Design and fabrication of niobate and tantalate semiconductor-based photocatalysts for solar energy conversion and environmental remediation

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By

Ping Wang

From Hunan, China

Industrial Chemistry

Faculty of Chemistry and Biochemistry

Ruhr-University Bochum
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First Examiner: Prof. Dr. Michael Wark

Second Examiner: Prof. Dr. Martin Muhler

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Abstract

The heterogeneous photocatalysis and semiconductor-based photocatalytic processes have attracted worldwide attention in recent years for potential applications, including solar hydrogen production by photocatalytic water splitting and the treatment of industrial effluents and wastewater through the photodegradation of contaminants. Over the past 40 years, a wide variety of semiconductor-based materials have been investigated, of which titania is proved to be one of the best candidates because of its chemical stability, low cost, and nontoxicity. However, the major limitations for its wide practical application are low conversion efficiencies and poor reliability, etc. Furthermore, the serious problems of attendant formation of effective charge-carrier recombination centers have also remained unsolved yet. Therefore, this work focused on the search for efficient niobate and tantalate based mixed metal oxide semiconductor materials as potential substitutes of TiO$_2$.

Owing to considerations of nontoxicity, thermal stability, recyclability and economic efficiency, the simple and cost-effective molten salts method was employed for materials synthesis, compared with solid state reaction method under high temperature ($>1000$ °C) and liquid-phase method, such as sol-gel polymerizable complex method, etc, using expensive precursors and complicated processing routes. Therefore, by aid of the mixtures of NaCl and KCl salts as eutectic medium, a series of phase-controlled and composition-tuned calcium tantalate composite photocatalysts had been prepared by adjusting the initial atomic ratio of Ta/Ca precursors. Without any co-catalysts, these composites with the optimized phase composition of either cubic α-CaTa$_2$O$_6$/hexagonal Ca$_2$Ta$_3$O$_7$, or cubic CaTa$_2$O$_6$/hexagonal Ca$_2$Ta$_3$O$_7$/orthorhombic β-CaTa$_2$O$_6$, or cubic α-CaTa$_2$O$_6$/orthorhombic β-CaTa$_2$O$_6$ showed very high photocatalytic H$_2$ production activities in the presence of methanol. A strong correlation was demonstrated between the photocatalytic H$_2$ production activities of calcium tantalate nanocomposite photocatalysts for hydrogen evolution and respective phase compositions. Then
in the next step, a comprehensive study carried out for demonstrating the photocatalytic properties of these different calcium tantalate nanocomposite photocatalysts with optimized phase-composition after modification with double-layered NiO\textsubscript{x} (Ni/NiO) co-catalyst and without the addition of any co-catalysts. Photocatalytic performance in overall water splitting, and reforming of different alcohols and biomass derivatives were detailed investigated, respectively. Moreover with the addition of noble metal (Pt and Rh) co-catalysts in the presence of methanol, the photocatalytic activities of these calcium tantalate nanocomposite photocatalysts were further investigated for hydrogen evolution.

Novel tetragonal tungsten bronze-type Ta substituted-Sr\textsubscript{2}KNb\textsubscript{5}O\textsubscript{15} nanorod photocatalysts with tunnel structure were synthesized by molten salts method using salt combinations including potassium chloride (KCl). Ta substitution effects on the physicochemical properties and photocatalytic behavior were systematically investigated for photocatalytic hydrogen production by aqueous methanol reforming. The average H\textsubscript{2} formation rates of Sr\textsubscript{2}KNb\textsubscript{5-x}Ta\textsubscript{x}O\textsubscript{15} first decrease with tantalum substitution for x < 2.5, presumably due to a decreased amount of absorbed photons and an obvious reduction of their exposed surface areas, whereas the activity is significantly improved for samples containing more Ta (x > 2.5) and especially the fully substituted Sr\textsubscript{2}KTa\textsubscript{5}O\textsubscript{15}. This can be explained by a stronger driving force for photogenerated conduction band electrons to reduce water. Furthermore, although all native photocatalysts did not possess any detectable activity in pure water splitting, after deposition of NiO\textsubscript{x} (double-layered Ni/NiO) as co-catalysts, it is found that samples of Sr\textsubscript{2}KNb\textsubscript{5}O\textsubscript{15} and Sr\textsubscript{2}KTa\textsubscript{5}O\textsubscript{15} can split pure water into H\textsubscript{2} and O\textsubscript{2} in a stoichiometric amount (≈ 2:1), which can be ascribed to the improved charge carrier separation and transfer in the presence of NiO\textsubscript{x}.

By direct growth of g-C\textsubscript{3}N\textsubscript{4} on Sr\textsubscript{2}KNb\textsubscript{5}O\textsubscript{15} and Sr\textsubscript{2}KTa\textsubscript{5}O\textsubscript{15} nanorods, respectively, the g-C\textsubscript{3}N\textsubscript{4}/Sr\textsubscript{2}KNb\textsubscript{5}O\textsubscript{15} and g-C\textsubscript{3}N\textsubscript{4}/Sr\textsubscript{2}KTa\textsubscript{5}O\textsubscript{15} nanocomposite photocatalysts were successfully prepared. Both of Sr\textsubscript{2}KNb\textsubscript{5}O\textsubscript{15} and Sr\textsubscript{2}KTa\textsubscript{5}O\textsubscript{15} have matching conduction and valence bands with g-C\textsubscript{3}N\textsubscript{4}, the coupling of g-C\textsubscript{3}N\textsubscript{4} with
Sr$_2$KNb$_5$O$_{15}$ or Sr$_2$KTa$_5$O$_{15}$ are thus expected to promote both visible light response and electron-hole pair separation. It is found that by coupling with g-C$_3$N$_4$, the moderate band-gap Sr$_2$KNb$_5$O$_{15}$ (ca. 3.20 eV) and broad band-gap Sr$_2$KTa$_5$O$_{15}$ (ca. 3.89 eV) were successfully sensitized into visible-light response. The photoactivity of the samples was evaluated by degradation of methylene blue under visible light irradiation ($\lambda > 400$ nm). Compared with their single components (g-C$_3$N$_4$, Sr$_2$KNb$_5$O$_{15}$ and Sr$_2$KTa$_5$O$_{15}$), the photocatalytic performance of g-C$_3$N$_4$/Sr$_2$KNb$_5$O$_{15}$ was significantly enhanced while the improvement of g-C$_3$N$_4$/Sr$_2$KTa$_5$O$_{15}$ was weaker. It is plausibly followed that the electron transfer driving-forces between Sr$_2$KNb$_5$O$_{15}$ and g-C$_3$N$_4$ from the CB of Sr$_2$KNb$_5$O$_{15}$ into that of g-C$_3$N$_4$ are larger than those between Sr$_2$KTa$_5$O$_{15}$ and g-C$_3$N$_4$. The other probable reason is that as comparison with Sr$_2$KTa$_5$O$_{15}$, Sr$_2$KNb$_5$O$_{15}$ nanorods have higher BET surface areas, which may be providing more surface active sites. Moreover, by a comparative investigation of their preparation method, the importance of the formed proper nano-interfaces in the nanocomposites was demonstrated for the fabrication of composite photocatalysts. Consequently, a possible mechanism was proposed, which was associated with double role of g-C$_3$N$_4$ as light absorber and sensitizer, and the close cooperation between their components via the nano-interfaces. Therefore, the study offers a route to green solar energy harvesting using a simple and cost-effective approach to conveniently fabricate highly active niobate and tantalate-based semiconductor materials for the potential applications of solar energy conversion and environmental remediation.
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<th>Symbol</th>
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<th>Unit</th>
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<tr>
<td>BE</td>
<td>Binding energy</td>
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<tr>
<td>D</td>
<td>Crystallite size</td>
<td>nm</td>
</tr>
<tr>
<td>d</td>
<td>Lattice spacing</td>
<td>nm</td>
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<td>Electron</td>
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<td>$E_g$</td>
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<td>eV</td>
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<td>$F(R_\infty)$</td>
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<td>$h$</td>
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<td>Js</td>
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<td>$h^+$</td>
<td>Hole</td>
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</tr>
<tr>
<td>I</td>
<td>Transmitted light</td>
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<tr>
<td>$I_o$</td>
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<tr>
<td>$N_A$</td>
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<tr>
<td>NHE</td>
<td>Normal hydrogen electrode</td>
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<tr>
<td>$p$</td>
<td>Pressure</td>
<td>mbar</td>
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<tr>
<td>$p/p_o$</td>
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<tr>
<td>S</td>
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<tr>
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<tr>
<td>$\Delta G$</td>
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<tr>
<td>$\theta$</td>
<td>Bragg angle</td>
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<tr>
<td>$\lambda$</td>
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<td>nm</td>
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### Abbreviations

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<th>Abbreviations</th>
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<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
</tr>
<tr>
<td>CB</td>
<td>Conduction band</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
</tr>
<tr>
<td>DRS</td>
<td>Diffuse reflection spectroscopy</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width at half maximum</td>
</tr>
<tr>
<td>HAADF</td>
<td>High angle-annular dark field</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>HRTEM</td>
<td>High resolution transmission electron microscope</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>LSPR</td>
<td>Local surface plasmon resonance</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>MFC</td>
<td>Mass flow controller</td>
</tr>
<tr>
<td>SAED</td>
<td>Selected area electron diffraction</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>STEM</td>
<td>Scanning transmission electron microscope</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscope</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
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<tr>
<td>---------</td>
<td>----------------------------------</td>
</tr>
<tr>
<td>TG</td>
<td>Thermo gravimetry</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermo gravimetric analysis</td>
</tr>
<tr>
<td>UHV</td>
<td>Ultra high vacuum</td>
</tr>
<tr>
<td>VB</td>
<td>Valence band</td>
</tr>
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<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
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<td>XRD</td>
<td>X-ray diffraction</td>
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1 Introduction

1.1 General background

In the present era of the cumulative depletion of fossil fuel reserves, the energy shortage and the wreaked environmental damage, particularly global warming, are serious issues.\(^1\) In order to reduce the dangerous energy reliance on fossil fuels and transform their energy sectors to encompass modern, efficient, clean and renewable sources of energy, it is indispensable to construct clean and renewable energy systems.\(^2\) Hydrogen (H\(_2\)) is predicted to be a promising energy storage medium or carrier, with the advantages of high energy density (140 MJ Kg\(^{-1}\)), which far exceeds those of gasoline and coal, and environmental friendliness without carbon emission, and a useful by-product of water from combustion. Currently, hydrogen is mainly produced from hydrocarbons such as fossil fuels or biomass by reforming or thermal cracking which is severely restricted by its high air emission and high cost. Another technique is electrolysis, which applies electrical current to decompose water into hydrogen and oxygen molecules, but the problem is that the electricity for electrolysis can still come from an external resource.\(^3\)

Solar energy has been considered as an ideal alternative energy source, since it is the most powerful, affordable (cost-free) and richest renewable and sustainable source of energy.\(^4\)-\(^6\) Water and sunlight are both renewable resources, and cheap, thus the combination of water and solar energy for hydrogen production give us hope to fulfill the present and future energy demand in an eco-friendly manner. Up to now, several methods have been applied for utilizing solar energy in splitting water.\(^7\)-\(^9\) Photovoltaic electrolysis of water driven by efficient solar photovoltaics (PV) system, the expensive proton exchange membranes and alkaline electrolytes were used.\(^10\)-\(^11\) Solar to thermochemical water splitting needs the high temperature of 700-1000 °C, the search for appropriate heat-resisting materials and large-scale solar concentrator systems has become the greatest challenge.\(^12\) Photobiological water splitting has to overcome the
natural short-term nature of biospecies hydrogen production, such as the poisoning effect of enzymes under the presence of oxygen, which produced simultaneously during biophotolysis, and the difficulty in designing and scaling up the bioreactor for the process.\textsuperscript{[13]} As a result, much attention has been focused on water splitting for hydrogen production by photoelectrochemical (PEC) or photocatalytic reaction systems. Compared with the above-mentioned systems, it has the following advantages: (1) reasonable solar-to-hydrogen efficiency; (2) the ability to achieve separate hydrogen and oxygen evolution during reaction; (3) low process cost; and (4) small reactor systems suitable for household applications, thus providing for a huge market potential.\textsuperscript{[8, 14]}

In 1972, Fujishima and Honda demonstrated the feasibility of an artificial analog to photosynthetic water splitting with UV light, using the semiconductor TiO\textsubscript{2} to absorb photons, separate charges, and catalyze water oxidation to generate O\textsubscript{2}. Electrons were pumped to a Pt counter electrode, which reduced protons to generate H\textsubscript{2}.\textsuperscript{[15]} It was the first demonstration that hydrogen could be obtained through water splitting using PEC system. Afterwards, through considerable simplification of the apparatus, the principle of PEC hydrogen production was successfully extended into particulate system by simple dispersions of semiconductor particles for heterogeneous photocatalysis by Allen J. Bard.\textsuperscript{[16]} It has prompted a flurry of worldwide activity aimed at the research and development of semiconductor photocatalysis. During this period, photocatalysis with TiO\textsubscript{2} was applied with varied success to a number of processes, including hydrogen production, effluents detoxification and disinfection, and organic synthesis, because of its relatively high activity, chemical stability, low cost, and non-toxicity, etc.\textsuperscript{[17-19]}

However, a fundamental problem has thwarted its practical implementation in such water-splitting systems, because the large band gap of TiO\textsubscript{2} (> 3.0 eV) allows it to absorb only the UVA (400–320 nm) and UVB (320–290 nm) ranges of sunlight spectra, leading to the low solar-to-hydrogen conversion efficiency. Since UV light only accounts for approximately 4% of solar energy, while visible
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light contributes about 50%, the inability to utilize visible light limits the efficiency of TiO$_2$ in solar photocatalytic hydrogen production. Furthermore, the photocatalytic reaction rates are moderate, and consequently this technology is not appropriate for high throughput processes. In consequence, a wide variety of simple and complex semiconductor materials have been reported as potential substitutes of TiO$_2$.\textsuperscript{[20-22]}

Some traditional metal oxides, such as Fe$_2$O$_3$ or WO$_3$, have smaller band gaps, the unsuitable band potential make the reaction thermodynamically unfavorable to reduce water to H$_2$ at a normal pressure of one atmosphere. ZnO has similar conduction and valence positions as anatase TiO$_2$, and therefore has been frequently considered an alternative to TiO$_2$ for photocatalytic applications, but the main drawback is its chemical instability in solution and easy photocorrosion, especially at low pH values. Although the metal (oxy)sulfide semiconductors (such as Sm$_2$Ti$_2$S$_2$O$_5$, CdS and CdSe, etc.) possess relatively narrow band gaps that are better matched to the spectral distribution of sunlight, they are initially discarded because of their poor photo-stability.\textsuperscript{[23-25]} Metal (oxy)nitrides consisting of Ti$^{4+}$, Nb$^{5+}$ or Ta$^{5+}$ metal ions (e.g. TaON and Ta$_3$N$_5$) are active for H$_2$ or O$_2$ evolution in the presence of sacrificial reagents. In the development of oxynitrides with d$^{10}$ electronic configuration, a solid solution of GaN and ZnO- (Ga$_{1-x}$ Zn$_x$)(N$_{1-x}$O$_x$) was first reported for spitting water under visible light irradiation.\textsuperscript{[26]} However, in most cases, the (oxy)nitride is partially decomposed by photogenerated holes (instead of water oxidation) at the initial stage of photocatalytic reactions.

The first example of niobate-based photocatalyst with a layered structure, K$_4$Nb$_6$O$_{17}$, was developed in 1986, which exhibited high photocatalytic activity.\textsuperscript{[27]} The potassium ions between the niobium oxide layers can be exchanged with many other cations including transition metal ions. Of particular note is the H$^+$-exchanged K$_4$Nb$_6$O$_{17}$, it showed the highest activity for H$_2$ evolution from an aqueous methanol solution and its quantum yield was up to ca. 50% at 330 nm.\textsuperscript{[28]} Kato and Kudo reported in 2003 that alkali tantalates ATaO$_3$ (A = Li, Na,
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and K) showed high activities for photocatalytic water splitting under UV light and the apparent quantum yield of the NiO/La-doped NaTaO$_3$ photocatalyst amounted to 56% at 270 nm.$^{[29]}$ The nature of connection of MO$_6$ octahedra (M= Nb or Ta) in crystal structure should be favorable for migration of photogenerated electrons and holes, and separation of surface reactions sites. The researches on various mixed oxide semiconductors with d$^0$ configuration of M=Ta or Nb have grown exponentially,$^{[21]}$ such as layered perovskite structure- (100) layering of Sr$_2$M$_2$O$_7$, (100) layering of KCa$_2$Nb$_2$O$_{10}$ and KBa$_2$Ta$_2$O$_{10}$, and (111) layering of Ba$_3$M$_4$O$_{15}$,$^{[30-33]}$ tunnel structure- tungsten bronze type PbNb$_2$O$_6$ and A$_2$BM$_5$O$_{15}$ (A=Sr, Ba; B= Na, K),$^{[34-35]}$ pyrochlore structure Ca$_2$Ta$_2$O$_7$, Bi$_2$NMO$_7$(N= Al, Ga, In, Fe, etc.),$^{[36-37]}$ wolframite-type structure InTaO$_4$,$^{[38]}$ etc. It is worth note that the NiO$_x$/In$_{0.9}$Ni$_{0.1}$TaO$_4$ belonging to the d$^0$ configuration family, was the first photocatalyst, which was reported by Zou, et al, for splitting water into H$_2$ and O$_2$ under visible light irradiation.$^{[38]}$
1.2 Motivation and Aims

Despite significant efforts to date, a practically viable semiconductor material with sufficient efficiency, stability and low cost is yet to be demonstrated. There is a changeling's motivation to improve and develop a multifunction photocatalyst for the heterogeneous photocatalysis process. In particular, the development of niobate and tantalate-based mixed metal oxide photocatalysts is possible and very attractive. Therefore, this thesis aims to produce new and highly photoactive niobate and tantalate-based semiconductor photocatalysts for water splitting and organic contaminants decomposition. The following questions need to be considered and answered, which includes:

1). What kind of methods is preferred for niobate and tantalate-based photocatalyst preparation?

2). Which design strategy is the preferred option for improving the photocatalytic activities?

3). Are the as-synthesized products really better than commercial TiO$_2$ (Evonik P25)?

4). How to understand Ta substitution effects for Nb on their physicochemical properties and photocatalytic behavior?

5). How to extend the light absorption of large band-gap semiconductor photocatalysts from the UV region into the visible-light region?

6). What are the key points for the design and fabrication of semiconductor composite systems?

The molten salts method will be introduced for the photocatalyst preparation, because of the comparable advantages of nontoxicity, thermal stability, recyclability and economic efficiency, etc. In the first part, a series of phase-controlled and composition-tuned calcium tantalate composite photocatalysts has been prepared by adjusting the initial atomic ratio of Ta/Ca precursors, instead of conventional temperature control. The strong correlation
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will be demonstrated between the photocatalytic activities of calcium tantalate nanocomposite photocatalysts for hydrogen evolution and respective phase compositions, thus the photocatalytic property can be optimized by adjusting the initial atomic ratio of Ta/Ca precursors. Design and fabrication of calcium tantalate nanocomposite photocatalysts with matching band structure is found to be an important strategy to improve charge separation of photogenerated electron-hole pairs.

In the second part, a comparative study to demonstrate the photocatalytic H₂ production activities of these calcium tantalate nanocomposite photocatalysts with optimized phase-composition for photocatalytic reforming of different alcohols and biomass derivates was performed in absence of any co-catalysts, And with the addition of noble metal co-catalysts, the photocatalytic activities of calcium tantalate nanocomposite photocatalysts were further investigated for hydrogen evolution. Furthermore, since NiOₓ (double-layer structure Ni/NiO) is a cheap and effective co-catalyst for overall water splitting, these calcium tantalate nanocomposite photocatalysts were studied after modification with double-layered NiOₓ (Ni/NiO) and the influence of NiOₓ loading as co-catalysts for overall water splitting is also investigated in detail.

In the third part, tetragonal tungsten bronze-type Ta substituted-Sr₂Knbo₁₅ nanorod photocatalysts with tunnel structure were prepared. Ta substitution effects on the physicochemical properties and photocatalytic behavior were systematically investigated for photocatalytic hydrogen production by aqueous methanol reforming. Furthermore, samples of Sr₂Knbo₁₅ and Sr₂Ktao₁₅ were studied for spitting water into H₂ and O₂ after deposition of double-layered NiOₓ as co-catalyst.

Finally, hybrid organic/inorganic nanocomposite photocatalysts of g-C₃N₄/Sr₂Knbo₁₅ and g-C₃N₄/Sr₂Ktao₁₅ heterojunctions were prepared. By coupling with g-C₃N₄, the moderate band-gap Sr₂Knbo₁₅ and broad band-gap Sr₂Ktao₁₅ was successfully sensitized. The photoactivity of the samples was
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evaluated by degradation of methylene blue under visible light irradiation (λ > 400 nm). The photocatalytic performance of g-C₃N₄/Sr₂K₅Nb₂O₁₅ was significantly enhanced while the improvement of g-C₃N₄/Sr₂KTa₂O₅ was relatively weak. Furthermore, by a comparative investigation of different preparation methods, the importance of the formed proper nano-interfaces in the nanocomposites was demonstrated. A proposed mechanism was associated with double role of g-C₃N₄ as light absorber and sensitizer, and the close cooperation between their components via the nano-interfaces.
2 Basic principles

2.1 Thermodynamic requirements for photocatalytic reactions

As depicted in Figure 2.1, photocatalytic reactions have been typically classified into two categories: uphill and downhill reactions. Thermodynamically, degradation reactions such as the photo-oxidation of organic compounds using oxygen molecules are generally downhill reactions. The reaction proceeds irreversibly. On the other hand, water splitting into H₂ and O₂ is classified as an uphill photocatalytic reaction. In this reaction, photon energy is converted into chemical energy, which is similar to natural photosynthesis.

Figure 2.1. Types of photocatalytic reactions. Adapted from ref. [39]

Photocatalytic water splitting is therefore referred to as an artificial photosynthesis and is an attractive and challenging theme in chemistry. The reaction requires the standard Gibbs free energy change $\Delta G^\circ$ of 237 kJ/mol or 1.23 eV, as shown in Equation 1.

oxidation: $\text{H}_2\text{O} + 2h\nu \rightarrow 2\text{H}^+ + \frac{1}{2}\text{O}_2$

reduction: $2\text{H}^+ + 2e^- \rightarrow \text{H}_2$

Overall reaction: $\text{H}_2\text{O} \xrightarrow{h\nu} \text{H}_2 + \frac{1}{2}\text{O}_2 \quad \Delta G = +237 \frac{\text{kJ}}{\text{mol}} \quad (1)$
In order to achieve the goal of solar water splitting, the band gap of photocatalytic materials and the edges of the conduction band (CB) and valence band (VB) must be suitable for decomposing water. As shown in Figure 2.2, the bottom edge of the conduction band must be more negative than the redox potential of \( \text{H}^+ / \text{H}_2 \) (0 V vs. NHE at PH 0), while the top edge of the valence band must be more positive than the redox potential of \( \text{O}_2 / \text{H}_2\text{O} \) (1.23 V vs. NHE). However, there is an activation energy or overpotential in the charge-transfer process between photocatalysts and water molecules, necessitating a photon energy greater than the band gap of the photocatalyst to drive the water splitting reaction at reasonable reaction rates. Therefore, the band gap energy \( (E_g) \) of the photocatalyst should be >1.23 eV (<1000 nm) to achieve water splitting. To use visible light, it should be <3.0 eV (>400 nm), it would appear to be possible to utilize the entire spectral range of visible light.

![Figure 2.2. Requirements of semiconductor materials for water splitting](image)

2.2 Fundamental mechanism of semiconductor photocatalytic water splitting

The process for photocatalytic water splitting is quite complicated because the reactions occur in the photocatalysts and on the interface of the photocatalysts and reactants solution, as illustrated in Figure 2.3. All of these processes affect the photocatalytic efficiency of the semiconductor photocatalyst system. They include light absorption of the semiconductor photocatalyst, generation of
Basic principles

excited charges (electrons and holes), recombination of the excited charges, separation of excited charges, migration of the charges, trap of excited charges, and transfer of excited charges to water or other molecules.

i. Photons absorption to form electron–hole pairs.

The electron-hole pairs are formed by excitation of the incident photons. When the energy of incident light is greater than that of a band gap, electrons in the valence bands can become excited and be promoted into the conduction bands. Simultaneously, holes are generated in the valence bands.

ii. Charges separation, recombination of charges

The excited charges separate and migrate to the surface of the photocatalyst, which is drastically affected by crystal structure, crystallinity, and by the particle size of the photocatalyst. The higher the crystallinity of the catalyst, the smaller the number of defects, and the better the charge migration can be achieved. Excited state conduction-band electrons and valence-band holes tend to recombine and dissipate the input energy as heat, get trapped in metastable surface states, or react with electron donors and electron acceptors adsorbed on the semiconductor surface or within the surrounding electrical double layer of the charged particles. In the absence of suitable electron and hole separation forces, the stored energy is dissipated within a few nanoseconds in the recombination process. If a suitable scavenger or surface defect state is available to trap the electron or hole, recombination is suppressed and subsequent redox reactions may occur.

iii. Migration to surface reaction sites for H₂ and O₂ evolution.

Water splitting reaction is achieved through the reduction of H⁺ ions to H₂ by photogenerated electrons and the oxidation of H₂O to O₂ by holes, respectively. In this step, the surface properties of the photocatalyst play key roles in achieving overall water splitting, i.e. the surface reaction sites, the surface states. Even when the potentials of the photogenerated electrons and holes are
Basic principles

thermodynamically sufficient for water splitting, they may not be able to split water into H₂ and O₂ if the surface of photocatalyst lacks active sites. Meanwhile, the backward reaction to form water from the reaction between evolved H₂ and O₂ proceeds readily because it is a downhill reaction.

All of these processes affect the overall efficiency of a semiconductor photocatalysis system. Clearly, taking into consideration the basic mechanism and processes of photocatalytic water splitting, there are two keys to developing a suitable high-efficiency semiconductor for photocatalytic splitting of water into H₂ and/or O₂. On the one hand, a photocatalyst should have a sufficiently narrow band gap (1.23 eV < $E_g$ < 3.0 eV) to both harvest visible light and possess the suitable band structure. On the other hand, photoinduced charges in the photocatalyst should be separated efficiently in order to avoid bulk/surface recombination of electron-hole pairs. They must migrate to the respective surface active sites for hydrogen and/or oxygen evolution, thus strictly inhibiting the backward reaction of water formation from H₂ and O₂. In addition, the photocatalysts themselves must be stable in the reaction.

Figure 2. 3. Fundamental principle of semiconductor-based photocatalytic water splitting
3 Literature review- design strategies of semiconductor-based photocatalysts

Various strategies to design efficient semiconductor-based photocatalysts towards solar energy utilization and environmental applications have been described in literature, and the related main concepts will be reviewed below.

3.1 Doping

In the development of visible-light active photocatalysts, doping engineering has been intensively investigated by tuning the electronic structure of wide band-gap semiconductors. So far, most metals and nearly all of non-metals have been explored as dopants for modification of the electronic structure, in order to retard the fast charge recombination and improve its visible-light photocatalytic activity by creating defect states in the band gap. In the former case, the CB electrons or VB holes are trapped in the defect sites, inhibiting the recombination and enhancing the interfacial charge transfer. In the latter case, the electronic transitions from VB to defect states (interband states or mid-gap level) or from defect states to CB are allowed under sub-bandgap irradiation. Thus, dopants are usually classified into cations (noble metal ions and transition metal ions) and anions (non-metal ions), and the selection of dopant is very crucial in determining overall photocatalytic activities.

As depicted in Figure 3.1a, the replacement of cations in the crystal lattice, may create impurity energy levels within the band gap of the photocatalyst that facilitates absorption in the visible range. Noble metal ions as dopants have received much less attention as compared to transition metals. Noble metals such as Pt, Au, and Ag are usually deposited on the TiO$_2$ surface as a metallic nanoparticle (not as an ionic dopant) to serve as both a CB electron trap and a cocatalyst. There are only a few reports that studied the effects of noble metal ion dopant on TiO$_2$. Because dopants act as visible-light absorption
Literature review- design strategies of semiconductor-based photocatalysts

centers, with an absorption coefficient dependent on the density of dopants doping with transition metal substantially increased photocatalytic activity and induced visible-light response, such as W, V, Fe, Mo and Cr, etc.[50-53] Nevertheless, some of these photocatalysts do not have photoactivity because dopants usually act as recombination sites and accelerate the recombination of photogenerated electrons and holes,[54-56] because the impurity levels created by dopants in the photocatalysts are usually discrete, which would appear disadvantageous for the migration of the photogenerated holes.[57] It is therefore important to carefully control both the content and the depth of the cation substitution in the structure of the host photocatalysts to develop visible-light-active photocatalysts. The metal ions may be incorporated into the photocatalysts by chemical methods (impregnation or precipitation) or using the advanced ion-implantation technique. The advanced ion-implantation technique is more effective than chemical methods for controlling the insertion of dopants into the photocatalyst structure.

Anion doping is another way of enhancing the visible-light response of wide band gap (UV-active) photocatalysts based on oxide semiconductors, since Asahi et al. reported in 2001 visible-light active N-doped TiO$_2$ for the degradation of volatile organic compounds. This study triggered the research attention on visible light-active anions doped oxide materials as substitutes for oxygen in the oxide lattice, such as C, S, B and F, etc.[58-62] In wide band-gap oxide photocatalysts, the top of the VB consists of O 2p atomic orbitals. In these anion-doped photocatalysts, the mixing of the p states of the doped anions with the O 2p states shifts the VB edge upward and narrows the band-gap energy of the photocatalyst as depicted in Figure 3. 1b. In contrast to the cationic dopant technique, the anionic replacement usually forms fewer recombination centers, and therefore, it is more effective for enhancing photocatalyst activity. However, in the anion-doped materials, it is necessary to control the number of oxygen defects due to the difference in the formal oxidation numbers of oxygen and the dopant anions, as these defects will act as
recombination centers that may reduce the efficiency of the anion-doped photocatalyst. Yet in some cases, their visible light activities were rather controversial and contradictory results were reported. For example, Gole et al.\cite{63} prepared TiO$_2$xN$_x$ using alkylammonium as a precursor, which successfully degraded methylene blue under visible light. Despite the same method employed, however, Mrowetz et al.\cite{64} could not observe the visible light activity of TiO$_2$xN$_x$ for the degradation of formic acid. The selective reactivity of TiO$_2$xN$_x$ is ascribed to the limited oxidation power of holes generated in the mid-gap states (associated with N dopants). Nakamura et al.\cite{65} raised the similar controversy in a photoelectrochemical study. They argued that the photocatalytic oxidation of organic compounds on nitrogen-doped TiO$_2$ under visible illumination is mainly induced by surface intermediates of water oxidation or the reductive activation of oxygen and not by direct reactions with holes trapped at the nitrogen-induced mid-gap level. The study and ensuing related publications have led to a lively debate on the root causes of the red shift of the absorption onset of TiO$_2$ to the visible region. Some key issues such as the origin of doping-induced visible-light absorption, the nature of the chemical states created, and the locations of the dopants are not yet well understood.

![Diagram](image1.png)

![Diagram](image2.png)
Literature review- design strategies of semiconductor-based photocatalysts

Figure 3.1. Band structure of oxide photocatalysts doped by cation (a) and anion (b), which are adapted from Ref. [39] and [17], respectively.

Co-doping TiO$_2$ with more than two elements has also been studied to further increase the photocatalytic activity under UV and visible light and to make the doped TiO$_2$ more stable through charge compensation.$^{[66]}$ There has been a large number of studies that tried various doping combinations of metal/metal (e.g., Pt/Cr,$^{[46]}$ Sb/Cr,$^{[67-69]}$), non-metal/non-metal (e.g., N/F,$^{[70-72]}$ N/S$^{[73]}$), and metal/non-metal pairs (e.g., Pt/N$^{[74]}$). As an example of the metal/non-metal doped TiO$_2$, Kim and Lee$^{[74]}$ prepared Pt-N-TiO$_2$, which exhibited enhanced photocatalytic activities for the degradation of 4-chlorophenol (4-CP) under UV and visible light irradiation. Moreover, it is also worth to mention that none of the co-doped TiO$_2$ samples were found to have enhanced photocatalytic activity for phenol degradation when compared to their single-doped TiO$_2$ counterparts. The visible light activity of co-doped TiO$_2$ is as well substrate-specific as the UV-light activity of bare TiO$_2$ is.$^{[75]}$ Therefore, the dopant effect observed with a specific substrate may not be generalized to other substrates in the field of environmental applications.

3.2 Co-catalyst modification

Most of current photocatalysts are generally obtained by randomly loading co-catalysts onto the surface of semiconductor particles. The co-catalysts play an important role in improving the photoactivity of the photocatalyst systems.$^{[76-77]}$ Proper cocatalysts loading on the light harvesting semiconductor could promote or accelerate the photocatalytic courses, which can serve as the reaction sites and catalyze the reactions, promote the charge separation and transport driven by junctions/interfaces formed between the co-catalyst and the light harvesting semiconductor.$^{[76]}$ In general, metal/semiconductor heterogeneous photocatalysts can offer potential benefits.$^{[78]}$

First of all, a Schottky junction can be formed between the metallic nanoclusters and the semiconductor. The equilibrium alignment of the Fermi
levels of the metal and semiconductor materials creates a built-in electric field in the space-charge region near the interface, which can promote the separation of photogenerated electrons and holes. Secondly, the metallic nanoclusters can function as effective cocatalysts to reduce the overpotential for surface electrochemical reactions or gas evolution processes. The first two benefits have been widely investigated and reviewed.\cite{79-80} Well-known noble metals (Pt, Rh, Ru, and Pd, etc.) have been widely used as proton reduction co-catalysts in semiconductor-based photocatalytic water splitting.\cite{29, 81-85} Pt is often regarded as the most efficient co-catalyst for H₂ evolution from the viewpoint of both electronic and catalytic properties,\cite{86-87} since its work function is also the largest going in line with one of the lowest overpotentials for hydrogen among the noble metals. Alternatively, many low-cost and environmentally friendly metal oxide and metal sulfides are also developed as co-catalysts for photocatalytic water splitting reactions, such as the dual co-catalysts (NiO and RuO₂, etc.),\cite{88-89} proton reduction-type co-catalysts (MoS₂ and WS₂, etc.)\cite{90-92} and oxidation-type co-catalysts (IrOₓ, CoOₓ, CoPi, CoBi, and B₂O₃-Nₓ, etc.).\cite{93-99} In particular, it is worth to note that double-layered structures of metal/metal oxide co-catalysts such as NiOₓ (Ni/NiO)\cite{100-101} and Rh/Cr₂O₃\cite{102-103} were found playing dual functional roles, in presence of metallic core at the interfaces between the photocatalyst and metal oxide, favoring extraction of the photogenerated electrons to the surface of metal oxide and thus reduction of electron-hole recombination.

Lastly, the metallic components in the metal/semiconductor heterostructure could also enhance the light absorption of semiconductors through a plasmonic enhancement effect.\cite{104} On the one hand, they can function as strong scattering elements to scatter and trap freely propagating light within the semiconductor material. On the other hand, for certain metallic nanostructures, the optical excitation can create a coherent oscillation of the free electrons in resonance with the electrical field component of the incoming electromagnetic irradiation, to form so called local surface plasmon resonance (LSPR). A dipolar
oscillation of all electrons in the metallic nanostructures induces strong absorption of the electromagnetic energy, which can greatly enhance the local optical field and thereby enhance the absorption and photocatalytic activity of the nearby semiconductor material. The frequency of the surface plasmon absorption is highly dependent on the size and morphology of the metal nanostructures, as well as their dielectric environment. Au and Ag represent two typical metals with tunable plasmonic resonance frequencies in the visible light range. A wide range of metas/semiconductor heterostructures, including Au/TiO$_2$, Ag/TiO$_2$, and Au/CdS, have been explored to achieve enhanced photocatalytic activity. The investigation on plasmonic enhanced photocatalytic materials is intriguing but not always straightforward because of multiple convoluting factors that could impact the photocatalytic activity.

### 3.3 Crystal growth engineering

Greatly motivated by the development of controlling the morphologies of materials in nanoscience and nanotechnology, the interest has emerged in tuning crystal growth of photocatalysts in order to optimize the photocatalytic reactivity.$^{[108]}$ Many efforts have focused on changing phases of TiO$_2$ by mediating mineralizers with common titanium (III/IV) halide or alkoxide precursors.$^{[109-111]}$ The morphology of anatase TiO$_2$ has been investigated for sphere, rod, wire, tube, slightly and heavily truncated octahedron, belt and sheet structures.$^{[112]}$ Some of these morphologies are enclosed with recognizable facets such as (001), (101) and (010). The preparation of shape-controlled anatase TiO$_2$ crystals with specific reactive facets exposed is greatly desired to improve the reactivity. The average surface energies of anatase TiO$_2$ (0.90 J m$^{-2}$ for (001), 0.53 J m$^{-2}$ for (100), 0.44 J m$^{-2}$ for (101) have been demonstrated extensively.$^{[113]}$ By tuning the ratio of different facets, the photocatalytic reactivity would be correspondingly changed and the minority surfaces such as (001) ones with a higher surface energy (0.90 J m$^{-2}$) attract extensive interest. Unfortunately, (101) surfaces, normally the majority of the external surface of anatase TiO$_2$ (more
than 94% percent, according to the Wulff construction), are thermodynamically stable with a low surface energy (0.44 J m$^{-2}$), which determines its low reactivity.$^{[114]}$

Barnard and Curtiss $^{[115]}$ systematically studied the effects of surface chemistry in terms of acidic and alkaline conditions on the morphologies of anatase and rutile nanoparticles. Surface chemistry plays a decisive role in realizing the fine-tuning of morphology of well-defined anatase crystals, as shown in Figure 3. 2a-e. The surface termination by hydrogen (acidic conditions) results in little change in the shapes of both polymorphs relative to vacuum. However, in water terminated surfaces and hydrogen-poor surfaces, in particular oxygenated surfaces, both polymorphs are apparently elongated. These predictions are very important to experimentally realize the fine tuning of morphology by controlling surface chemistry.

![Figure 3. 2. Morphology predicted for anatase crystals with (a) hydrogenated surfaces, (b) with hydrogen-rich surface adsorbates, (c) hydrated surfaces, (d) hydrogen-poor adsorbates and (e) oxygenated surfaces. Adapted from Ref. [115]](image)

Yang et al.$^{[116]}$ successfully prepared well-defined anatase single crystals with 47% of the highly reactive (001) facets by using hydrofluoric acid (HF) as a capping agent under hydrothermal conditions. This work has triggered the subsequent intensive research interests in preparing faceted anatase (001), (101) and (010) $^{[117-118]}$ and also other photocatalysts.$^{[119]}$ Following this breakthrough, extensive efforts have been made in the preparation, modification, and application of TiO$_2$ with (001) facets. Among them, Pan et al. $^{[120]}$ prepared anatase single crystals with a respective predominance of (001), (101) and (010) by controlling carefully
the preparation parameters (concentrations of precursor and morphological controlling agent and reaction time) to satisfy the surface energy requirement for each facet. These products made it possible to compare the relative photocatalytic activity of each facet and then determine the photoreactivity order of facets. However, reactive facets usually have a relatively high surface energy. They are therefore unstable during the crystal growth as a result of reducing total surface energy of crystals. Acquiring a high percentage of reactive facets by crystal facet engineering is highly desirable for improving the photocatalytic reactivity.

3.4 Heterostructure

Light absorption and charge generation/separation are the two most important steps in photoconversion of solar energy for water splitting. In addition to increasing the absorbance of light, improving the transportation of charge carriers after the charges are generated and separated is the second critical step in increasing photocatalytic activity. It is often difficult to simultaneously achieve these different performance metrics with a single-semiconductor component. As one of promising solutions for converting solar energy include preventing the trapping of carriers on semiconductor surfaces, and improving the capability for instantaneous charge collection, separation, and transportation, rational design and nanoscale integration of multiple semiconductor components can enable efficient channeling of the photogenerated charge carriers for the desired redox chemistry, compared to single-semiconductor photocatalysts. In general, the semiconductor heterostructures can be divided into three different types: straddling bandgap (type-I), staggered bandgap (type-II) or broken bandgap (type-III), as shown in Figure 3.3. Considering a type-II band alignment, the energy gradient existing at the interfaces tends to spatially separate electrons and holes on different sides of the heterojunction, where electrons may be confined to one side and holes to the other. The spatially localized charges in the type-II nanostructures
should make these materials more suitable for photocatalytic applications. Such semiconductor heterostructures can easily integrate small and wide band gap materials to drive water oxidation/reduction processes simultaneously via multiple combinations. The semiconductor p–n junction is another one of effective architectures for the highly efficient charge separation and transportation by a built-in electrical potential that can direct the electrons and holes to travel in the opposite direction.

Figure 3.3. Schematic energy band diagram of three types of semiconductor heterojunctions categorized by band alignments.

In 1984, Serpone et al.\textsuperscript{[122]} showed for the first time that coupling the two semiconductors CdS and TiO\textsubscript{2} led to significant increases in process efficiencies as the charges formed upon light absorption by CdS were vectorially separated, $e^-$ on TiO\textsubscript{2} and $h^+$ on CdS through a pathway that we referred to as interparticle electron transfer. Several combinations of semiconductor couples have since been examined extensively, especially TiO\textsubscript{2} based semiconductor composite systems by combining with other different materials have been explored and demonstrated to efficiently promote charge separation via the interfaces between the combined semiconductors.\textsuperscript{[123-131]}
Figure 3.4. Charge separation and transfer process from the CB of photoexcited CdS to that of TiO$_2$. Hole transfer occurs from the VB of TiO$_2$ to that of CdS. Adapted from Ref. [132].

On the other hand, TiO$_2$ as one of the most important photocatalysts, has three crystalline polymorphs in nature: anatase, rutile and brookite. The structure of the three main phases is well characterized by the two complementary Ti$_x$O$_y$ building block representations pictured in Figure 3.5. The most common representation is the view of the crystal structures as networks of edge- and/or corner-linked distorted TiO$_6$ octahedron building blocks. Rutile and brookite exhibit corner-as well as edge-sharing TiO$_6$ units. The manner of such connections determines the crystal structure, surface structure and electronic structure of TiO$_2$, and thus the bulk diffusion, surface transfer capability and redox potentials of photoinduced charge carriers. The surface terminations in various orientations and thus the equilibrium morphologies of the crystals are completely different. The homo-semiconductor composites consisting of different polymorphic phase, have attracted a lot of research attention, such as anatase/rutile TiO$_2$. Recently, other elemental homosemiconductor composites have been developed as well (Figure 3.6), such as α/β-Ga$_2$O$_3$, α/γ-Bi$_2$O$_3$, Ba$_3$Ta$_5$O$_{15}$/Ba$_5$Ta$_4$O$_{15}$ and (La, Cr co-doped) Sr$_2$TiO$_4$/SrTiO$_3$. 

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Similarly, under irradiation, their potential difference of the polymorphic phases give rise to the charge transfer and redistribution behavior, i.e. via polymorphic phase junctions, the photogenerated electrons can easily transfer in the side of the one with a more positive CB potential, simultaneously, the photogenerated holes tend to migrate in the side of the other one with a more negative VB potential. Although such a potential difference is small, it can still serve as the driving force for efficient charge separation and transfer. Compared with hetero semiconductor composites composed of different elemental components, they were more easily obtained from nature by tailored polymorphic phase junctions on the surface. Integration of multiple semiconductor materials or multiple co-catalysts with proper architecture can open up opportunities not possible within a single material, and address some critical fundamental challenges in photocatalyst materials.
Figure 3.6. The speculated model of the charge transfer and separation on the interfaces of α/β-Ga₂O₃[135] and α/γ-Bi₂O₃[136].

However, there still remains a great challenge concerning the methodologies for constructing the semiconductor composites with matching band potentials for efficient charge carrier separation. The more complicated multi-components composite systems are rarely mentioned[139-140]. Proper and intimate interfacial junction architecture among these components is still another difficulty in the composite photocatalysts approach.
4 Experimental

4.1 Characterization

4.1.1 Powder X-ray diffraction

The powder X-ray diffraction (XRD) patterns of all as-synthesized samples were recorded with a PANalytical MPD diffractometer using Cu-Kα radiation ($\lambda=0.1541$ nm), and the data were collected from $10^\circ$ to $60^\circ$ ($2\theta$). XRD technique is among of the most widely applied methods used for the identification of bulk phases, especially in mixtures. X-ray diffraction is the elastic scattering of X-ray photons by atoms in a periodic lattice. The scattered monochromatic X-rays that are in phase produce a constructive interference, which will be observed for X-rays that are reflected from the lattice planes at the specular angle, if the path length difference for scattering off of two adjacent planes is an integer number of wavelength, shown in Figure 4.1. This condition is summarized in the Bragg's law:

$$2d \sin \theta = n \lambda$$

(2)

where $d$ is the spacing between diffracting planes; $\theta$ is the incident angle; $n$ is any integer called the order of the reflection.; $\lambda$ is the wavelength of the beam.

Figure 4.1. Schematic illustration of X-rays scattered by atoms in an ordered
lattice interfere constructively in directions given by Bragg’s law. (Two beams with identical wavelength and phase approach a crystalline solid and are scattered off two different atoms within it. The lower beam traverses an extra length of \(2dsin\theta\). Constructive interference occurs when this length is equal to an integer multiple of the wavelength of the radiation.)

In essence, the phase identification and quantification, characterization of the ideal and real structure, determination of crystallite size and strain can be analyzed on the powder diffraction pattern of lines if a reference set of patterns is consulted. In this case classical Scherrer equation is used for crystallite size determination.\textsuperscript{[141]}

\[
D = \frac{K\lambda}{\beta \cos \theta} \quad \text{(3)}
\]

where \(D\) is the crystallite size, \(K\) is the Scherrer constant, \(\lambda\) is the X-ray wavelength, \(\beta\) is the width of the peak (full width at half maximum (FWHM)) after correcting for instrumental peak broadening (\(b\) expressed in radians), and \(\theta\) is the Bragg angle. The Scherrer equation gives volume-weighted mean column length. The \(d\) value calculated for \((hkl)\) peak should be understood as mean crystallite size in the direction that perpendicular to the \((hkl)\) plane.

However, XRD has some serious disadvantages. Because it depends on interference between X-rays reflecting from lattice planes, the technique requires samples that possess sufficient long-range order. Amorphous phases and small particles give either broad and weak diffraction lines or no diffraction at all, with the consequence that if materials contain particles with a size distribution, XRD may detect only the larger ones.

4.1.2 Electron microscope

Electron microscope has been a valuable tool in the development of scientific theory and it contributed greatly to biology, medicine and material sciences. Since its invention, this wide spread use of electron microscopes is based on the fact that they permit the observation and characterization of materials on a
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nanometer (nm) to micrometer (μm) scale. Electron microscopy is a rather straightforward technique that can be used to determine the size and shape of supported particles. It can also reveal information on the composition and internal structure of the particles, for example by detecting the characteristic X-rays that are produced by the interaction of the electrons with matter, or by analyzing how the electrons are diffracted, shown schematically in Figure 4.3.

Figure 4.2. The interaction between the primary electron beam and the sample in an electron microscope leads to a number of detectable signals.

The operational modes of three types of electron microscope are shown schematically in Figure 4.3. In transmission electron microscopy (TEM), which uses transmitted and diffracted electrons, the instrument is in a sense similar to an optical microscope, if one replaces optical lenses with electromagnetic lenses. In TEM, a primary electron beam of high energy and high intensity passes through a condenser to produce parallel rays, which impinge on the sample. As the attenuation of the beam depends on the density and the thickness, the transmitted electrons form a two-dimensional projection of the sample mass, which is subsequently magnified by the electron optics to produce a so-called bright-field image. The dark-field image is obtained from the diffracted electron beams, which are slightly off-angle from the transmitted beam. Typical operating conditions of a TEM instrument are 100 to 200 keV
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electrons, $10^{-6}$ mbar vacuum, 0.3 nm resolution, and a magnification of $3 \cdot 10^5$ to $10^6$. Scanning electron microscopy (SEM) is carried out by rastering a narrow electron beam over the surface, and detecting the yield of either secondary or backscattered electrons as a function of the position of the primary beam. Contrast is caused by the orientation: parts of the surface facing the detector appear brighter than parts of the surface with their surface normal pointing away from the detector. The secondary electrons have mostly low energies (~5 to 50 eV), and originate from the surface region of the sample. Backscattered electrons come from deeper and carry information on the composition of the sample, because heavy elements are more efficient scatterers and appear brighter in the image. While, scanning transmission electron microscopy (STEM) combines the TEM and SEM modes of operation. the scanning coils are used to illuminate a small area of the sample, from which either bright- or dark-field images are obtained. If the primary beam is generated with a field emission gun, the resolution is comparable to that in TEM, with the advantage that selected regions of the sample (e.g., a supported catalyst particle) can be investigated separately.

![Schematic set-up of an electron microscope in the transmission (TEM), scanning (SEM), and combined (STEM) modes.](image)

Figure 4.3. Schematic set-up of an electron microscope in the transmission (TEM), scanning (SEM), and combined (STEM) modes.
Experimental

In the study, the techniques of SEM (along with EDX) and TEM were used to study the morphologies and microstructures of the as-prepared photocatalysts. They were sputter-coated with a thin layer of Au particles and then examined in scanning electron microscopes using a LEO (Zeiss) 1530 Gemini field-emission equipped with an energy-dispersive spectrometer (EDS) (an Oxford Aztec system) for elemental analysis on a microscopic scale. The high-resolution TEM images were collected with a Philips/FEI Tecnai F20 S-TWIN TEM instrument operating at 200 kV. High angle-annular dark field (HAADF) scanning transmission electron microscope (STEM) imaging and EDX chemical analysis was conducted using a JEOL JEM-2200FS transmission electron microscope. The samples were prepared by ultrasonicating the finely ground samples in ethanol and then dispersing them on carbon film supported copper grids.

4.1.3 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is based on the photoelectric effect, that is, a sample which is irradiated with light of sufficiently high energy emits electrons. XPS is a highly surface-sensitive technique with a probing depth of a few nanometers due to the limited escape depth of the emitted electrons, thus can provide information on the elemental composition, on the oxidation state of surface species, and on the dispersion of metal nanoparticles supported on solid substrates. As is shown in Fig. 24, an x-ray photon incident on a sample can ionize an atom producing an ejected free electron. The photoelectron will be emitted with a kinetic energy given by:

\[ KE = h\nu - BE - \Phi \]  

where KE is the kinetic energy of the photoelectrons, \( h\nu \) is the photon energy, BE is the binding energy of the electron to the atom concerned and \( \Phi \) is the spectrometer work function.

In the history of research on photocatalysis, use of XPS was not frequent before 2000. The reason may be that XPS gives information on valency of elements on
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and near the surface of photocatalysts, but the valency of doped (or attached) elements in the bulk of photocatalysts can be elucidated by analyzing the crystal structure by X-ray diffraction (XRD) analysis. The exception was determination of valency of a loaded co-catalyst, such as platinum. In 2001, Asahi et al. reported doping of titania with typical-elements could induce photocatalytic activity under visible-light irradiation (see 3.1 section), and the chance of using XPS has explosively increased, since analysis of valency of doped (or attached) element(s) is important to understand the structures and physical properties of doped samples. In this study, XPS measurements of the as-synthesized products were carried out in an ultrahigh vacuum (UHV) setup equipped with a monochromatic Al-Kα X-ray source (1486.6 eV; anode operating at 14.5 kV and 45 mA) and a high-resolution Gammadata-Scienta SES 2002 analyzer. Charging effects were compensated by applying a flood gun. The XPS spectra were obtained in the fixed transmission mode with pass energy of 200 eV, resulting in an overall energy resolution better than 0.5 eV. The binding energies were calibrated based on the graphite C 1s peak at 284.5 eV. The CASA XPS program with a Gaussian-Lorentzian mix function and Shirley background subtraction were used to analyze the XPS spectra quantitatively.

Figure 4.4. Schematic diagram showing the basic principle of XPS.
4.1.4 Ultraviolet-visible diffuse reflectance spectroscopy

Light cannot penetrate opaque (solid) samples, since it is at least partly is reflected on the surface of the samples. As shown in Figure 4.5, incident light reflection symmetrically with respect to the normal line is called "specular reflection," while incident light scattering in different directions is called "diffuse reflection." Diffuse Reflectance and Ultraviolet-Visible Absorption Spectrometry are some of the most fundamental ways to probe the excited state of a wide variety of species.

![Figure 4.5. General reflection mechanisms.](image)

Diffuse reflectance measurements are usually made by using a UV-visible spectrophotometer equipped with a diffuse reflectance accessory (integrating sphere) capable of collecting the reflected radiation over almost the entire solid angle. Inside integrating spheres, which is with coating a reference high-reflectance standard material inside, for example, MgO, BaSO4, or polytetrafluoroethylene (PTFE). Radiation is diffusely reflected multiple times.\(^{[142]}\)

Measurement is performed by placing the sample in front of the incident light window, and concentrating the light reflected from the sample on the detector. Although spheres collect almost all the light, the measurement area (labeled \(f_m\) in Figure 4.6) that determines the flux reaching the detector is actually small. A baffle (screen) can prevent direct reflection of light from the sample onto the measurement area, which simplifies the equations that need to be applied to describe reflection inside the sphere. With the aid of a gloss trap, the
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contribution of regularly reflected light can be determined. Generally, integrating spheres are used to measure materials properties with high accuracy and precision.

Figure 4.6. Schematic drawing of an integrating sphere with incident light from source (L), screen, and gloss trap. The area imaged on to the detector, \( f_m \), is relatively small.

Based upon the onset of the diffuse reflectance spectra of the powdered materials, the absorption edge and band gap energies were determined by analysis of the Tauc-plots resulting from Kubelka-Munk transformation of diffuse reflectance spectra.\(^{143-145}\) The Kubelka–Munk function \( F(R) \) relates the reflectivity \( R \) (\( R_{\text{sample}}/R_{\text{standard}} \): unitless) of a sample to an absorption coefficient \( \alpha \) (1 cm\(^{-1}\)) and a scattering coefficient \( S \) (1 cm\(^{-1}\)). Many measurements are routinely made on layers thick enough to ensure that a further increase in thickness will fail to change the reflectivity, and Equation 5 yields:

\[
F(R) = \frac{(1 - R)^2}{2R} = \frac{\alpha}{S}
\]

(5)

Based on the assumption of a wavelength-independent scattering coefficient \( S \), \( F(R) \) is proportional to \( \alpha \) and represents the absorbance of a powder material. The absorption spectra of the samples were calculated using the
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Kubelka–Munk function. The band gap of the samples was also calculated by fitting the absorption band edge of the spectra using the following remission Equation 6:

\[ h\nu\alpha \sim (h\nu - E_g)^{1/2} \]  

(6)

Since \( F(R) \) is equivalent to absorbance in the spectrum, the linear portion of a plot \([F(R) h\nu]^2\) (for a direct band gap material) against \( h\nu \) (eV) has an intercept at \( h\nu = E_g \) (eV). Such a plot is frequently utilized to estimate the band gap energy of semiconductors. UV-Vis diffuse reflectance spectra were measured using BaSO\(_4\) or MgO as a reference on a Perkin Elmer Lambda 650 UV-Vis spectrometer equipped with a Praying-Mantis mirror construction or a UV/Vis Varian Cary 4000 spectrophotometer. Band gap energies were calculated by analysis of the Tauc-plots resulting from Kubelka-Munk transformation of diffuse reflectance spectra.

4.1.5 Nitrogen physisorption

The specific surface area of a powder is determined by physical adsorption of a gas on the surface of the solid and by calculating the amount of adsorbate gas corresponding to a monomolecular layer on the surface. Physical adsorption results from relatively weak forces (van der Waals forces) between the adsorbate gas molecules and the adsorbent surface area of the test powder. The determination is usually carried out at the temperature of liquid nitrogen. For powders of low specific surface area (< 1 m\(^2\)·g\(^{-1}\)) the proportion adsorbed is low. Thus, the use of krypton at 87K is preferred in such cases since the low vapour pressure exerted by this gas greatly reduces the error. The amount of gas adsorbed can be determined by the measurements of the amount of gas leaving the gas phase (i.e. gas volumetric methods), the uptake of the gas by the adsorbent (gravimetric method, e.g. direct determination of increase in mass by an adsorption balance), or the concentration changes of gas in a continuous flow system under defined conditions of temperature and pressure (continuous
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flow method), respectively.

Based on a simplified model of physisorption and the adsorption isotherm, the Brunauer–Emmett–Teller (BET) method is widely used for evaluating the surface area of catalysts and solid supports. Assuming that (a) gas molecules can be physically adsorbed on a solid in layers infinitely, (b) there is no interaction between each adsorption layer and (c) the Langmuir theory can be applied to each layer, which is a theory for monolayer molecular adsorption. The data can be treated according to the Brunauer-Emmett-Teller (BET) adsorption isotherm equation:

$$\frac{1}{V_a(\frac{P}{P_0} - 1)} = \frac{C}{V_m C} \times \frac{P}{P_0} + \frac{1}{V_m C}$$  \hspace{1cm} (7)

where $P$ (Pa) is partial vapour pressure of adsorbate gas in equilibrium with the surface at 77.4 K - b.p. of liquid nitrogen;

$P_0$ is saturation pressure of adsorbate gas;

$V_a$ is volume of gas adsorbed at standard temperature and pressure (STP) [273.15 K and atmospheric pressure (1.013 x 105 Pa)];

$V_m$ is volume of gas adsorbed at STP to produce an apparent monolayer on the sample surface,

C is dimensionless constant that is related to the enthalpy of adsorption of the adsorbate gas on the powder sample, depending on the temperature and the gas/solid system.

$$c = \exp\left(\frac{E_1 - E_L}{RT}\right)$$  \hspace{1cm} (8)

where $E_1$ is the heat of adsorption for the first layer, and $E_L$ is that for the second and higher layers and is equal to the heat of liquefaction.

A value of $V_a$ is measured at each of not less than 3 values of $P/P_0$. Then the BET value is plotted against $P/P_0$ according to equation (8):
Then the values of $C$ and $V_m$ can be easily calculated from the slope and intercept of the line. The specific surface area, $a_{BET}$, in m$^2$·g$^{-1}$, is calculated by the equation (8):

$$a_{BET} = V_m N_A \sigma$$

where $\sigma$ is the area occupied by a single adsorbate molecule (i.e. the effective molecular cross-sectional area) in the completed monolayer and $N_A$ is the Avogadro constant.

In my study, the gas adsorption/desorption techniques by gas volumetric method were used to determine the surface area of the as-prepared photocatalysts. Static N$_2$ physisorption measurements were carried out at 77 K using an Autosorb-1 MP Quantachrome system. Before the measurements, the samples were degassed at 200 °C for 2-6 h.

4.1.6 Thermogravimetry

Thermogravimetry (TG) is the thermal analysis of the mass variations of a sample versus time or temperature in a controlled atmosphere, which provides information related to a mass loss (e.g. drying, desorption, reduction) or a mass gain (e.g. wetting, oxidation, adsorption). TG relies on highly precise measurements of mass change, temperature and temperature change, which, therefore, requires a precision balance with a crucible loaded with sample and a precisely programmable furnace. A schematic diagram of a commonly used TG apparatus is shown in Figure 4.7. The derivative processing of the thermogravimetric signal allows one to distinguish more accurately the mass variations. In thermogravimetric analysis (TGA) is the weight of material studied as a function of time and temperature in various atmospheric conditions. This makes possible the study of the thermal stability of materials, the functionality of anti-oxidants, solvent evaporation, degradation of materials,
patterns, and others. TG is commonly coupled with other techniques, e.g., mass spectroscopy, differential scanning calorimetry and infrared spectroscopy, in order to obtain more information on the physical and chemical phenomenon under thermal conditions. The TGA is also the perfect tool for quality control checks on precious metals such as oxidation, the determination of the conversion reaction, fire retarded composites.

Thermalgravimetric analyses were conducted with a TG/DSC NETZSCH STA 409 PC instrument from room temperature to 1000 °C at a heating rate of 5 °C·min⁻¹ under nitrogen flow of 300 mL/min. As will be discussed below in Chapter 8 and 9, the content of graphitic carbon nitride in the as-synthesized hybrid composite sample was calculated by this technique.

Figure 4. 7. Schematic diagram of a commonly used TG apparatus.
4.2 Photocatalytic performance evaluation

4.2.1 Photocatalytic water splitting

Photocatalytic hydrogen production was performed in a typical double-walled inner irradiation-type quartz reactor connected to a closed gas evolution system shown in Figure 4.8. The reaction temperature was maintained at 283 K to prevent any thermal catalytic effect with a double-walled quartz jacket filled with a flow of cooling water from a thermostat (LAUDA). A 500 W Hg mid-pressure immersion lamp (Peschl UV-Consulting, operated at 72% power of 700 W) was used as a light source for irradiation considering the potential hazards by UV rays from the lamp. Gas evolution was measured online using a multichannel analyser (Emerson) equipped with a detector for the determination of the concentration of hydrogen (thermal conductivity detector), oxygen (paramagnetism) and carbon dioxide (IR). High-purity Argon (99.9999%) was used as a carrier gas for the reaction products, of which continuous gas flow was set to 50 NmL/min controlled by a Bronkhorst mass flow controller (MFC). The evolved gases were analyzed online using an analyzer (Emerson) equipped with a thermal conductivity detector for the determination of the concentration of hydrogen. Typically, an adequate amount of the photocatalyst powder was suspended in 500 mL pure water. Prior to irradiation, the whole system including the photocatalysts was purged with argon at 100 NmL/min to remove air completely.
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Figure 4.8. Schematic diagram of reaction setup for photocatalytic water splitting and photograph of quartz reactor (Inset).

4.2.2 Photocatalytic degradation

The photocatalytic reaction system consisted of a 300 W Xe arc lamp, a GG400 filter (providing the visible light of different wavelength, > 400 nm) and a Schott KG3 IR filter (preventing from thermal catalytic effect). The suspension was irradiated from the top of photoreactor with a fixed distance of around 9.5 cm. All experiments were conducted at room temperature in air. As a hazardous organic pollutant, methylene blue (MB) was adopted to evaluate the photocatalytic performance of as-prepared samples presented in Chapter 8 and 9. Typically, 0.05 g of catalysts was added into 100 mL of 10.0 mg·L⁻¹ MB solution. Prior to irradiation, the suspension was magnetically stirred in the dark for 40 min to reach the adsorption-desorption equilibrium of MB on photocatalysts. Under irradiation, approximately 4 mL suspension was collected at given time intervals and separated through a syringe driven filter unit (Millex, Millipore Corp., USA). The degradation of MB was detected by measuring its maximum absorption at 665 nm on a Cary 4000 UV/Vis Varian spectrophotometer or Perkin-Elmer Lambda 650 UV-Vis spectrometer.
Figure 4.9. (Left) Schematic diagram of reaction setup for photocatalytic degradation of methylene blue; (Right) a photograph of reaction setup equipped with 300 W xenon arc lamp and arc lamp power controller (Newport Corporation).
5 Fabrication of calcium tantalate nanocomposite photocatalysts by control of phase coexistence

5.1 Brief introduction

Due to the coexistence phenomenon commonly occurring in preparation of calcium tantalate, it is difficult to prepare phase-pure calcium tantalates by conventional methods.\cite{146-149} Until now only pure cubic Ca$_2$Ta$_2$O$_7$\cite{150} and orthorhombic β-CaTa$_2$O$_6$\cite{151} phases were prepared under unfavorable synthetic conditions, thus leading to very low photocatalytic activities. Herein, we report a series of phase-controlled and composition-tuned calcium tantalate photocatalyst composites, namely α/hex.-type composite (cubic α-CaTa$_2$O$_6$ /hexagonal Ca$_2$Ta$_2$O$_7$), α/hex./β-type composite (cubic α-CaTa$_2$O$_6$/hexagonal Ca$_2$Ta$_2$O$_7$/orthorhombic β-CaTa$_2$O$_6$) and α/β-type composite (cubic α-CaTa$_2$O$_6$/orthorhombic β-CaTa$_2$O$_6$). Taking the advantage of phase coexistence, they are easily prepared via adjusting the initial atomic ratio of Ta/Ca precursors in eutectic mixtures of NaCl and KCl salts. Without any co-catalysts, these composites with optimum phase composition exhibit drastically enhanced photocatalytic hydrogen evolution activities from an aqueous methanol solution. The presented data show how important a controlled construction of composites of different phases is for the development of efficient photocatalysts for conversion of solar energy to chemical energy.

5.2 Photocatalysts preparation

All chemicals used were of analytical grade and used without further purification. In a typical procedure, the calcium tantalate composite systems were prepared by molten salt synthetic method (Figure 5.1). The desired Ta/Ca atomic ratio of Ta$_2$O$_5$ (99.85%, Alfa Aesar) and Ca$_2$CO$_3$ (99.5%, Alfa Aesar) precursors were grinded together with a mixture of 45:55 wt% NaCl/KCl salts (NaCl: 99.0%, Alfa Aesar; KCl: 99.5%, Honeywell Riedel-de Haën) at a weight ratio of 1 to 2, and calcined at 1123 K for 2 h in air using a corundum crucible.
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The resulting white powder was extensively washed with distilled water, and then dried at 353 K for 6 h. The as-synthesized samples at different Ta/Ca atomic ratio are defined as 0.9TC-2.0TC, with reference to the Ta/Ca atomic ratio from 0.9 to 2.0.

![Figure 5.1. Experimental flow chart of molten salts synthesis procedure.](image)

5.3 Results and discussion

5.3.1 Synthesis parameters determination

Owing to considerations of nontoxicity, thermal stability, recyclability and economic efficiency,\textsuperscript{[152]} the chloride salts were chosen as eutectic medium. Especially, the mixture of NaCl and KCl salts with a 0.45/0.55 eutectic composition has the lowest melting point (mp) at 918 K, compared with the pure salts (NaCl, mp= 1078 K, KCl, mp= 1047 K).\textsuperscript{[153]} In order to determine the appropriate reaction temperature, the typical sample with the Ta/Ca ratio of 1.0 was first prepared under different reaction temperatures at a constant reaction time of 2 h. Powder X-ray diffraction (XRD) was used to determine the temperature-dependent phase transformations. As shown in Figure 5. 2, the XRD patterns within the angular range (2θ) of 20–40° show at a low reaction temperature (973 K, which is higher than the melting point of the salt mixture), the formation of a Ca-rich monoclinic Ca$_4$Ta$_2$O$_9$ phase compound (JCPDS No.31-0103) and residue Ta$_2$O$_5$ precursor were observed. When the reaction temperature was increased to 1123 K, the hexagonal Ca$_2$Ta$_2$O$_7$ phase with the distorted pyrochlore structure (JCPDS No.44-1008) was dominantly formed accompanied with low amounts of Ca-riched monoclinic Ca$_4$Ta$_2$O$_9$ and Ta-rich
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cubic $\alpha$-CaTa$_2$O$_6$ (JCPDS No.36-0805). Whereas at higher reaction temperature (> 1123 K), the diffraction peaks of the hexagonal Ca$_2$Ta$_2$O$_7$ phase become much sharper and stronger, indicating higher reaction temperatures giving rise to the growth of larger crystallines. Meanwhile, it is effective in favoring phase transitions of monoclinic Ca$_4$Ta$_2$O$_9$ and cubic $\alpha$-CaTa$_2$O$_6$ to hexagonal Ca$_2$Ta$_2$O$_7$ phase compound. Therefore, I decided to use the reaction temperature of 1123 K for preparation of calcium tantalate composite with different Ta/Ca atomic ratios.

![XRD patterns](image)

Figure 5.2. XRD patterns of the samples with the Ta/Ca ratio of 1.0 prepared at different reaction temperatures within the angular range (2$\theta$) of 20–40$^\circ$.

5.3.2 Nanocomposite characterization

The samples with different Ta/Ca atomic ratios prepared at 1123 K in the range of 0.9-2.0 were denoted as 0.9TC-2.0TC hereafter. The XRD patterns within the angular range (2$\theta$) of 10-60$^\circ$ indicate that all diffraction peaks can be indexed with the corresponding standard diffraction patterns. No evident shifts in the peak positions were observed in these composites (Figure 5.3). The diffraction patterns of these samples within the angular range (2$\theta$) of 22–30.5$^\circ$ are presented in Figure 5.4. As shown in Figure 5.4A, in 0.9TC sample, hexagonal Ca$_4$Ta$_2$O$_9$ phase compound was identified as the main phase with very few coexisting monoclinic Ca$_4$Ta$_2$O$_9$ phase compound. The strongest intensity of
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[201] plane, which disappeared in samples with higher Ta/Ca ratios than 1.0, was observed as well in the 0.9TC sample. Along with the increase of Ta/Ca ratio from 1.0 to 1.3, the phase proportion of the cubic $\alpha$-CaTa$_2$O$_6$ phase compound with respect to hexagonal Ca$_2$Ta$_2$O$_7$ is increasing, shown by the increasing intensive cubic $\alpha$-CaTa$_2$O$_6$ diffraction peak at $2\theta=22.8^\circ$. It reveals that the $\alpha$/hex.-type composite system could be finely tuned by controlling the Ta/Ca ratio in the range of 1.0-1.3, further increasing the Ta/Ca ratio from 1.3 to 1.7 (Figure 5.4B), it can be clearly observed that the increasing intensities of $\alpha$-CaTa$_2$O$_6$ and $\beta$-CaTa$_2$O$_6$ phase compound (JCPDS No.39-1430) reflections were accompanied with a decrease of hexagonal Ca$_2$Ta$_2$O$_7$ phase. Interestingly, in the samples with higher Ta/Ca ratio samples of 1.8-2.0 (Figure 5.4C), the hexagonal Ca$_2$Ta$_2$O$_7$ phase compound disappeared, and instead, a polymorphic composite consisting of the predominately present $\alpha$-CaTa$_2$O$_6$ and $\beta$-CaTa$_2$O$_6$ was obtained. However, a new Ta-rich phase, i.e.-hexagonal CaTa$_4$O$_{11}$ (JCPDS No.15-0679) appeared when the Ta/Ca ratio was increased to 2.0 or higher.

As displayed in Figure 5.5A, along with the increase of Ta/Ca ratio, the Kubelka-Munk transformation of UV-Vis diffuse reflectance spectra of the samples show an obvious red shift of the absorption edge and Tauc plots (inset) provide an estimate of the optical band gap energies. The estimated band gap values (Figure 5.5B) decreased gradually from ca. 4.75 eV to ca. 4.50 eV. This tendency is in good agreement with the variation in the phase composition demonstrating the hexagonal Ca$_2$Ta$_2$O$_7$ gradually disappearing accompanied by the dominance of the CaTa$_3$O$_6$ polymorphs, provided the band energies of as-synthesized phases are in accordance with the reported band gap of cubic Ca$_2$Ta$_2$O$_7$ and $\beta$-CaTa$_2$O$_6$ at 4.4 eV and 4.0 eV, respectively. It is important to note that samples with a narrower band gap can always absorb more photons and consequently excite more electrons to the conduction band. Thus, this might have a considerable effect on the higher Ta/Ca ratio of samples with enhanced photocatalytic activity (see below). A slight increase of the estimated band gap from 1.4TC to 1.8TC is probably affected by the
Formation of β-CaTa₂O₆, presumably indicating that the band gap of β-CaTa₂O₆ is slightly larger than that of α-CaTa₂O₆. The measured band gap values are slightly larger than the ones reported for the corresponding polymorphs.
Figure 5.3. XRD patterns of the as-synthesized different Ta/Ca ratio samples within the angular range of 10-60°: a) 0.9TC-1.3TC, b) 1.3TC-1.7TC, c) 1.8TC-2.0TC.
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Figure 5.4. XRD patterns of samples with different Ta/Ca ratio within the angular range (2θ) of 22–30.5°: A) 0.9TC-1.3TC, B) 1.3TC-1.7TC, C) 1.8TC-2.0TC. This can be attributed to different degrees of disorder and different amounts of crystal defects in these different calcium tantalate polymorphs. Meanwhile, with increasing initial Ta/Ca ratio, it was found that the BET surface areas significantly increase to a maximum value of about 9.8 m²/g for 1.5TC and then negligibly decrease to about 7.8 m²/g for 2.0TC (Figure 5.5C). It is believed, by employing eutectic salts medium, the significant improvement in BET surface of the samples could provide more active sites as a light-harvesting
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unit and a photocatalytic active center, and thus have a beneficial effect on photocatalytic H₂ production.

![Graph A](image)

- **Graph A**: Plot of F(R) / a.u. against Wavelength / nm for different Ta/Ca atomic ratios (0.9 TC to 2.0 TC).

![Graph B](image)

- **Graph B**: Plot of Estimated band gap (eV) against Initial Ta/Ca atomic ratio.

**Estimated band gap (eV)**

<table>
<thead>
<tr>
<th>Initial Ta/Ca atomic ratio</th>
<th>Estimated band gap (eV)</th>
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</tr>
<tr>
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<td>4.60</td>
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</tbody>
</table>
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High angle-annular dark field (HAADF) STEM micrographs and EDX elemental mappings of the 1.2TC (a), 1.6TC (b) and 1.8TC (c) samples are shown in Figure 5.7. The distributions of Ca, Ta and O in 1.2TC (a 1-3) and 1.6TC (b 1-3) samples are inhomogeneous, due to the phase components with different chemical composition (Ca$_2$Ta$_2$O$_7$ and CaTa$_2$O$_6$). Quantitative EDX spot analysis further confirmed that the Ta/Ca atomic ratio are different in the selected spots and varied from the empirical Ta/Ca ratio of 1:1 for Ca$_2$Ta$_2$O$_7$ to 2:1 for CaTa$_2$O$_6$ in the samples of 1.2TC (a4) and 1.6TC (b4), indicating that the different calcium tantalate phases are combined by junctions in the aggregated particles. As shown in the elemental maps (c 1-3) and spot analysis (c4) of 1.8TC, which are composed of polymorphic $\alpha$-CaTa$_2$O$_6$ and $\beta$-CaTa$_2$O$_6$ phases, the component elements of Ca, Ta and O distributed uniformly and the calculated elemental ratios are in good agreement with the chemical composition of CaTa$_2$O$_6$.

Figure 5.7 shows representative SEM images of as-synthesized 1.2TC (a), 1.6TC (b) and 1.8TC(c) samples, displaying the distinct morphological evolution. The
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1.2 TC is mainly composed of truncated hexagonal bipyramids of 0.2-0.5 µm in size, surrounded by a small portion of irregular particles. With the increasing of Ta/Ca ratio to 1.8TC, we can clearly see that an increasing number of elongated “truncated pyramid-like” shape microrods with a length of about 1.5 µm is formed, attached by a larger number of ordered and uniform nanocuboid aggregates. It indicates that the nano-crystallization of constituent particles occurred along with the phase transformation in the higher Ta/Ca ratio samples, in good agreement with their increased specific surface areas as mentioned above. It shortens the transport paths for photo-induced electrons and holes to the reactive surface sites, thus reducing lattice recombination.\textsuperscript{154}

From the representative lattice-resolved HRTEM images of 1.2TC of $\alpha$/hex.-type composite (d), 1.6TC of $\alpha$/hex./$\beta$-type composite (e) and 1.8TC of $\alpha$/$\beta$-type composite (f) samples in Figure 5. 7, the lattice fringes can be clearly observed, suggesting the well-defined crystal structure. The interplanar spacings observed are consistent with the values in the standard JCPDS cards as mentioned above. From the HRTEM image of 1.2TC (Figure 5. 7 d), the interplanar spacings at 0.29(9) nm and 0.38(8) nm can be assigned to the [202] plane of hexagonal Ca$_2$Ta$_2$O$_7$ (marked as Hex.) and the [200] plane of $\alpha$-CaTa$_2$O$_6$ (marked as $\alpha$), respectively. As displayed in Figure 5. 7 e, an intimate contact of the [200] plane of a $\alpha$-CaTa$_2$O$_6$ particle (lattice spacing: 0.38(7)), the [003] plane of a hexagonal Ca$_2$Ta$_2$O$_7$ particle (spacing: 0.60(3)) and the [020] plane of a $\beta$-CaTa$_2$O$_6$ particle (marked as $\beta$, lattice spacing: 0.37(5) nm) is observed in 1.6TC sample. Similarly, the HRTEM image of 1.8TC (Figure 5. 7f), shows the fringes of d=0.38(8) nm and d=0.29(6) nm matching the [200] plane of $\alpha$-CaTa$_2$O$_6$ and the [121] plane of $\beta$-CaTa$_2$O$_6$, respectively. These results further demonstrate the existence of interface junctions among the phase components being in close contact in these composites, and playing a vital role in the interfacial charge transfer processes.\textsuperscript{155}
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Figure 5.6. High angle-annular dark field (HAADF) STEM micrographs of as-synthesized samples: 1.2TC (a), 1.6TC (b) and 1.8TC (c); the corresponding elemental maps of Ca K, Ta M and O K and the elemental composition analysis of the selected area orderly presented from 1 to 4, respectively.

Figure 5.7. SEM and HRTEM images of the as-synthesized samples with different Ta/Ca ratio: (a, d) 1.2TC, (b, e) 1.6TC, (c, f) 1.8TC, respectively.

The XPS survey spectra of the 1.2TC (a), 1.6TC (b) and 1.8TC (c) samples are presented in Figure 5.8, show that the surface components of Ca, Ta, O, and Na.
The Ca 2p, Ta 4f and O 1s spectra, obtained by region scans (Figure 5. 9), show no detectable changes regarding the oxidation states, and each element is present in the expected state in accordance with reference data.\cite{156-157} Surface compositions are derived from quantitative analysis of the recorded XPS results (see Table 5. 1), which are in good agreement with the EDX results. In addition to Ca and Ta, a relatively weak signal of sodium from the residual salts was also found on the surface of the composites shown by the Na 1s and Na KLL peaks (centered at 1072.0 and 493.0 eV, respectively). The concentration of Na varied randomly at a low level, probably caused by the adsorption of Na\textsuperscript{+} on the surface from the molten salts that cannot be readily washed out with distilled water.\cite{158-160}

Figure 5. 8. X-ray photoelectron spectrum of survey scans for samples with different Ta/Ca ratio: a) 1.2TC, b) 1.6TC, b) 1.8TC.
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![Graphical representation of Ca 2p, Ta 4f and O1s regions for 1.2TC, 1.6TC and 1.8TC samples.](image)

**Figure 5.9.** Narrow scans of Ca 2p, Ta 4f and O1s regions for 1.2TC, 1.6TC and 1.8TC samples.

**Table 5.1.** Calculated elemental compositions of Ca, Ta, O and Na from the surface of the samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>At.%</th>
<th>Ca</th>
<th>Ta</th>
<th>O</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2TC</td>
<td>15.2</td>
<td>26.2</td>
<td>57.3</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>1.6TC</td>
<td>14.3</td>
<td>27.1</td>
<td>57.6</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>1.8TC</td>
<td>13.5</td>
<td>27.6</td>
<td>57.4</td>
<td>1.5</td>
<td></td>
</tr>
</tbody>
</table>

Based on the reasonable assumption as the calculated band gaps close to the corresponding band gap of reported modifications (cubic Ca$_2$Ta$_2$O$_7$, 4.4 eV, $^{[150]}$ orthorhombic CaTa$_2$O$_6$, 4.0 eV$^{[151]}$), the theoretical predictions of the position of band edges of Ca$_2$Ta$_2$O$_7$ and CaTa$_2$O$_6$ by Butler and Ginley method$^{[161]}$ using the equation related to Mulliken electronegativity. Thereby, the conduction band (CB) edge positions can be calculated according to the following empirical equation:

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\[ E_{CB} = E^e - X + 0.5E_g \]  

where \( E_{CB} \) is the CB edge potential, \( X \) is the Sanderson electronegativity of the semiconductor, which is the geometric mean of the electronegativity of the constituent atoms, \( E^e \) is the energy of free electrons on the hydrogen scale (4.44 eV), and \( E_g \) is the band gap energy of the semiconductor. The \( X \) values for \( \text{Ca}_2\text{Ta}_2\text{O}_7 \) and \( \text{CaTa}_2\text{O}_6 \) are about 5.73 and 5.96 eV, respectively. The bottom CB level of \( \text{Ca}_2\text{Ta}_2\text{O}_7 \) (~ -0.91 eV) is much more negative than that of \( \text{CaTa}_2\text{O}_6 \) (~ -0.48 eV), therefore, the photoinduced electron-transfer pathways among the conduction band edges of these phase components are proposed in Figure 5.10.

The photoinduced electrons on the surface of \( \text{Ca}_2\text{Ta}_2\text{O}_7 \) particle can easily transfer to \( \text{CaTa}_2\text{O}_6 \) particle via pathway I (from hexagonal \( \text{Ca}_2\text{Ta}_2\text{O}_7 \) to \( \alpha\)-\( \text{CaTa}_2\text{O}_6 \)) and pathway II (from hexagonal \( \text{Ca}_2\text{Ta}_2\text{O}_7 \) to \( \beta\)-\( \text{CaTa}_2\text{O}_6 \)). That means under UV irradiation, the \( \text{CaTa}_2\text{O}_6 \) phases act as more reactive unit in the composite and its surfaces provide much more active sites for \( \text{H}_2 \) production. It is believed that the enhanced photocatalytic performance of \( \text{CaTa}_2\text{O}_6/\text{Ca}_2\text{Ta}_2\text{O}_7 \) composite system is attributed mainly to improved charge transfer via the interface junctions between \( \text{CaTa}_2\text{O}_6 \) and \( \text{Ca}_2\text{Ta}_2\text{O}_7 \). Moreover, trusting that the band gaps of polymorphic \( \text{CaTa}_2\text{O}_6 \) phases are \( \beta \) type > \( \alpha \) type, a difference of CB edge potentials exists between the two materials and thus the photoinduced synergetic effect will greatly favor for the electron transfer pathway III (from \( \beta\)-\( \text{CaTa}_2\text{O}_6 \) to \( \alpha\)-\( \text{CaTa}_2\text{O}_6 \)), due to the same estimated electronegativity for \( \alpha\)-\( \text{CaTa}_2\text{O}_6 \) and \( \beta\)-\( \text{CaTa}_2\text{O}_6 \) (5.96 eV). The CB electrons of \( \beta\)-\( \text{CaTa}_2\text{O}_6 \) can be injected into \( \alpha\)-\( \text{CaTa}_2\text{O}_6 \), suppressing the recombination of photoinduced electron-hole pairs. Presumably, more active \( \text{H}_2 \) production sites will be generated on the surface of \( \alpha\)-\( \text{CaTa}_2\text{O}_6 \).
Figure 5.10. The photoinduced electron transfer pathways among the conduction bands of these phase components (pathway I, from hexagonal Ca$_2$Ta$_2$O$_7$ to α-CaTa$_2$O$_6$; pathway II, from hexagonal Ca$_2$Ta$_2$O$_7$ to β-CaTa$_2$O$_6$; pathway III, from β-CaTa$_2$O$_6$ to α-CaTa$_2$O$_6$).

### 5.3.3 Correlations between photocatalytic activity and phase compositions

Photocatalytic activities for H$_2$ production of the as-synthesized samples from 0.9TC to 2.0TC were carried out in the presence of methanol as electron donor. Based on the above theoretical predictions of the conduction band edge of Ca$_2$Ta$_2$O$_7$ and CaTa$_2$O$_6$, a correlation between the suggested trend of phase composition of calcium tantalate composites from XRD results and average photocatalytic H$_2$ production steady rates is presented in Figure 5.11. For the α/hex.-type composites from 1.0 TC to 1.4TC, it is mentioned above that more photons were absorbed with the narrower band gap of these samples and more active sites were available as the increase of special surface areas. However, the photocatalytic H$_2$ evolution from the 1.2TC reach the maximum rate (up to ca. 6.1 mmol/h), rapidly decreased in 1.3TC, and then dropped to a quite low level in 1.4TC. This, which goes not in line with changes in the band gaps (Figure 5.5), can only be ascribed to the synergistic effect of different phases. The inappropriate phase proportion of α-CaTa$_2$O$_6$/hexagonal Ca$_2$Ta$_2$O$_7$ obviously
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led to a significant reduction of the number of their interfaces and thus to a decrease of electron transfer efficiency via pathway I. Besides, in 1.3TC and 1.4TC, the possibility of the formation of \( \beta\)-CaTa\(_2\)O\(_6\) phase in the boundary between \( \alpha\)-CaTa\(_2\)O\(_6\) and hexagonal Ca\(_2\)Ta\(_2\)O\(_7\) phase gives rise to an increased electron diffusion length and hinder the key electron transfer pathway I. With the further increase of the Ta/Ca ratio, the formation of a higher amount of \( \beta\)-CaTa\(_2\)O\(_6\) phase produces more favorable interfaces for electron transfer via pathway II and pathway III, leading to an increase in the synergetic effect. Consistently, another local maximum of the \( \text{H}_2\) evolution rate was observed from 1.6TC. The photocatalytic \( \text{H}_2\) activity of 1.7TC is low again, because the low content of hexagonal Ca\(_2\)Ta\(_2\)O\(_7\) phase results in a serious loss of available interfaces for electron transfer pathways I and II, probably even hampering pathway III as a blocker. Therefore, it can be proposed that the hexagonal Ca\(_2\)Ta\(_2\)O\(_7\) phase acts in a dual-role as photocatalyst but also influences the electron transfer efficiency significantly via its amount in the formed \( \alpha/\text{hex./}\beta\)-composites.

More interestingly, in absence of hexagonal Ca\(_2\)Ta\(_2\)O\(_7\), the polymorphic \( \alpha/\beta \)-type composite of 1.8TC possesses the highest photocatalytic \( \text{H}_2\) evolution rate (ca. 10.3 mmol/h) of all samples. That is, without the blocking effect of a low amount of hexagonal Ca\(_2\)Ta\(_2\)O\(_7\), the dominant electron transfer pathway transforms to pathway III and promotes electron transfer via interfaces between \( \alpha\)- and \( \beta\)-CaTa\(_2\)O\(_6\). Unfortunately, with further incorporation of Ta, the more Ta-rich hexagonal CaTa\(_4\)O\(_{11}\) phase forms in the \( \alpha/\beta \)-type composite, as clearly seen in the XRD pattern of 2.0TC, and consequently leads to the blocking of the electron transfer pathway III. This is probably the primary reason for the decreased photocatalytic \( \text{H}_2\) activity in the \( \alpha/\beta \)-type composite of 1.9TC and 2.0TC. Although in 1.9TC no clear diffraction peaks of the CaTa\(_4\)O\(_{11}\) phase are visible, it is very likely that a small quantity of it being below the detection limit of XRD is already present. In fact, there are also additional reasons to be responsive for the enhanced photoactivity for \( \text{H}_2\) evolution of composites. As
presented above, with the increase of Ta/Ca ratio, the enhanced light harvesting efficiency and the increased surface areas, and the formation of nano-crystallized particles all favor the enhancement of hydrogen production activity. Since these trends, however, go not in line with the H\textsubscript{2} production, it is undoubted that the synergistic effects among the phase components of the calcium tantalate composites are the major factor in the photogenerated charge carrier separation affecting the photocatalytic H\textsubscript{2} production activity. Figure 5.12 depicts the photocatalytic H\textsubscript{2} production yield over the 1.2TC, 1.6TC and 1.8TC samples, respectively. The continuous and stable H\textsubscript{2} evolution was observed during the reaction course by an intermittent irradiation and purging the evolved gases. The slight deactivation of H\textsubscript{2} evolution after the intermittent evacuation was typically due to the surface absorption of some byproduct arising from the sacrificial agent decomposition.\textsuperscript{[93,105]} No change was observed in these XRD patterns of the recycled samples after the photocatalytic reaction. Therefore, it can be concluded that these composite photocatalysts have considerable photostability during the reaction.

Figure 5.11. Dependence of photocatalytic H\textsubscript{2} production rates on the phase composition of calcium tantalate composite photocatalysts (Reaction conditions: Catalyst, 0.5 g; Water, 500 mL; methanol, 50 mL). Error bars show
the range of evolution rates in at least 3 times reproduced measurements.

Figure 5.12. Photocatalytic H₂ production yield by an intermittent irradiation over 1.2TC, 1.6TC and 1.8TC samples (Reaction conditions: catalyst, 0.5 g; Water, 500 mL; methanol, 50 mL).
5.4 Conclusions

In summary, by aid of the simple and cost-effective molten salts method, a series of phase-controlled and composition-tuned calcium tantalate composite photocatalysts has been prepared by adjusting the initial atomic ratio of Ta/Ca precursors. Without any co-catalysts, these composites with the optimized phase composition of either cubic $\alpha$-CaTa$_2$O$_6$/hexagonal Ca$_5$Ta$_2$O$_7$, or cubic CaTa$_2$O$_6$/hexagonal Ca$_5$Ta$_2$O$_7$/orthorhombic $\beta$-CaTa$_2$O$_6$, or cubic $\alpha$-CaTa$_2$O$_6$/orthorhombic $\beta$-CaTa$_2$O$_6$ showed very high photocatalytic H$_2$ production activities in the presence of methanol. It is attributed mainly to a significantly improved photo-excited charge carrier separation via the junctions and interfaces in the composites. Moreover, a strong correlation between the phase composition of the calcium tantalate composites and the photocatalytic hydrogen activities was demonstrated. HRTEM, STEM-EDX spot analysis and elemental mapping provide reliable evidence for the formation of phase junctions. A resulting synergistic effect of phase components on the phase-coexisted calcium tantalate composites significantly enhances the photogenerated charge carrier separation and thereby improves the photocatalytic H$_2$ production activity. As phase-coexistence phenomena are quite common in nature, fabrication of a composite photocatalyst can be conveniently achieved by fine-tuning the ratio of raw materials. This strategy will open up new avenues of fabrication of efficient H$_2$ evolution photocatalysts for the conversion of solar energy to chemical energy.
6 Calcium tantalate nanocomposites photocatalysts for overall water splitting, alcohol and biomass reforming

6.1 Brief introduction

As an alternative strategy for effective enhancing charge carrier separation and improving photocatalytic efficiency, the rational fabrication of semiconductor composites comprising multicomponent or multiphase heterojunctions have attracted increasing attention.[121] Three different kinds of calcium tantalate composite photocatalysts with optimum phase composition were prepared, as presented above, by control of the initial ratio of Ta/Ca precursors at 1.2, 1.6 and 1.8, respectively, i.e. 1.2TC of cubic $\alpha$-CaTa$_2$O$_6$/hexagonal Ca$_2$Ta$_2$O$_7$ composite, 1.6TC of cubic CaTa$_2$O$_6$/hexagonal Ca$_2$Ta$_2$O$_7$/orthorhombic $\beta$-CaTa$_2$O$_6$ composite, and 1.8TC of cubic $\alpha$-CaTa$_2$O$_6$/orthorhombic CaTa$_2$O$_6$ composite, respectively. A strong correlation has been demonstrated between the photocatalytic hydrogen production activities of the calcium tantalate composite photocatalysts in aqueous methanol solution under UV irradiation and the synergistic effect of the coexisting phases. Therefore, the objective of this work was to extend use these calcium tantalate composite photocatalysts with optimum phase-composition for overall water splitting, and alcohol and biomass reformation. In absence of any co-catalysts, a comparative study to demonstrate the photocatalytic H$_2$ production activities of these nanocomposites for photocatalytic reforming of different alcohols and biomass derivates was also performed. By in-situ photodeposition of noble metal nanoparticles (Pt or Rh) as co-catalysts, the photocatalytic activity of these composites was studied for H$_2$ production in presence of methanol. Furthermore, since NiO$_x$ is a cheap and effective co-catalyst for overall water splitting, the influence of NiO$_x$ loading as co-catalysts for overall water splitting is investigated in detail.
6.2 Experimental

6.2.1 Photocatalysts preparation

As described in Section 5.2, calcium tantalate composite photocatalysts with optimum phase-composition were prepared by use of molten salts method. The samples with the optimum Ta/Ca atomic ratio of 1.2, 1.6 and 1.8 are denoted as 1.2TC, 1.6TC and 1.8TC, respectively.

6.2.2 Co-catalyst loading

The noble metal of platinum Pt or rhodium Rh was loaded as co-catalysts by in situ photodeposition method using H₂PtCl₆.6H₂O (Sigma-Aldrich) or Na₃RhCl₆ (Sigma-Aldrich), respectively.

The photocatalysts with different loading amount of Ni/NiO double-layered structure co-catalysts (denoted as NiOₓ hereafter) as a function of Ni content (between 0.2, and 2.0 wt%) were prepared by impregnation method. The powder samples were dispersed in a freshly prepared Ni(NO₃)₂ solution (99.9985%, STREM Chemicals) and heated under constant stirring until the water was completely evaporated. The resulting powder was dried at 353 K in air, followed by calcination at 473 K for 2 h, and further treated by reduction under H₂ flow at 573 K for 2 h and re-oxidation under O₂ flow at 473 K for 1 h. The NiOₓ loaded calcium tantalate composite photocatalysts are generally denoted by NiOₓ/TCs. For example, the 1.2TC composite photocatalyst with loading of 0.5 wt% NiOₓ co-catalysts are described in shorthand by 0.5 wt% NiOₓ/1.2TC.

6.3 Results and discussion

6.3.1 Characterization of nanocomposite photocatalysts

Figure 6.1 shows the XRD patterns of 1.2TC (a), 1.6TC (b) and 1.8TC (c) composite photocatalysts: bare, as-synthesized 0.5 wt% NiOₓ loaded, and recycled 0.5 wt% NiOₓ loaded after reaction, respectively. The crystalline phases were identified in reference to standard JCPDS cards. In good agreement with
our previous results, the XRD patterns indicate that the 1.2TC, 1.6TC and 1.8TC samples were composed of cubic $\alpha$-CaTa$_2$O$_6$ (JCPDS No.36-0805)/hexagonal Ca$_2$Ta$_2$O$_7$ (JCPDS No.44-1008) phase compounds, cubic CaTa$_2$O$_6$/hexagonal Ca$_2$Ta$_2$O$_7$/orthorhombic $\beta$-CaTa$_2$O$_6$ (JCPDS No.39-1430) phases and cubic $\alpha$-CaTa$_2$O$_6$/orthorhombic CaTa$_2$O$_6$ phase compounds, respectively. Moreover, no diffraction peaks of NiO$_x$ were observed in the XRD patterns of 0.5 wt% NiO$_x$ loaded composite samples, probably due to low loading below the detection limit of XRD analysis and/or a high dispersion of NiO$_x$ on the surface of composite photocatalysts. After the photocatalytic reaction, no significant change was observed in the XRD patterns of the recycled NiO$_x$ loaded samples. This indicates that the nanocomposite photocatalysts are stable during the water splitting reaction.

Figure 6.1. XRD patterns of bare TCs, as-synthesized and recycled 0.5 wt% NiO$_x$/TCs: a) 1.2TC b) 1.6TC, and c) 1.8TC.
Figure 6.2. SEM (left) and EDX (right) images of the 0.5 wt% NiO$_x$ loaded these TCs: a) 1.2TC, b) 1.6TC and c) 1.8TC.

Figure 6.2 shows SEM (left) and EDX images (right) of these as-synthesized 0.5 wt% NiO$_x$/TCs composites: 1.2TC (a), 1.6TC (b) and 1.8TC (c), respectively. After loading of NiO$_x$ particles on the surface of these composites, no significant changes in morphology were observed from their SEM images. As mentioned above, examination of these samples by XRD only revealed reflections attributable to calcium tantalate phases. However, these composites were examined on a microscopic scale by EDX confirm the presence of nickel species, as shown in the corresponding EDX images. Furthermore, the identification of
nickel species on the surface of the as-synthesized 0.5 wt% NiO$_x$/TCs nanocomposites was performed by XPS analysis. As shown in Figure 6.3, the XP spectra of Ni 2p display a typical Ni$^{2+}$ line-shape with the Ni 2p$_{3/2}$ and Ni 2p$_{1/2}$ peaks located at 853.5 and 871.0 eV and characteristic satellite peaks at 860.5 and 879.0 eV, respectively. The main Ni 2p$_{3/2}$ peak is slightly shifted towards lower binding energy compared to pure NiO. This are consistent with the data previously reported by Chiou, et al.\textsuperscript{[164]} which observed a similar shift of the Ni 2p$_{3/2}$ peak after mild re-oxidation at 473 K compared to a fully oxidized and a reduced sample. The shift is attributed to a combination of NiO and Ni, indicating a core-shell like structure with a thin layer of NiO covering the metal Ni core of particles. Thus, presumably the formation of a Ni metal at the surface of calcium tantalate composite results in the formation of a Schottky barrier at the interface, which decreases the energy position of the calcium tantalate oxides conduction band to its minimum potential level, and thus offers an opportunity to facilitate electron transport to NiO shell and then effectively suppress the backward reaction between H$_2$ and O$_2$ as will be discussed below.\textsuperscript{[165]}
Calcium tantalate nanocomposites photocatalysts for overall water splitting, alcohol and biomass reforming

Figure 6.3. Ni 2p XP spectra of as-synthesized 0.5 wt% NiOx/TCs.

6.3.2 Photocatalytic reforming of alcohols and biomass derivatives without any co-catalysts

The effective utilization of the solar energy for photocatalytic H₂ production is of great importance in order to reduce high production cost and avoid serious environmental issue, while addressing industrial production. Accordingly, the green approach to photochemical synthesis is to develop more efficient photocatalyst materials but abuse expensive and rare noble metals as co-catalysts in order to achieving high efficiency photocatalysis. Therefore, as shown in Figure 6.4, without employing any co-catalysts, additional studies were performed on the photocatalytic activity of the optimized Ta/Ca nanocomposite photocatalysts for H₂ production by photocatalytic reforming of some alcohols, including methanol (MeOH), ethanol (EtOH), isopropyl alcohol (IPOH) and ethylene glycol (EG). Alcohols are known to show the current-doubling effect and the reaction sequence is highly irreversible, and are hence greatly favorable for H₂ production. The hydrogen production efficiency decreased over these different phase-composition composite photocatalysts in the following order: MeOH > EtOH > IPOH > EG. The use of MeOH always provides the best photocatalytic ability for H₂ production, probably because of its highest abilities to donate electrons to scavenge the valence band holes to preventing photogenerated charge recombination. This agrees well with the reported order of hydrogen production efficiency over prototypical photocatalyst of Pt-loaded KCa₂Nb₃O₁₀. Among these different phase-composition composite photocatalysts, the 1.8TC composite photocatalyst possesses the highest hydrogen production rate in these aqueous alcohols solution.

To use by-products from biomass conversion for hydrogen production could be a useful intermediate step between the current fossil fuel energy structure and
Calcium tantalate nanocomposites photocatalysts for overall water splitting, alcohol and biomass reforming

efficient water splitting.\textsuperscript{[169]} The pioneering work of Kawai and Sakata in 1980 showed that hydrogen can be produced from the carbohydrate over RuO\textsubscript{2}/TiO\textsubscript{2}/Pt photocatalyst under light irradiation.\textsuperscript{[170]} Subsequently, they claimed that hydrogen can also be acquired from some other kind of biomasses, such as cellulose, starch, dead insects, and waste materials.\textsuperscript{[171-173]} These works demonstrate the feasibility of producing hydrogen from biomass by the photocatalytic process. The 1.8TC composite photocatalyst (i.e. cubic $\alpha$-CaTa\textsubscript{2}O\textsubscript{6}/$\beta$-orthorhombic CaTa\textsubscript{2}O\textsubscript{6} phases) was further employed toward H\textsubscript{2} production by reforming of typical biomass derivatives. As shown in Figure 6.4c, without using any co-catalysts, the continuous H\textsubscript{2} evolution was observed from reforming of glycerol (GL, 50 mL) and glucose (Glu, 0.1 M). After irradiation for 180 min, the yield of evolved H\textsubscript{2} was measured to be ca. 7.3 mmol and 5.6 mmol from aqueous GL and Glu solutions, respectively. Although be lower than yields from alcohols these results reveal an efficient and noble metal-free photocatalytic biomass reforming system for H\textsubscript{2} production. Despite of major efforts in improving biomass characteristics and conversion efficiency,\textsuperscript{[174-176]} the determination and analysis of the intermediates during photocatalytic reforming process of biomass resources remains an appealing challenge. It is believed that a better understanding of true mechanism will open up many new opportunities in field of photocatalytic biomass conversion.
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(a) Yield of H₂ production (mmol) vs. Time (min.) for different alcohols: MeOH, EtOH, IPOH, EG.

(b) Similar graph as (a) but with updated data and labels.
Figure 6.4. Hydrogen evolution from different alcohols over different optimized phase-composition composite photocatalysts: a) 1.2TC, b) 1.6TC and c) 1.8TC, respectively. (Conditions: 0.5 g of photocatalyst, 500 mL of water, 50 mL of alcohols, 0.1 M of Glu).

6.3.3 Effect of noble metal as co-catalysts

As shown in Figure 6.5, by in situ photodeposited 0.2 wt% of noble metal (platinum Pt or rhodium Rh) as co-catalyst, unsurprisingly, the activities of the composites for photocatalytic H₂ production were greatly improved. The results indicate that the addition of noble metal can directly influence the interfacial charge transfer processes, provide effective sites for electron collection and reduction reactions and thus improve the photocatalytic efficiency. In addition, Rh metal as the auxiliary catalyst also exhibit high photocatalytic performance for H₂ production, comparable to Pt. Nevertheless, Pt is rare and quite expensive. Rh can therefore be considered as cheaper alternative to Pt co-catalysts. [84]
Figure 6.5. Effect of noble metal loading (0.2 wt% of platinum Pt or rhodium Rh) on photocatalytic H$_2$ production rate of these composite photocatalysts (catalyst, 0.5 g; water, 500 mL; methanol, 50 mL).

6.3.4 Effect of NiO$_x$ as co-catalysts

Figure 6.6 shows the photocatalytic activity for overall water splitting of composite photocatalysts with optimized phase-compositions (1.2TC, 1.6TC and 1.8TC) after loading with different amounts of NiO$_x$ (between 0.2 and 2.0 wt%). Without the deposition of NiO$_x$ co-catalysts (i.e. 0 wt% NiO$_x$), the composites exhibit low ability for water splitting into stoichiometric amount of H$_2$ and O$_2$, probably due to the fast recombination of photogenerated electron-hole pairs. With increasing amount of NiO$_x$ as co-catalyst their water splitting activity is markedly enhanced reaching a maximum for a loading of 0.5 wt% NiO$_x$. The results indicate that the NiO$_x$ as co-catalysts not only greatly promotes the transfer of electrons which results in an enhancement of the separation efficiency for photogenerated electron-hole pairs, but also effectively suppresses the backward reaction between H$_2$ and O$_2$. Therefore, it can be explained by cooperative effects between the formation of a Schottky barrier at
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the metallic Ni/calcium tantalate contact region and the existing heterojunctions between nanoparticles of the different phases in these calcium tantalate composites. However, NiO\textsubscript{x} loading above 0.5 wt% lowered the photocatalytic activity, because with higher loading, the light masking by NiO particles might have a considerable detrimental effect on the photoreactivity. The number of surface sites responsive for light absorption is reduced if more NiO\textsubscript{x} is present.

![Diagram showing the effect of NiO\textsubscript{x} loading on photocatalytic activity.](image)

Figure 6.6. Effect of the NiO\textsubscript{x} loading amount on photocatalytic activity of these composites for overall water splitting into an approximately stoichiometric amounts of H\textsubscript{2} and O\textsubscript{2}.

Taking the advantage of our used gas-flow through system, the variations of the evolved H\textsubscript{2} and O\textsubscript{2} rates can be on-line determined. Figure 6.7 illustrates the simultaneous evolution of H\textsubscript{2} and O\textsubscript{2} over the optimum phase-composition composite photocatalysts with optimum loading of 0.5 wt% NiO\textsubscript{x} as a function of irradiation time. The steady evolution of H\textsubscript{2} and O\textsubscript{2} in an approximately stoichiometric amount can be observed.
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Figure 6.7. Steady photocatalytic overall water splitting into stoichiometric amounts of H\textsubscript{2} and O\textsubscript{2} over these 0.5 wt% NiO\textsubscript{x} loaded composite photocatalysts.
6.4 Conclusions

The photocatalytic properties of different calcium tantalate composite photocatalysts with optimized phase-composition were studied after modification with noble metal (Pt or Rh) or double-layered NiOₓ (Ni/NiO) co-catalyst and without the addition of any co-catalysts. Photocatalytic performance in water splitting, and reforming of different alcohols and biomass derivatives is reported. By in-situ photodeposited noble metal nanoparticles (Pt and Rh) in the aqueous MeOH solution, the activities of these composites were further improved for photocatalytic H₂ production. Different amounts of NiOₓ loading were investigated to identify the most favorable conditions. 0.5 wt% NiOₓ loaded composite photocatalysts were found to exhibit the best photocatalytic activities with stable stoichiometric H₂ and O₂ evolution rates. The results indicate that the loading of NiOₓ as co-catalyst is beneficial to the formation of Schottky barriers at metallic Ni/calcium tantalate phases contact regions, and then results in a joint cooperation between the formed Schottky barriers and the interfacial phase junctions in these calcium tantalate composites. Thus, the enhanced electron-hole separation and interfacial charge transfer can account for the improved photocatalytic activities. Moreover, in the absence of any co-catalysts, the efficient photocatalytic H₂ production can also be achieved for photocatalytic reforming of other alcohols and biomass derivatives over these optimized phase-composition composite photocatalysts, as comparison with the highest ability of MeOH as electron donor. We believe that this study offers a route to green solar energy harvesting using a simple and cost-effective approach to fabricate highly active semiconductor composite materials with simple, versatile and scalable techniques.
7 Tetragonal tungsten bronze-type nanorod photocatalysts with tunnel structure: Ta substitution for Nb and overall water splitting

7.1 Brief introduction

During the past few years, several types of semiconductor photocatalysts such as bulk-type simple oxides (TiO$_2$, Nb$_2$O$_5$, Ta$_2$O$_3$, ZnO and ZrO$_2$, etc.) as well as perovskite-type oxides (SrTiO$_3$, K$_4$Nb$_6$O$_{17}$, NaTaO$_3$, and A$_2$La$_2$Ti$_3$O$_{10}$, (A=Ca, Sr, and Ba), etc.) have been widely studied.\textsuperscript{[40, 177-179]} It is well known that the superior photocatalytic ability of layered oxides can be attributed to the unique structure, compared to the above-mentioned bulk-type oxides.\textsuperscript{[180]}

Besides the above layered oxides, the past two decades have also witnessed great efforts on the tunnel oxides (BaTi$_4$O$_9$ and A$_2$Ti$_6$O$_{13}$ (A = Na, K, Rb), etc.).\textsuperscript{[181-182]} The deficient perovskite tetragonal tungsten bronze-type (TTB) niobates-(A$_1$)$_4$(A$_2$)$_2$(A$_3$)$_4$Nb$_{10}$O$_{30}$, consisting of corner-sharing NbO$_6$ octahedra arrays and three different tunnels (A$_1$, A$_2$ and A$_3$) for cation filling have been widely investigated as ferroelectric and piezoelectric materials in view of their large spontaneous polarization and high dielectric constants.\textsuperscript{[183-187]} They also exhibit dominant electron-hole separation and transport via static electric fields between structure-induced dipole moments in distorted metal-oxygen polyhedron. Therefore, a slight structural modification by altering the cation-site occupancy has a dramatic effect on the charge mobility (Figure 7.1). To our knowledge, there have been no reports on photocatalytic properties of the modified tunnel-structure niobates, except for Wu, et al.\textsuperscript{[35]}
Figure 7.1. Crystal structure of tungsten bronze niobate \((A_1)_4(A_2)_2(A_3)_4Nb_{10}O_{30}\) viewed down [001], consisting of corner-sharing \(NbO_6\) octahedra arrays and three different tunnels.

In principle on all the three cation positions \(A_1, A_2\) and \(A_3\) a cation exchange can be done, but since recent studies have shown that the substitution of the Nb site with tantalum (Ta) could considerably improve the photocatalytic activity.\[^{188-189}\] However, most reports of substitution effects are focused on the photodegradation of organic compounds. It still remains a great challenge to directly split water into \(H_2\) and \(O_2\) and determine the variation of the Ta substitution induced-structure properties and photocatalytic behaviour. In present work, by employment of a simple and cost-effective molten salt technique, the \(Sr_2KNb_{5-x}Ta_xO_{15}\) nanorod photocatalysts with different Ta substitution molar ratios were synthesized. The determination of the Ta substitution effect on the photocatalytic behavior for photocatalytic hydrogen production by methanol reforming was systematically investigated.

### 7.2 Experimental

#### 7.2.1 Photocatalysts preparation

Powders of \(Sr_2KNb_{5-x}Ta_xO_{15}\) with \(x = 0, 1, 2.5, 4\) and 5 were prepared by molten salt method. \(SrCO_3\) (≥99.99%, Aldrich), \(K_2CO_3\) (>99.9%, Alfa Aesar), \(Nb_2O_5\)
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(99.99%, Alfa Aesar), and Ta$_2$O$_5$ (99.85%, Alfa Aesar) were used as starting materials. The desired molar ratio of starting materials were grinded together with potassium chloride (KCl: 99.5%, Honeywell Riedel-de Haén) at a weight ratio of 1:2 and then the well-mixed powders were heated at different calcination temperatures for 2 h in air using a corundum crucible. After cooling down to room temperature, the mixture was intensively washed with distilled water in order to remove any residual salts and then dried in air at 80 °C. The 1.0 wt% NiO$_x$ loaded samples were prepared by impregnation method: the powder dispersed in an approximate amount of Ni(NO$_3$)$_2$ (99.9985%, STREM Chemicals) solution and heated under constant stirring until the water was completely evaporated. The resulting powder was dried at 80 °C in air, followed by calcination at 200 °C for 2 h, and further treated by reduction under H$_2$ flow at 300 °C for 2 h and re-oxidation under O$_2$ flow at 200 °C for 1 h.

7.2.2 Photocatalytic activity tests

In a typical run, 0.1 g of photocatalyst powder was suspended in 500 mL pure water. In case of the photocatalytic reforming, methanol (50 mL) was added as a sacrificial reagent. Prior to irradiation, the whole system including the photocatalysts was purged with argon at 100 NmL/min to remove air completely.

7.3 Results and Discussion

7.3.1 Synthesis of materials

In order to determine the optimum calcination temperature, the Sr$_2$KTa$_5$O$_{15}$ was prepared under different calcination temperatures from 850 to 1050 °C (higher than melting point of KCl, 774 °C) and the photocatalytic reactivity of these samples was probed by photocatalytic methanol reforming for H$_2$ production. As shown in Figure 7.2, the diffraction peaks of the Sr$_2$KTa$_5$O$_{15}$ (JCPDS 40-0345) peaks become sharper and stronger, indicating the increase of the average crystallite size and the improvement of the crystallinity of Sr$_2$KTa$_5$O$_{15}$ crystals. As seen from Table 7.1, the average crystallite size of the samples with the
increased calcination temperature were estimated to be about 24, 39 and 46 nm, respectively, according to the well-known Scherrer’s equation from the full width at half maximum (FWHM) of the X-ray diffraction peak at 2θ= 29.47°,[191] which was indexed as (410) reflection. Also, as presented in Table 1, the sample calcined at 850 °C show a high BET surface area of 8.5 m²/g, and an increase in calcination temperature resulted in the significantly decreased surface area of 5.3 and 2.7 m²/g for samples calcined at 950 °C and 1050 °C, respectively. Undoubtedly, the decreased photocatalytic activity for H₂ production can be attributed to the large crystallite size and the decreased specific surface areas as the increase of calcination temperature. Thus, we decided on the preparation temperature for Sr₂KNb₅₋ₓT maxxO₁₅ (x=0, 1, 2.5, 4 and 5) at 850 °C as will be discussed later.

Table 7.1. Effect of calcination temperature on average crystallite size, BET surface area and photocatalytic activity for H₂ production.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Crystallite size (nm)[a]</th>
<th>BET surface area (m²/g)[b]</th>
<th>Rate of H₂ production (mmol/h)[c]</th>
</tr>
</thead>
<tbody>
<tr>
<td>850</td>
<td>35.6-36.4</td>
<td>8.5</td>
<td>1.24</td>
</tr>
<tr>
<td>950</td>
<td>38.2-40.6</td>
<td>5.3</td>
<td>1.23</td>
</tr>
<tr>
<td>1050</td>
<td>45.1-46.2</td>
<td>2.7</td>
<td>1.14</td>
</tr>
</tbody>
</table>

[a] estimated by Scherrer’s method. [b] measured by the Brunauer-Emmett-Teller (BET) method. [c] reaction of conditions: 0.1 g of photocatalysts; 50 mL of methanol dissolved in 500 mL of water; Hg lamp).
Figure 7.2. XRD patterns of typical Sr$_2$KTa$_5$O$_{15}$ samples synthesized under different calcination temperatures for 2 h.

### 7.3.2 Structural properties

X-ray powder diffraction patterns of Sr$_2$KNb$_{5-x}$Ta$_x$O$_{15}$ (x = 0, 1, 2.5, 4 and 5) with different molar ratios of Ta substitution prepared at 850 °C for 2 h are shown in Figure 7.3. All the powders are well-crystallized and no significant shifts are observed in the diffraction patterns. This indicates that Ta$^{5+}$ has diffused into the tetragonal tungsten bronze (TTB) structure to form a solid solution in which Ta$^{5+}$ occupies the Nb lattice sites, because the effective ionic radii of Nb$^{5+}$ and Ta$^{5+}$ ions in the Sr$_2$KNb$_{5-x}$Ta$_x$O$_{15}$ are similar (64 pm), and on the contrary, the effective ionic radius of the Ta$^{5+}$ ion is remarkably smaller than those of the Sr$^{2+}$ ion and the K$^+$ ion.[192] The pattern of our Sr$_2$KNb$_5$O$_{15}$ can be indexed to a TTB structure on basis of the reported data of bulk Sr$_2$KNb$_5$O$_{15}$ crystals (JCPDS 34-0108). However, the most intense reflection is (410), instead of (311, 420), and the intensity of (211) reflection decreases by more than half. This agrees very well with reported results,[193-195] and can be attributed to the anisotropic growth of the Sr$_2$KNb$_5$O$_{15}$ particles leading to a strong (001) orientation. It is important to note that some unknown impurity (< 3%) was observed for Sr$_2$KNb$_5$O$_{15}$, as indicated by the arrows in Figure 7.3a, it means the impurity...
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phases will not significantly modify the properties of the Sr$_2$KNb$_5$O$_{15}$ photocatalyst. Interestingly, no impurity peaks were detected with the increasing x and the phenomenon of the preferred (001) orientation growths of these solid solutions become weaker, indicating that the anisotropic grain growth can be limitedly inhibited by Ta$^{5+}$ substitution. As complete substitution of Ta$^{5+}$ for Nb$^{5+}$, the Sr$_2$KTa$_5$O$_{15}$ phase (JCPDS 40-0345) was derived. On the other hand, the diffraction peak at about 46.3° splits into two peaks (Figure 7.3b). This suggests that the crystal structure transition with symmetric center appeared when substituting Nb$^{5+}$ with Ta$^{5+}$.[196]

![Figure 7.3](image)

Figure 7.3. a) XRD patterns of Sr$_2$KNb$_{5-x}$Ta$_x$O$_{15}$ with x=0, 1, 2.5, 4 and 5 prepared at 850 °C for 2 h, b) Enlarged XRD patterns of the Sr$_2$KNb$_{5-x}$Ta$_x$O$_{15}$ ranging from 2θ = 45°-47°.

Representative SEM images of Sr$_2$KNb$_5$O$_{15}$ (a), Sr$_2$KNb$_{2.5}$Ta$_{2.5}$O$_{15}$ (b) and Sr$_2$KTa$_5$O$_{15}$ (c) samples are shown in Figure 7.4. The samples display a nanorod-shaped morphology with the diameters in the range of 100-400 nm and the length goes up to a few microns, suggesting that the foreign eutectic KCl salt favors the formation of nanorod morphology. With the increase of Ta molar ratio, most of nanorods became more uniform but more agglomerated,
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and grew shorter in length. The results show that the Ta$^{5+}$ substitution is certainly effective in suppressing the grain growth and avoiding abnormal grain growth behavior. The similar suppressing behavior caused by Ta$^{5+}$ substitution was also found in other ceramics systems like $(K_{0.44}Na_{0.52}Li_{0.04})(Nb_{0.96-x}Ta_xSb_{0.04})O_3$, and $Sr_{0.53}Ba_{0.47}Nb_{2-x}Ta_xO_6$. [197-198]
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Figure 7.4. Representative SEM images of Sr$_2$KNb$_5$O$_{15}$ nanorods (a) Sr$_2$KNb$_{2.5}$Ta$_{2.5}$O$_{15}$ (b) and Sr$_2$KTa$_5$O$_{15}$ nanorods (c), respectively.

The microstructure, the lattice parameters and growth properties of the Sr$_2$KNb$_5$O$_{15}$ and Sr$_2$KTa$_5$O$_{15}$ nanorod samples were further studied by TEM, high-resolution TEM (HRTEM), and selected area electron diffraction (SAED). As shown in Figure 7.5a, we can clearly see a TEM image of a typical Sr$_2$KNb$_5$O$_{15}$ nanorod at low magnification. The HRTEM image of the Sr$_2$KNb$_5$O$_{15}$ sample taken from the top part of the Sr$_2$KNb$_5$O$_{15}$ nanorod (as marked by a white rectangle in Figure 7.5a) and the corresponding SAED pattern are presented in Figure 7.5b and Figure 7.5c, respectively. The lattice fringes of the Sr$_2$KNb$_5$O$_{15}$ [001] and [400] planes are found to be about 0.39(0) nm and 0.31(2) nm, respectively and the SAED pattern can be also assigned to tetragonal Sr$_2$KNb$_5$O$_{15}$ single crystals with the electron beam closely parallel to [010] direction. These observations unambiguously indicate that the Sr$_2$KNb$_5$O$_{15}$ nanorod is a high quality single crystal with tetragonal structure and grew along the [001] direction (marked by a white arrow in Figure 7.5b). Moreover, a typical Sr$_2$KTa$_5$O$_{15}$ nanorod can be observed in the low-magnification TEM image of Figure 7.6a, and in the HRTEM image of Figure 7.6b, which corresponds to the area marked by a white rectangle in Figure 7.6a, it shows the same crystal planes and the same growth direction (as indicated by a white arrow) as illustrated in Figure 7.5b. Therefore, clear evidence for preferential
growth direction of Sr$_2$KNb$_5$O$_{15}$ and Sr$_2$KTA$_5$O$_{15}$ nanorod samples could be further found and both of them have the same [001] growth direction. Therefore, it is suggested that the use of molten salt as a reaction medium plays a dominant role for the formation of nanorod morphology and their preferential growth, while presumably the growth inhibition caused by Ta substitution in these Ta substituted samples, as observed in above XRD and SEM results, is limited.

Figure 7.6c shows a representative TEM image of a typical 1.0 wt.% NiO$_x$ loaded Sr$_2$KTA$_5$O$_{15}$ sample. It can be clearly seen that distinguishable nano-NiO$_x$ co-catalyst particles are anchored on an individual Sr$_2$KTA$_5$O$_{15}$ nanorod. The nano-NiO$_x$ co-catalyst particles consist of a solid Ni metal core and a brighter NiO outer layer. Furthermore, the inset on the lower right shows a lattice resolved HRTEM image of a nano-NiO$_x$ particle, in which the lattices of the outer layer-cubic NiO can be determined to be the [111] and [200] crystal planes with d-spacings of 0.24 nm and 0.21 nm, respectively. The results demonstrate that the double-layered structure of metallic Ni and metal oxide NiO is created on the surface of the Sr$_2$KTA$_5$O$_{15}$ nanorods photocatalyst by reduction-reoxidation processes. The formation of a Ni metal at the surface of photocatalyst results in the formation of a Schottky contact at the interface, and thus provides an opportunity to facilitate electron transport to the NiO shell to enhance the photocatalytic activity of the photocatalysts for overall water splitting as will be discussed below.
Figure 7.5. TEM images of the Sr$_2$KNb$_5$O$_{15}$ sample: (a) Low-magnification TEM image of a typical Sr$_2$KNb$_5$O$_{15}$ nanorod, (b) HRTEM taken from the top part of the Sr$_2$KNb$_5$O$_{15}$ nanorod as marked by a white rectangle in (a). The white arrow indicates the growth direction of the Sr$_2$KNb$_5$O$_{15}$ nanorod along the [001] planes. (c) Corresponding SAED pattern.
Figure 7.6. TEM images of the Sr$_2$KTa$_5$O$_{15}$ sample: (a) Low-magnification TEM image of a typical Sr$_2$KTa$_5$O$_{15}$ nanorod, (b) HRTEM taken from the edge of the Sr$_2$KTa$_5$O$_{15}$ nanorod as marked by a white rectangle in (a). The white arrow indicates the growth direction of the Sr$_2$KTa$_5$O$_{15}$ nanorod along the [001] planes. (c) The TEM image of the 1.0 wt.% NiO$_x$ loaded Sr$_2$KTa$_5$O$_{15}$ nanorod with inset
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of a NiO₃ particle.

7.3.3 Optical and physical properties

The UV-Vis diffuse reflectance spectra of Sr₂KNb₅₋ₓTaₓO₁₅ with x= 0, 1, 2.5, 4 and 5 are shown in Figure 7.7a. The absorption edges of Sr₂KNb₅₋ₓTaₓO₁₅ obviously shift to shorter wavelength with the increased Ta content. On basis of Kubelka–Munk transformation of the diffuse reflectance spectra, the band-gap energies from Tauc plots were larger than the apparent band-gap energies if direct transition is assumed for light absorption by the samples. As indicated in Figure 7.7b, the assumption of indirect transition is in good agreement with apparent band-gap energies, thus suggesting that the as-prepared oxides are indirect band gap semiconductors. Figure 7.7d shows the band gaps of Sr₂KNb₅O₁₅, Sr₂KNb₄Ta₁O₁₅, Sr₂KNb₂.₅Ta₂.₅O₁₅, Sr₂KNb₁Ta₄O₁₅ and Sr₂KTa₅O₁₅ were estimated to be about 3.19, 3.24, 3.32, 3.51 and 3.89 eV, respectively. The band gap of Sr₂KNb₅O₁₅ is consistent with the reported value (3.24 eV).³⁵ The data indicate that the band gaps do not linearly increase with the Ta substitution; for high Ta contents the band gap widening is more prominent.

On the other hand, the BET surface areas of Sr₂KNb₅₋ₓTaₓO₁₅ with x= 0, 1, 2.5, 4 and 5 decreased almost linearly with the substitution of Ta, as shown in Figure 7.7c. The surface area of as-prepared Sr₂KNb₅O₁₅ (19.1 m²/g) was improved by more than 61 times compared with that of the sintered sample (0.31 m²/g) by the conventional solid state reaction method,³⁵ which may provide more active sites, reduce the recombination of photogenerated electron-hole pairs, and thus greatly enhance photocatalytic efficiency. This can be ascribed to the lower reaction temperature and the shorter reaction times (at 850 °C for 2 h) possible due to the intimate contacts in the molten salt moderated reaction.

The band structure of photocatalysts is one of the important factors affecting the photonic efficiency. The valence band (VB) potentials of all Sr₂KNb₅₋ₓTaₓO₁₅ solid solutions should be quite similar because of the same crystal structure and the same orbitals (O 2p orbitals) comprising the VB. Thus, the difference of
band gap energies is due to the orbitals forming the conduction band (CB). According to the report by Scaife,\textsuperscript{[199]} for oxides not containing partly filled d-levels, the following equation can be used to approximately determine the flat band potential:

\[ V_{fb}(\text{NHE}) = 2.94 - E_g \] (12)

where \( V_{fb} \) and \( E_g \) represent a flat band potential and a band gap, respectively. The band structures of \( \text{Sr}_2\text{KNb}_{3-x}\text{Ta}_x\text{O}_{15} \) with \( x = 0, 1, 2.5, 4 \) and 5 are schematically illustrated in Figure 7.8. The CB of \( \text{Sr}_2\text{KNb}_6\text{O}_{15} \) consists of Nb 4d, while that of \( \text{Sr}_2\text{KTa}_5\text{O}_{15} \) is from Ta 5d. The CB formed by the empty Ta 5d orbitals lies at a considerably more negative potential than the Nb 4d orbitals. Thus, with increasing Ta substitution, the larger band gap will lead to the decreased amount of absorbed photons. On the contrary, it also means that the CB potential becomes more negative than the water reduction potential (\(<0 \text{ V vs. NHE at pH 0}\)), suggesting that the driving force of \( \text{Sr}_2\text{KNb}_{3-x}\text{Ta}_x\text{O}_{15} \) for water reduction by electrons in the CB becomes larger, thus promoting the transfer of photoelectrons. It can be concluded that the Ta substitution molar ratio has a great effect on the band structures and thus plays a crucial role in determining the efficiency of \( \text{H}_2 \) production.\textsuperscript{[200]} Furthermore, the bottom level of the CB was much more negative than the reduction potential of \( \text{H}^+/\text{H}_2 \) (0 eV), while the top level of the VB was more positive than the oxidation potential of \( \text{O}_2/\text{H}_2\text{O} \) (+1.23 eV). It is therefore reasonable to infer that these photocatalysts might be able to split water into \( \text{H}_2 \) and \( \text{O}_2 \) by the appropriate excited energy.
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Figure 7.7. (a) UV-Vis diffuse reflection spectra of Sr$_2$KNb$_{5-x}$Ta$_x$O$_{15}$ with x= 0, 1, 2.5, 4 and 5, (b) Tauc plots (for indirect band gap transition) calculated from the Kubelka-Munk transformation, (c) Band gap energies of Sr$_2$KNb$_{5-x}$Ta$_x$O$_{15}$.
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with $x=0, 1, 2.5, 4$ and $5$, and (d) BET surface areas of Sr$_2$KNb$_{5-x}$Ta$_x$O$_{15}$ with $x=0, 1, 2.5, 4$ and $5$.

Figure 7.8. A schematic illustration of band structures of Sr$_2$KNb$_{5-x}$Ta$_x$O$_{15}$ with $x=0, 1, 2.5, 4$ and $5$.

### 7.3.4 Ta substitution effect on photocatalytic H$_2$ production

The photocatalytic H$_2$ production rates over co-catalyst-free Sr$_2$KNb$_{5-x}$Ta$_x$O$_{15}$ with $x=0, 1, 2.5, 4$ and $5$ from photocatalytic reforming of methanol are shown in Figure 7.9. Note that the activities of photocatalysts with different Ta substitution molar ratio were compared by the average rate of H$_2$ production in the first 1 h and the same photocatalytic trend can be obtained by at least three repeated measurements. For comparison, commercial TiO$_2$ nanoparticles (Evonik P25) were also tested for photocatalytic H$_2$ production under the same conditions. The Sr$_2$KNb$_{5-x}$Ta$_x$O$_{15}$ solid solutions photocatalysts exhibited superior photocatalytic activity than P25. And it is clearly seen that the photocatalytic activity of Sr$_2$KTa$_5$O$_{15}$ is much higher than that of Sr$_2$KNb$_3$O$_{15}$. With the increased content of Ta substitution, the average formation rates of H$_2$ decreased first, the lowest activity was observed for the Sr$_2$KNb$_{2.5}$Ta$_{2.5}$O$_{15}$. 

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and then began to increase in the case of $x > 2.5$. It might be possible that the crystal sizes and crystallinity of the solid solutions negligibly influence the photocatalytic activity because their crystal sizes and high crystallinity were not significantly changed by Ta substitution from the XRD results. Therefore, the obvious decrease of $H_2$ formation rate ($x < 2.5$) can be related to the decreased number of absorbed photons and lower specific surface areas. With higher Ta substitution ($x > 2.5$), the increase of $H_2$ formation rate can be mainly attributed to the stronger driving force and more effective photoelectron transfer from the CB as described above.

![Graph showing rate of $H_2$ production vs. $x$](image)

Figure 7.9. Formation rates of hydrogen over $\text{Sr}_2\text{KNb}_{3-x}\text{Ta}_x\text{O}_{15}$ nanorod photocatalysts with $x=0, 1, 2.5, 4$ and $5$ (Conditions: $0.1 \text{ g}$ of photocatalysts; $50 \text{ mL}$ of methanol dissolved in $500 \text{ mL}$ of water, $500 \text{ W}$ Hg lamp).

### 7.3.5 Photocatalytic overall water splitting

All native photocatalysts did not possess photocatalytic activity in pure water, probably due to the low charge separation and transfer efficiency. While $1.0 \text{ wt\%}$ NiO$_x$ was loaded as co-catalyst, the photocatalytic overall water splitting into stoichiometric amounts of $H_2$ and $O_2$ can be effectively promoted over prototypical examples of $\text{Sr}_2\text{KNb}_{3}\text{O}_{15}$ and $\text{Sr}_2\text{KTa}_{3}\text{O}_{15}$ photocatalysts. Figure 7.10
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shows the time course of H₂ and O₂ evolution from pure water over 1.0 wt% NiOₓ/Sr₂KNb₅O₁₅ and 1.0 wt% NiOₓ/Sr₂KTa₅O₁₅ photocatalysts under UV light irradiation for 5 h. After some short induction period of about 15 minutes of irradiation, the formation of H₂ and O₂ in a stoichiometric ratio (H₂/O₂ ≈ 2/1) was observed and there was no appreciable decrease by on-line monitoring of gas evolution, indicating that the samples are stable under UV light irradiation. Therefore, it is demonstrated that the presence of the double-layered nano-NiOₓ particles on the surface of photocatalysts, as shown above, can facilitate electron migration and suppress the backward reaction of water formation, leading to an enhancement of photocatalytic activity for overall water splitting. Furthermore, the average rates of H₂/O₂ evolution over Sr₂KNb₅O₁₅ and Sr₂KTa₅O₁₅ photocatalysts were estimated to be about 36.2/15.2 and 84.5/46.3 μmol/h, respectively, thus the latter was more than 2 times higher than the former, in agreement with the above-presented comparison value from photocatalytic H₂ production by methanol reforming. These experimental results not only proved the photocatalytical abilities of the tunnel structured photocatalysts for overall water splitting, but also consistently confirmed the above reasonable prediction resulting from the theoretical calculation of the band structures.
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Figure 7.10. H₂ and O₂ evolution from pure water over 1 wt% NiOₓ loaded Sr₂KNb₅O₁₅ and Sr₂KTA₅O₁₅ for 5 h (Conditions: 0.1 g of photocatalysts; 500 mL of H₂O, Hg lamp).
7.4 Conclusions

Novel tetragonal tungsten bronze-type tantalum (Ta) substituted Sr$_2$KNb$_5$O$_{15}$ nanorod photocatalysts with tunnel structure were prepared by a facile and low-cost molten salt method using potassium chloride (KCl) at 850 °C for only 2 h. Ta substitution effects on the photocatalytic behaviour were systematically investigated for hydrogen production by aqueous methanol reforming. The average H$_2$ formation rates of Sr$_2$KNb$_{5-x}$Ta$_x$O$_{15}$ first decrease with tantalum substitution for $x < 2.5$, presumably due to a decreased amount of absorbed photons and an obvious reduction of their exposed surface areas, whereas the activity is significantly improved for samples containing more Ta ($x > 2.5$) and especially the fully substituted Sr$_2$KTa$_5$O$_{15}$. This can be explained by a stronger driving force for photogenerated conduction band electrons to reduce water. Compared to a bulk TiO$_2$ sample, the Sr$_2$KNb$_5$Ta$_{5-x}$O$_{15}$ nanorod photocatalysts showed much higher activity. Moreover, although all native photocatalysts did not possess any detectable activity in pure water splitting, after deposition of NiO$_x$ (double-layered Ni/NiO) as co-catalysts, samples of Sr$_2$KNb$_5$O$_{15}$ and Sr$_2$KTa$_5$O$_{15}$ can split pure water into H$_2$ and O$_2$ in a stoichiometric amount ($\approx 2:1$), which can be ascribed to the improved charge carrier separation and transfer in the presence of NiO$_x$. Therefore, it can be concluded that the tunnel structure photocatalysts are a new type of photocatalyst materials for overall water splitting from the view point of the tunable components because it consists of three different tunnels and octahedral arrays. Our ongoing work will continue to study on band gap engineering by controlling cation filling of three different tunnels and octahedral arrays, for extending the photosensitivity of photocatalytic oxides into the visible-light region.
Construction of visible light-driven graphitic carbon nitride-sensitized hybrid composite photocatalysts — a moderate band-gap

8 Construction of visible light-driven graphitic carbon nitride-sensitized hybrid composite photocatalysts — a moderate band-gap

8.1 Brief introduction

Recently, polymeric graphitic carbon nitride (g-C₃N₄) which was firstly reported by Wang, et al, can splitting water for the production of hydrogen or oxygen under visible light irradiation as a metal-free photocatalyst [204-205]. It possesses several characteristics, properties and advantages as a promising candidate for the fabrication of nanocomposite systems, such as a small band gap (~2.70 eV) capable of visible light absorption, a highly negative conduction band minimum (~1.12 eV vs. NHE) and high thermal and chemical stability, etc. Consequently, a lot of efforts have been devoted to the fabrication of g-C₃N₄-based hybrid nanocomposite photocatalysts. Up to now, coupling of g-C₃N₄ with another narrow band gap photocatalysts have been widely investigated, such as N-TiO₂ [206], N-H₂Ta₂O₆ [207], N-In₂TiO₅ [208], TaON [209], BiPO₄ [210], and Bi₂WO₆ [211], BiOX (X= Cl, Br, I) [212-213], etc. On the other hand, owing to the delocalized π electrons from the conjugated π structure of g-C₃N₄ [214], the combination of g-C₃N₄ as a visible light sensitizer with a wide band gap semiconductor has been also developed, such as TiO₂ [215-216], ZnO [217], SrTiO₃ [218] and Zn₄GeO₄ [219].

However, the challenge in photocatalytic efficiency still remains and more efficient photocatalytic structures need to be developed.

In spite of extensive research in the past, the efficient heterostructured composite photocatalysts are still rare in literature concerning the methodologies for constructing the semiconductor composites. There are several important factors to be carefully considered in rational design of heterostructured nanocomposites: i) efficient “primary impetus” for carrier separation among these semiconductor components, is that, the suitable band
Construction of visible light-driven graphitic carbon nitride-sensitized hybrid composite photocatalysts — a moderate band-gap alignment yielding a spatial carrier separation, and rational adjustment of carrier concentrations in each semiconductor component applied as a “secondary impetus”. 2) the intimate and tight adherence between these semiconductor components by control of their microstructures, to ensure the smooth charge transfer and good stability during the catalytic reaction; 3) another is excellent physical and chemical properties of these single-semiconductor components, enabling efficient charge carrier separation and transportation, such as high crystallinity, large surface areas and low defect density, etc. Furthermore, in the previous chapter (i.e. Chapter 7), the prepared Sr$_2$KNb$_5$O$_{15}$ and nanorod photocatalysts with tunnel structure have the similar band gap as TiO$_2$ (3.20 eV). However, surprisingly, they showed much higher H$_2$ production activity than a bulk TiO$_2$ sample. The results provide an extra motivation to work on the combination of g-C$_3$N$_4$ with Sr$_2$KNb$_5$O$_{15}$. Additionally, from the viewpoint of their band diagrams, the Sr$_2$KNb$_5$O$_{15}$ has matching conduction and valence bands with g-C$_3$N$_4$, belonging to type II band structure (see Figure 3. 3), the coupling of moderate band-gap Sr$_2$KNb$_5$O$_{15}$ with g-C$_3$N$_4$ is thus expected to promote both visible light response and electron-hole pair separation. Therefore, in this chapter, preparation and characterization of g-C$_3$N$_4$/Sr$_2$KNb$_5$O$_{15}$ nanocomposite photocatalysts and their photocatalytic performance will be investigated in detail.

8.2 Photocatalysts preparation

All reagents used in this study were analytically pure and used without further purification. The Sr$_2$KNb$_5$O$_{15}$ nanorods were synthesized according to molten salt method using KCl as a molten medium, as described in Section 7.2.1 of Chapter 7. The g-C$_3$N$_4$ in this study was prepared by directly heating melamine (C$_3$H$_6$N$_6$, Alfa Aesar, > 99 %) to 520 °C in a covered porcelain crucible for 4 h.[220]

The direct growth method was used for preparation of g-C$_3$N$_4$/Sr$_2$KNb$_5$O$_{15}$ nanocomposite photocatalysts. Briefly, an appropriate weight ratio of melamine
and Sr₂KNb₅O₁₅ was added into ethanol. The bottle was placed in an ultrasonic bath for 30 min for complete dispersion and then stirred in a fume hood. After drying at 80 °C overnight, the resulting mixture was heated to 520 °C in a covered porcelain crucible for 4 h. According to this method, different weight ratios of g-C₃N₄/Sr₂KNb₅O₁₅ photocatalysts were synthesized and the g-C₃N₄ content in the final product of g-C₃N₄/Sr₂KNb₅O₁₅ composite sample was roughly estimated to about 24 wt%, 55 wt%, 77 wt% and 99 wt% by balance measurement, denoted as 24CNNb, 55CNNb, 77CNNb and 99CNNb, respectively. For comparison, the physical mixture of the pre-synthesized g-C₃N₄ and Sr₂KNb₅O₁₅ was also prepared without heating treatment (denoted by M77CNNb).

8.3 Results and discussion

8.3.1 Physicochemical properties

The estimates of the g-C₃N₄ content in the g-C₃N₄/Sr₂KNb₅O₁₅ composite samples were carried out by thermogravimetric analysis (TGA, see Figure 8.1). The g-C₃N₄ content of the composite samples is more or less the same as the corresponding values calculated from balance measurement (see Table 8.1), and all TGA weight losses have similar profiles within the experimental error. For example, the content of g-C₃N₄ in the 77CNNb sample is calculated to be approximately 80 wt% from the TG curve. The slight weight loss being observed before 300 °C is corresponding to the desorption of water. The major weight loss starts at around 540 °C, and finished at around 730 °C, which can be attributed to the decomposition of g-C₃N₄. After 730 °C, no mass change is observed and the mass residue of the Sr₂KNb₅O₁₅ material is determined. Furthermore, the exposed surface areas of these nanocomposite samples were determined by the Brunauer-Emmett-Teller (BET) method of nitrogen adsorption-desorption measurements. As seen in Table 8.1, only for contents higher than 55 wt% of g-C₃N₄, a slight decrease of the BET surface area is
Construction of visible light-driven graphitic carbon nitride-sensitized hybrid composite photocatalysts — a moderate band-gap

observed, thus it could reasonably be considered that the surface area of composite samples might impact the photocatalytic performance only to a small degree.

Table 8.1. The g-C$_3$N$_4$ content, BET surface area, and band gaps of the g-C$_3$N$_4$/Sr$_2$KNb$_5$O$_{15}$ nanocomposite samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C$_3$N$_4$ content (wt%)$^a$</th>
<th>S$_{\text{BET}}$$^b$ (m$^2$ g$^{-1}$)</th>
<th>E$_g$$^c$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr$_2$KNb$<em>5$O$</em>{15}$</td>
<td>0</td>
<td>19.1</td>
<td>3.21</td>
</tr>
<tr>
<td>24CNNb</td>
<td>30%</td>
<td>17.1</td>
<td>3.22 / 2.64</td>
</tr>
<tr>
<td>55CNNb</td>
<td>54%</td>
<td>19.6</td>
<td>2.66</td>
</tr>
<tr>
<td>77CNNb</td>
<td>80%</td>
<td>14.6</td>
<td>2.66</td>
</tr>
<tr>
<td>99CNNb</td>
<td>98%</td>
<td>13.2</td>
<td>2.65</td>
</tr>
<tr>
<td>g-C$_3$N$_4$</td>
<td>100%</td>
<td>11.2</td>
<td>2.66</td>
</tr>
</tbody>
</table>

$^a$ Estimated by TGA; $^b$ measured by the BET method; $^c$ determined from the extrapolated straight line portion of the Tauc plot at $(F(R) \cdot h\nu)^{1/2} = 0$ (see Figure 8.4)
Figure 8.1. TG curves of the g-C$_3$N$_4$/Sr$_2$KNb$_5$O$_{15}$ nanocomposite samples with different g-C$_3$N$_4$ content.

8.3.2 Crystal Structure

The X-ray powder diffraction (XRD) patterns of the g-C$_3$N$_4$/Sr$_2$KNb$_5$O$_{15}$ nanocomposite samples with different content of g-C$_3$N$_4$ are shown in Figure 8.2. The samples were well-crystallized and no significant peak shift can be observed, indicating that the possible behavior of the Sr$_2$KNb$_5$O$_{15}$ component doped by N and (or) C specials, which originated from the melamine-derived sources, were completely eliminated at low calcination temperature condition. The bare Sr$_2$KNb$_5$O$_{15}$ sample can be indexed to the tetragonal tungsten bronze structure (JCPDS 34-0108). The XRD pattern of bare g-C$_3$N$_4$ shows two distinct peaks at 13.2$^\circ$ and 27.4$^\circ$, which can be indexed as the (100) and (002) diffraction planes, respectively. The small angle peak at 13.2$^\circ$ agrees with (100) interplanar structural packing of tri-triazine units. The strong peak at 27.4$^\circ$ is the characteristic (002) interplanar stacking peak, corresponding to the interlayer distance of aromatic systems, indicating the formation of well-built g-C$_3$N$_4$ layer structure.\cite{221} When the content of C$_3$N$_4$ was lower than 55 wt% in the C$_3$N$_4$/Sr$_2$KNb$_5$O$_{15}$ composite samples, it is very difficult to differentiate the diffraction peak of g-C$_3$N$_4$ at 27.4$^\circ$ and the peak of Sr$_2$KNb$_5$O$_{15}$ at 27.7$^\circ$ solely, because of the broad peak of g-C$_3$N$_4$ at 27.4$^\circ$ with lower diffraction intensity. While with the increased content of g-C$_3$N$_4$, the sharp peak appearing at around 27.5$^\circ$ in the 77CNNb and 99CNNb samples mostly result from the superimposition of the peak of Sr$_2$KNb$_5$O$_{15}$ at 27.7$^\circ$ and the board peak of g-C$_3$N$_4$ at 27.4$^\circ$. Furthermore, the nanocomposite samples, which were prepared by direct growth (77CNNb) and by physically mixing (M77CNNb), respectively, gave similar XRD patterns (Figure 8.2), indicating that in either case, there are no observed structural interaction between g-C$_3$N$_4$ and Sr$_2$KNb$_5$O$_{15}$.
Figure 8.2. XRD patterns of the g-C$_3$N$_4$/Sr$_2$KNb$_5$O$_{15}$ composite samples.

8.3.3 Microstructure

Figure 8.3 shows the representative transmission electron microscopy (TEM) images of bare Sr$_2$KNb$_5$O$_{15}$ (a), bare C$_3$N$_4$ (b), 77CNNb composite (c), and the high resolution transmission electron microscopy (HRTEM) image of 77CNNb composite (d). The bare Sr$_2$KNb$_5$O$_{15}$ sample was composed of nanorods with the diameters in the range of 100-400 nm and the length goes up to a few microns, while the bare C$_3$N$_4$ particles are irregular aggregated. As compared with bare Sr$_2$KNb$_5$O$_{15}$ and g-C$_3$N$_4$, it can be clearly seen that the g-C$_3$N$_4$ intimately grew on the surface of the Sr$_2$KNb$_5$O$_{15}$ nanorods for 77CNNb nanocomposite (Figure 8.3c). It indicates that the intimate contact between g-C$_3$N$_4$ and Sr$_2$KNb$_5$O$_{15}$ favors the formation of sufficient interfaces between the two components. As shown in the representative HRTEM image of 77CNNb composite (Figure 8.3d), the representative HRTEM image of the 77CNNb nanocomposite sample
obviously reveals the formation of smooth interfaces between g-C$_3$N$_4$ and Sr$_2$KNb$_5$O$_{15}$ and an interplanar spacing of 0.32 nm confirms to the [211] crystal planes of Sr$_2$KNb$_5$O$_{15}$. Apparently, the heterojunction structure forms in the as-synthesized nanocomposites. Presumably the charge transfer between the two semiconductor components is spatially smooth and is fundamental for improving the photocatalytic activity, as will be discussed in detail below.

Figure 8.3. The representative TEM images of bare Sr$_2$KNb$_5$O$_{15}$ (a), bare g-C$_3$N$_4$ (b), 77CNNb composite (c), and the HRTEM image of the 77CNNb nanocomposite (d), respectively.

8.3.4 Optical properties

Figure 8.4 shows Tauc plots for Kubelka-Munk transformed UV-Vis diffuse reflection spectra (UV-DRS) of the g-C$_3$N$_4$/Sr$_2$KNb$_5$O$_{15}$ nanocomposites. The band gap of bare Sr$_2$KNb$_5$O$_{15}$ and g-C$_3$N$_4$ can be estimated to be about 3.21 eV and 2.66 eV, repectively. A shoulder structure of absorption band was clearly observed for the g-C$_3$N$_4$/ Sr$_2$KNb$_5$O$_{15}$ nanocomposites with low g-C$_3$N$_4$ content.
Construction of visible light-driven graphitic carbon nitride-sensitized hybrid composite photocatalysts — a moderate band-gap (24CNNb) and M77CNNb sample. As estimated from the Tauc plots, the two different band gaps can be assigned to their corresponding components (see above Table 8.1). Along with increasing of g-C₃N₄ content, their absorption curves become almost parallel to that of bare g-C₃N₄. The results imply that the coupled g-C₃N₄ indeed functions not only as a visible light absorber, but also as a sensitizer to subsequently transfer of energy to the SrₓKnbxO₁₅.

![Figure 8.4. Tauc plots for Kubelka-Munk function transformed UV-Vis diffuse reflection spectra of the g-C₃N₄/SrₓKnbxO₁₅ nanocomposite samples](image)

8.3.5 XPS analysis

The X-ray photoelectron spectroscopy (XPS) was employed to analyze the oxidization state and the chemical environment of constituent elements on the surface of the bare SrₓKnbxO₁₅, 24CNNb and 77CNNb samples. As can be seen from the XP spectra in Figure 8.5A a, the main constituent elements on the surface of bare SrₓKnbxO₁₅ sample are Sr, K, Nb, O with sharp photoelectron peaks and low amount of absorbed C species in the form of carbonates. Compared with the XPS spectrum of bare SrₓKnbxO₁₅, there are no changes in binding energy of these constituent elements in the XPS spectra of 24CNNb and 77CNNb nanocomposites(Figure 8.5A b-f). With the increasing g-C₃N₄ content,
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the signals of C1s and N 1s are obviously stronger in intensity, while at the same time the content of Nb, Sr, O and K elements significantly decreases. As depicted in Table 8.2, with the increasing g-C3N4 content from 24CNNb to 77CNNb samples, the atom concentration of N element increase ca. 2.67 times, which is in good agreement with the increased content of g-C3N4. However, the atom concentration of Sr and Nb elements decreased by a factor of ca. 12.7 and 16.6, respectively. Thus, the results can be attributed to the increased g-C3N4 coating, i.e. larger g-C3N4 coverage form on the surface of Sr2KNb5O15 nanorods.

Table 8.2. Atom concentration (at%) for N, Sr and Nb derived from XPS spectra.

<table>
<thead>
<tr>
<th>Sample</th>
<th>N (at%)</th>
<th>Sr (at%)</th>
<th>Nb (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr2KNb5O15</td>
<td>0</td>
<td>11.97</td>
<td>21.80</td>
</tr>
<tr>
<td>24CNNb</td>
<td>19.78</td>
<td>7.77</td>
<td>14.46</td>
</tr>
<tr>
<td>77CNNb</td>
<td>52.79</td>
<td>0.61</td>
<td>0.87</td>
</tr>
</tbody>
</table>

The typical XPS data of the regional N1s, C1s, K 2p, Sr 3d, Nb 3d and O 1s spectra for the 77CNNb nanocomposite sample are further shown in Figure 8.5B b-f, respectively. The N1s XPS spectrum (Figure 8.5B a) can be deconvoluted into three peaks at 397.9, 399.2, and 400.2 eV, which can be ascribed to C-N-C, N-(C)3 and N-H group of g-C3N4.[222-223] The regional C 1s XPS spectrum in Figure 8.5B b can be fitted into three peaks at 284.3, 286.1 and 287.7 eV, respectively. The XPS peak with binding energy of 284.3 eV can be assigned to the C-C and/or adventitious carbon, while the peaks at 286.1 and 287.7 eV can be ascribed to the C-N-C and the C-(N)3 group, respectively.[223-224] Therefore, the above results confirm the presence of graphite-like sp2-bonded graphitic carbon nitride. The XPS spectra of K 2p (Figure 8.5B b), Sr 3d (Figure 8.5B c) and Nb 3d (Figure 8.5B d) can be fitted well into two peaks. The K 2p3/2 and K 2p1/2 bands are observed at 292.7 and 294.3 eV, respectively, the Sr 3d5/2 and Sr
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$3d_{3/2}$ bands are located at 132.5 and 134.2 eV, respectively, and the Nb 3d bands at the binding energies of 206.4 and 290.1 eV can be attributed to Nb $3d_{3/2}$ and $3d_{5/2}$ levels, respectively. Furthermore, Figure 8.5B e shows the asymmetric O1s spectrum can be deconvoluted into three peaks at 529.3, 531.0 and 532.4 eV, respectively. The main peak positioned at a low binding energy of 529.3 eV can be attributed to lattice oxygen in the form of $O^{2-}$. While the other minor and broad peaks centered at 531.0 and 532.4 eV, may be assigned to the surface adsorbed oxygen in form of $CO_3^{2-}$, $OH^-$, and $H_2O$.\[225-228\]
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Figure 8.5. A: survey XPS spectra of bare Sr$_2$KNb$_5$O$_{15}$, 24CNNb and 77CNNb nanocomposites (a), binding energy of N 1s (b), C 1s and K 2p (c), Sr 3d (d), Nb 3d (e) and O 1s (f) in the XPS spectra of bare Sr$_2$KNb$_5$O$_{15}$, 24CNNb and 77CNNb nanocomposites. B: the regional scan XPS spectra of N 1s (a), C 1s and K 2p (b), Sr 3d (c), Nb 3d (d) and O 1s (e) for the 77CNNb nanocomposite, respectively.

### 8.3.6 Photocatalytic abilities

As shown in Figure 8.6, the photocatalytic measurements were explored under visible light irradiation ($\lambda > 400$ nm) for degradation of methylene blue (MB).
Figure 8.7 depicts the photocatalytic abilities of $\text{C}_3\text{N}_4/\text{Sr}_2\text{KNb}_5\text{O}_{15}$ composite with different content of g-$\text{C}_3\text{N}_4$. After irradiation for 6 h, bare $\text{Sr}_2\text{KNb}_5\text{O}_{15}$ nanorods sample shows almost no activity for degradation of MB, indicating that the self-sensitized degradation of MB over $\text{Sr}_2\text{KNb}_5\text{O}_{15}$ did not exist in the system and the self-decomposition of MB can be also regarded to be negligible under visible light irradiation. Under the same conditions, only ca. 16.2 % MB was photodegraded over the bare g-$\text{C}_3\text{N}_4$ sample. By coupling of g-$\text{C}_3\text{N}_4$ with the $\text{Sr}_2\text{KNb}_5\text{O}_{15}$, the photocatalytic activity was significantly increased and then decreased in the following order: 77CNNb $>$ 55CNNb $>$ 24CNNb $>$ 55CNNb $>$ 99CNNb $>$ M77CNNb $>$ g-$\text{C}_3\text{N}_4$. This implies that g-$\text{C}_3\text{N}_4$ acts as a visible-light harvesting unit and a sensitizer of the UV-active $\text{Sr}_2\text{KNb}_5\text{O}_{15}$ component, and the high g-$\text{C}_3\text{N}_4$ content in the nanocomposites is very essential to get sufficient surface coverage of the $\text{Sr}_2\text{KNb}_5\text{O}_{15}$ nanorods, which presumably plays a crucial role in formation of proper nano-interfaces, thereby leading to the significant improvement of the photocatalytic abilities. Figure 8.7b illustrates the variations in characteristic absorbance band of MB at 665 nm, which was assigned to the absorption of the conjugated p-system.$^{[229]}$ The absorbance of MB obviously decreased with the increasing visible-light irradiation time over the 77CNNb nanocomposite. Apparently, the 77CNNb nanocomposite exhibited the excellent photocatalytic activity.
Figure 8.6. The wavelength distribution of the irradiation light employed in the MB decomposition experiments.

Figure 8.7. a) Photodegradation of MB under visible light (λ > 400 nm) irradiation over g-C₃N₄/Sr₂K Nb₅O₁₅ composite samples. Bare Sr₂K Nb₅O₁₅, g-C₃N₄, mixture of 77CNNb composite are also tested for comparison. b) Absorption changes of MB solution over 77CNNb composite sample during photocatalytic process. (Inset is the MB structural formula).

In order to determining the photocatalytic reaction rate, the first-order kinetics was confirmed by making a linear plot of ln (C₀/C) against time. The kinetic equation could be expressed as follows:
Construction of visible light-driven graphitic carbon nitride-sensitized hybrid composite photocatalysts — a moderate band-gap

\[ \ln \frac{C_0}{C} = k \cdot t \]  \hspace{1cm} (13)

where \( C_0 \) and \( C \) are the concentrations of MB solution at times \( 0 \) and \( t \) in Equation 13, the first order rate constant of \( k \) (h\(^{-1}\)) is equal to the corresponding slope of the fitting line, and \( t \) is the illumination time (min). The MB photodegradation on each sample follows the first-order kinetics model. The rate constant of \( g\text{-C}3\text{N}4/\text{Sr}2\text{KNb}5\text{O}15 \) nanocomposite with different content of \( g\text{-C}3\text{N}4 \), \( M77\text{CNNb} \) nanocomposite, bare \( \text{Sr}2\text{KNb}5\text{O}15 \) and \( g\text{-C}3\text{N}4 \) are illustrated in Figure 8.8. The photooxidation rate constant of \( g\text{-C}3\text{N}4/\text{Sr}2\text{KNb}5\text{O}15 \) nanocomposites increased with the increasing content of coupled \( g\text{-C}3\text{N}4 \). The highest photocatalytic activity was observed for \( 77\text{CNNb} \) nanocomposite with the photooxidation rate constant of ca. 0.183 h\(^{-1}\), which was about 6.2 times higher than that of bare \( g\text{-C}3\text{N}4 \) (0.029 h\(^{-1}\)) and 3.4 times that of \( M77\text{CNNb} \) nanocomposite (0.053 h\(^{-1}\)). While the activity decreased with further increasing the \( g\text{-C}3\text{N}4 \) content. Interestingly, the photooxidation rate constant of \( 99\text{CNNb} \) (0.067 h\(^{-1}\)) is still higher than that of bare \( g\text{-C}3\text{N}4 \) and \( M77\text{CNNb} \) nanocomposite. The results indicated that the improper weight ratio of \( g\text{-C}3\text{N}4/\text{Sr}2\text{KNb}5\text{O}15 \) lead to the loss of favorable interfaces between \( g\text{-C}3\text{N}4 \) and \( \text{Sr}2\text{KNb}5\text{O}15 \). The \( g\text{-C}3\text{N}4/\text{Sr}2\text{KNb}5\text{O}15 \) nanocomposite prepared by direct grown method was more beneficial for the formation of the intimate contact between the \( g\text{-C}3\text{N}4 \) and \( \text{Sr}2\text{KNb}5\text{O}15 \), thus the enhanced photocatalytic activity can be attributed to the improved charge transfer via the proper interfaces.
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Figure 8.8. First-order rate constant for the photodegradation of MB under visible light irradiation ($\lambda > 400$ nm) over the g-$\text{C}_3\text{N}_4$/Sr$_2$Nb$_5$O$_{15}$ nanocomposite photocatalysts with different C$_3$N$_4$ content, M77CNNb nanocomposite, bare Sr$_2$Nb$_5$O$_{15}$ and g-$\text{C}_3\text{N}_4$.

8.3.7 Recyclability

The recyclability of the photocatalyst is an important parameter of the photocatalytic process for practical application. After each cycle, fresh MB solution was used for next photocatalytic experiment, and taking into account the loss of photocatalyst during the sampling process, the photocatalyst was collected from previous parallel experiments followed by washing and drying. As shown in Figure 8.9a, the 77CNNb nanocomposite sample did not show a significant decrease in degradation efficiency after three cycles. From their XRD patterns of the 77CNNb sample before and after photoreaction (Figure 8.9b), no significant change was observed. Thus, it can be confirmed that g-$\text{C}_3\text{N}_4$/Sr$_2$Nb$_5$O$_{15}$ could be used as stable photocatalysts for decomposing organic contaminant pollutants exposed to visible irradiation.$^{[230-232]}$
Figure 8.9. (a) Recyclability of MB photodegradation over the 77CNNb nanocomposite photocatalyst and (b) their XRD patterns before and after photoreaction.

8.3.8 Proposed photocatalytic mechanism

According to the report from Scaife for oxides not containing partly filled d-levels,[199] as described by the Equation 12 in Section 7.3.3, can be used to approximately determine the flat band potential. The conduction band (CB) and valance band (VB) edge potentials of Sr$_2$KNb$_5$O$_{15}$ were roughly estimated to be about -0.25 and 2.95 eV, respectively. On the other hand, it was reported by Wang, et al.[204] using density functional theory (DFT) calculations, the LUMO and HOMO energy levels of g-C$_3$N$_4$ are estimated at -1.12 and 1.57 eV, respectively. The energy levels of C$_3$N$_4$/Sr$_2$KNb$_5$O$_{15}$ hybrid nanocomposite photocatalysts are schematically illustrated in Figure 8.10. Since the LUMO energy level of g-C$_3$N$_4$ is more negative than the CB potential of Sr$_2$KNb$_5$O$_{15}$, the excited-state electrons in the LUMO energy level of g-C$_3$N$_4$ can inject into the CB potential of Sr$_2$KNb$_5$O$_{15}$ and thus the photo-inactive Sr$_2$KNb$_5$O$_{15}$ was sensitized effectively. Under irradiation, the electron transfer and redistribution behavior of photogenerated electrons in the side of Sr$_2$KNb$_5$O$_{15}$ nanorods - photogenerated holes in the side of g-C$_3$N$_4$ would greatly reduce the possibilities of electron-hole pairs recombination, thus enhancing the photocatalytic abilities of these as-synthesized composites. Thus, the “gear effect” between g-C$_3$N$_4$ and Sr$_2$KNb$_5$O$_{15}$ was proposed to account for the enhanced visible-light...
Construction of visible light-driven graphitic carbon nitride-sensitized hybrid composite photocatalysts — a moderate band-gap photocatalytic activity, which was associated with the double role of g-C$_3$N$_4$ as light absorber and sensitizer, and the cooperation between g-C$_3$N$_4$ and Sr$_2$KNb$_5$O$_{15}$ with the aid of smooth nano-interfaces.

Figure 8.10. Proposed energy levels of heterostructure C$_3$N$_4$/Sr$_2$KNb$_5$O$_{15}$ composite.
Construction of visible light-driven graphitic carbon nitride-sensitized hybrid composite photocatalysts — a moderate band-gap

8.4 Conclusions

In summary, a novel visible light-driven g-C_3N_4/Sr_2KNb_5O_15 hybrid nanocomposite photocatalyst was simply prepared by directly grown graphitic C_3N_4 on Sr_2KNb_5O_15 nanorods at 520 °C. The structure properties, surface morphology and element chemical states have been investigated. Compared to bare Sr_2KNb_5O_15, and g-C_3N_4, the photocatalytic property was significantly enhanced by coupling of g-C_3N_4 with Sr_2KNb_5O_15 for degradation of methylene blue (MB) under visible light irradiation (\( \lambda > 400 \) nm), and the optimal g-C_3N_4 content is about 77 wt%. By a comparative investigation of the direct growth method with physical mixing method of pre-synthesized g-C_3N_4 and Sr_2KNb_5O_15, the photodegradation rate of the former is found to be about 3.4 times higher than of the latter. The results indicate how important the formation of proper nano-interfaces between g-C_3N_4 and Sr_2KNb_5O_15 is, which play a vital role in their cooperative effects. Therefore, it demonstrated that g-C_3N_4 acts not only as an efficient visible-light-harvesting unit, but also as an effective sensitizer for the Sr_2KNb_5O_15, thus enabling greatly enhanced the spatial charge separation via the formed nano-interfaces between g-C_3N_4 and Sr_2KNb_5O_15 components. The work may provide further insight for rational construction of C_3N_4 sensitized another wide band-gap semiconductor and offer an alternative strategy to develop novel visible-light-driven photocatalyst system for the potential application of water treatment and other environmental remediation.
9 Construction of visible light-driven graphitic carbon nitride sensitized hybrid composite photocatalysts — a broad band gap

9.1. Brief introduction

As discussed in the Chapter 7, the Sr$_2$KTa$_5$O$_{15}$ nanorod material obtained from the complete substitution of Sr$_2$KNb$_5$O$_{15}$ by Ta possess the similar structure properties with Sr$_2$KNb$_5$O$_{15}$. The main difference in optical property is that the former have a broader band gap (3.89 eV) than that of the latter (3.20 eV). It is because the CB formed by the empty Ta 5d orbitals lies at a considerably more negative potential than the Nb 4d orbitals. On the other hand, in the Chapter 8, the sensitized Sr$_2$KNb$_5$O$_{15}$ by coupling with g-C$_3$N$_4$ had been extended into the visible light response. Compared with bare Sr$_2$KNb$_5$O$_{15}$, and g-C$_3$N$_4$, the photocatalytic property of the g-C$_3$N$_4$/Sr$_2$KNb$_5$O$_{15}$ nanocomposites was significantly enhanced for degradation of methylene blue under visible light irradiation ($\lambda > 400$ nm).

Therefore, strongly motivated by these previous studies, the g-C$_3$N$_4$ sensitized the broad band-gap Sr$_2$KTa$_5$O$_{15}$ nanocomposites were prepared by the same direct growth method. The band structure of the g-C$_3$N$_4$/Sr$_2$KTa$_5$O$_{15}$ composite also belongs to type II band structure (see Figure 3.3) and the coupling of Sr$_2$KTa$_5$O$_{15}$ with g-C$_3$N$_4$ is expected to promote both visible light response and electron-hole pair separation. Therefore, on basis of the previous studies in Chapter 7 and Chapter 8, comparative results of g-C$_3$N$_4$ sensitizing the broad band-gap Sr$_2$KTa$_5$O$_{15}$ vs. g-C$_3$N$_4$ sensitizing the moderate band-gap Sr$_2$KNb$_5$O$_{15}$ will be discussed in the present chapter, in order to promote a better understanding of the possible factors affecting their photocatalytic performance.

9.2. Photocatalysts preparation

The g-C$_3$N$_4$/Sr$_2$KTa$_5$O$_{15}$ nanocomposite photocatalysts were prepared by the
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same direct growth method, as previously described in experimental section 8.2. The samples with different C₃N₄ content of 62 wt%, 77 wt% and 89 wt% were synthesized, and denoted as 62CNTa, 77CNTa and 89CNTa, respectively.

9.3. Results and discussion

9.3.1. Structure properties

The g-C₃N₄ content in the g-C₃N₄/Sr₂KTₐ₅O₁₅ nanocomposite samples were estimated by balance measurement and thermogravimetric analysis. In the TG curves of the nanocomposite samples (Figure 9.1), the major weight loss from ca. 540 °C to ca. 730 °C can be attributed to the and decomposition of g-C₃N₄, and match closely with the g-C₃N₄ content obtained from the balance measurements. For example, the nominal content of g-C₃N₄ in the 62CNTa sample is calculated to be approximately 65 wt% from the TG curve.

Figure 9.1. TG curves of the g-C₃N₄/Sr₂KTₐ₅O₁₅ nanocomposite samples with different g-C₃N₄ content.

The XRD patterns of g-C₃N₄/Sr₂KTₐ₅O₁₅ nanocomposite samples with different content of g-C₃N₄ are shown in Figure 9.2. The results showed the samples were well-crystallized and no significant peak shift can be observed. The bare Sr₂KTₐ₅O₁₅ sample can be indexed to the tetragonal tungsten bronze structure
Construction of visible light-driven graphitic carbon nitride sensitized hybrid composite photocatalysts — a broad band gap (JCPDS 40-0345). With the increased content of g-C₃N₄ in these C₃N₄/Sr₂KTa₅O₁₅ nanocomposite samples, the intensity of diffraction peak at 27.4° obviously increased, which can be assigned to the (002) diffraction plane of g-C₃N₄.

![XRD patterns of the g-C₃N₄/Sr₂KTa₅O₁₅ nanocomposite samples.](image)

Figure 9.2. XRD patterns of the g-C₃N₄/Sr₂KTa₅O₁₅ nanocomposite samples.

Figure 9.3 shows that Tauc plots for the transformed Kubelka-Munk function of UV-Vis diffuse reflectance spectra (UV-DRS) of the g-C₃N₄/Sr₂KTa₅O₁₅ nanocomposite photocatalysts. Compared with the bare Sr₂KTa₅O₁₅ with a band gap of 3.89 eV and g-C₃N₄ with a band gap of 2.66 eV in our study, the absorption edges of the g-C₃N₄/Sr₂KTa₅O₁₅ nanocomposites with high content of g-C₃N₄ are nearly the same as that of bare g-C₃N₄ and their absorption curves are almost parallel to that of bare g-C₃N₄. The results imply that the possible doping behavior of anions, such as N and (or) C species were completely limited because of the low calcination temperature of 520 °C. Similarly with the case of g-C₃N₄/Sr₂KNb₅O₁₅ nanocomposites (see Section 8.3.4), the coupled g-C₃N₄ indeed functions not only as a visible light absorber to enhance visible-light absorption, but also as a sensitizer to subsequently transfer of energy to the Sr₂KTa₅O₁₅ semiconductor.
Construction of visible light-driven graphitic carbon nitride sensitized hybrid composite photocatalysts — a broad band gap

![Graph](image)

Figure 9.3. Tauc plots for Kubelka-Munk transformed UV-Vis DRS of g-C₃N₄/Sr₂KTa₅O₁₅ nanocomposite samples.

9.3.2. Photocatalytic abilities

Photocatalytic activity of the as-synthesized g-C₃N₄/Sr₂KTa₅O₁₅ nanocomposite samples have been evaluated by degradation of MB under visible light irradiation (λ > 400 nm). As shown in Figure 9.4, after irradiation for 6 h, bare Sr₂KTa₅O₁₅ nanorods sample was almost photo-inactive because of its wide band gap (E₉ = 3.89 eV) while only 16.2 % MB was photodegraded over the bare g-C₃N₄ sample. With the increasing content of coupled g-C₃N₄ with the Sr₂KTa₅O₁₅, their photocatalytic performance was improved and the photocatalytic activity reached the maximum in the 77CNTa sample and then decreased in 89CNTa sample. The photocatalytic trend is in good agreement with that of g-C₃N₄/Sr₂KNb₅O₁₅ nanocomposites, as presented in Section 8.3.6. Therefore, in the g-C₃N₄/Sr₂KTa₅O₁₅ nanocomposite photocatalysts, g-C₃N₄ acts similarly as a visible-light harvesting unit and a sensitizer, thereby enhancing the photocatalytic abilities. While compared with 77CNNb, the improvement of 77CNTa in photocatalytic activity was relatively weak. It is plausibly resulted from their different driving-force electron transfer as will be discussed later.
Construction of visible light-driven graphitic carbon nitride sensitized hybrid composite photocatalysts — a broad band gap

![Graph](image)

Figure 9.4. Photodegradation of MB under visible light irradiation (λ > 400 nm) over the g-C₃N₄/Sr₂KTa₅O₁₅ nanocomposite samples, bare Sr₂KTa₅O₁₅ and g-C₃N₄.

According to the Equation 11 as described before, reported by Scaife for oxides not containing partly filled d-levels,[199] the conduction band (CB)/valance band (VB) edge potentials of Sr₂KNb₅O₁₅ and Sr₂KTa₅O₁₅ were roughly estimated to be about -0.25 eV/2.95 eV, -0.95/2.95, respectively. The LUMO and HOMO energy levels of g-C₃N₄ are at -1.12 and 1.57 eV, respectively. A comparison diagram of heterojunction g-C₃N₄ coupled with Sr₂KNb₅O₁₅ and Sr₂KTa₅O₁₅ nanocomposites are schematically illustrated in Figure 9.5. Similar with the case of g-C₃N₄/Sr₂KNb₅O₁₅, the photoinduced electrons from the conduction band (CB) of g-C₃N₄ inject into that of wide band gap Sr₂KTa₅O₁₅ (E₉ = 3.89 eV), while the holes in the valence band Sr₂KTa₅O₁₅ migrate to that of g-C₃N₄, leading to the electronic sensitization of Sr₂KTa₅O₁₅, thus promoting spatial separation of photoinduced electron-hole pairs. While compared with the CB potential of Sr₂KNb₅O₁₅, the CB potential of Sr₂KTa₅O₁₅ is much closer to that of g-C₃N₄, this suggests that the driving force for photo-induced electron transfer from g-C₃N₄ to Sr₂KTa₅O₁₅ is smaller. The inefficient improvement of g-C₃N₄/Sr₂KTa₅O₁₅ in photocatalytic activity seems to be caused mainly by their lower driving-force electron transfer, thus limiting electron flow into CB of Sr₂KTa₅O₁₅ to some extent.

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Figure 9.5. A proposed energy levels comparison diagram of heterojunction g-C\textsubscript{3}N\textsubscript{4} coupled with Sr\textsubscript{2}Nb\textsubscript{5}O\textsubscript{15} or Sr\textsubscript{2}Ta\textsubscript{5}O\textsubscript{15} nanocomposites.
9.4. Conclusions

The hybrid nanocomposite photocatalyst of g-C_3N_4/Sr_2KTa_5O_15 heterojunction was similarly prepared by direct grown of graphitic C_3N_4 on Sr_2KTa_5O_15 nanorod at 520 °C for 4 h. Compared to bare Sr_2KTa_5O_15 or g-C_3N_4, the visible light photocatalytic properties of the nanocomposites was indeed enhanced for degradation of methylene blue (MB) under visible light irradiation (λ > 400 nm), and the optimal g-C_3N_4 content in the nanocomposite is ca. 77wt%. It can be attributed to the same “photoinduced gear effect”. While compared to 77CNNb nanocomposites, the 77CNTa nanocomposites exhibited a relatively weaker in the improvement of photocatalytic activity. The CB potential of Sr_2KTa_5O_15 is closer to that of g-C_3N_4, compared with the CB potential of Sr_2KNb_5O_15, suggesting that the driving force electron transfer between Sr_2KTa_5O_15 with g-C_3N_4 becomes smaller. Thus the relatively weak improvement of g-C_3N_4/Sr_2KTa_5O_15 in photocatalytic activity is plausibly resulted from their different driving-force electron transfer.
10. Summary

Although much recent efforts have been devoted to the development of niobate and tantalate-based semiconductor photocatalysts, the improvement of photocatalytic efficiency remains a great challenge and certain critical problems that may influence the photocatalytic activity and photostability still need to be addressed. For example, concerning the methodologies for constructing the semiconductor composites with matching band potentials for efficient charge carrier separation, the important effect are still not yet sufficiently understood. The even more complicate multi-components composite systems are rarely mentioned in literature. Another difficulty will be encountered in the composite photocatalysts approach, i.e., how to fabricate proper and intimate interfacial junction architecture among the components. Therefore, the thesis is targeting on fabrication, characterization, of niobate and tantalite-based mixed metal oxide semiconductor nanocomposite photocatalysts. Their photocatalytic activities for photocatalytic water splitting and photodegradation of methylene blue (MB) were systematically evaluated.

Control of phase coexistence in calcium tantalate nanocomposite photocatalysts for highly efficient hydrogen production

By aid of the simple and cost-effective molten salts method, a series of phase-controlled and composition-tuned calcium tantalate composite photocatalysts has been prepared by adjusting the initial atomic ratio of Ta/Ca precursors. The strong correlation was demonstrated between their photocatalytic H₂ production activities and respective phase compositions. Without any co-catalysts, these composites with the optimized phase composition of either cubic α-CaTa₂O₆/hexagonal Ca₂Ta₅O₁₇, or cubic CaTa₂O₆/hexagonal Ca₅Ta₂O₇/orthorhombic β-CaTa₂O₆, or cubic α-CaTa₂O₆/orthorhombic β-CaTa₂O₆ showed very high photocatalytic H₂ production activities in the presence of methanol. It is attributed mainly to a
Summary

significantly improved photo-excited charge carrier separation via the junctions and interfaces in the composites.

Insights into the photocatalytic properties of calcium tantalate nanocomposite photocatalysts with optimized phase-composition

The comprehensive study to demonstrate the photocatalytic properties of these different calcium tantalate nanocomposite photocatalysts with optimized phase-composition were performed after modification of co-catalysts, without the addition of any co-catalysts for simultaneous photocatalytic reforming. The effect of double-layered NiOx (metallic Ni core /NiO shell) as co-catalysts for overall water splitting, noble metal (Pt, Rh) as co-catalysts in presence of methanol for H₂ production on their photocatalytic performance were detailed investigated. Different amounts of NiOx loading were investigated to identify the most favorable conditions. 0.5 wt% NiOx loaded composite photocatalysts were found to exhibit the best photocatalytic activities with stable stoichiometric H₂ and O₂ evolution rates. The results indicate that the loading of NiOx as co-catalyst is beneficial to the formation of Schottky barriers at metallic Ni/calcium tantalate phases contact regions, and then results in a joint cooperation between the formed Schottky barriers and the interfacial phase junctions in these calcium tantalate composites. Thus, the enhanced electron-hole separation and interfacial charge transfer can account for the improved photocatalytic activities. With the addition of noble metal (Pt, Rh) co-catalysts, the photocatalytic activities of these calcium tantalate nanocomposite photocatalysts were greatly promoted for for hydrogen evolution. And without the addition of co-catalysts, very efficient photocatalytic H₂ production activities of these composite photocatalysts can also be achieved by simultaneous photocatalytic reforming of different alcohols and biomass derivatives.

Tetragonal tungsten bronze-type Ta substituted-Sr₂KNb₅O₁₉ nanorod photocatalysts with tunnel structure for photocatalytic water splitting
Tetragonal tungsten bronze-type tantalum (Ta) substituted \( \text{Sr}_2\text{KNb}_5\text{O}_{15} \) nanorod photocatalysts with tunnel structure were prepared by a facile and low-cost molten salt method using potassium chloride (KCl) at 850 °C for only 2 h. Ta substitution effects on the photocatalytic behaviour were systematically investigated for hydrogen production by aqueous methanol reforming. The average \( \text{H}_2 \) formation rates of \( \text{Sr}_2\text{KNb}_{5-x}\text{Ta}_x\text{O}_{15} \) first decrease with tantalum substitution for \( x < 2.5 \), presumably due to a decreased amount of absorbed photons and an obvious reduction of their exposed surface areas, whereas the activity is significantly improved for samples containing more Ta (\( x > 2.5 \)) and especially the fully substituted \( \text{Sr}_2\text{KTa}_5\text{O}_{15} \). This can be explained by a stronger driving force for photogenerated conduction band electrons to reduce water.

Furthermore, although all native photocatalysts did not possess any detectable activity in pure water splitting, after deposition of \( \text{NiO}_x \) as co-catalysts, samples of \( \text{Sr}_2\text{KNb}_5\text{O}_{15} \) and \( \text{Sr}_2\text{KTa}_5\text{O}_{15} \) can split pure water into \( \text{H}_2 \) and \( \text{O}_2 \) in a stoichiometric amount (\( \approx 2:1 \)), which can be ascribed to the improved charge carrier separation and transfer in the presence of \( \text{NiO}_x \).

Construction of visible light-driven \( \text{g-C}_3\text{N}_4 \)-sensitized hybrid nanocomposite photocatalysts

The \( \text{g-C}_3\text{N}_4 \) coupled \( \text{Sr}_2\text{KNb}_5\text{O}_{15} \) with a moderate band-gap and \( \text{Sr}_2\text{KTa}_5\text{O}_{15} \) with a broad band-gap have been prepared by the same direct growth method. The photoactivity of the samples was evaluated by degradation of methylene blue under visible light irradiation (\( \lambda > 400 \text{ nm} \)). These results indicate that the moderate band-gap \( \text{Sr}_2\text{KNb}_5\text{O}_{15} \) as well as the broad band-gap \( \text{Sr}_2\text{KTa}_5\text{O}_{15} \) were successfully sensitized by coupling of \( \text{g-C}_3\text{N}_4 \) into visible-light response. However, compared to the corresponding single components (i.e. \( \text{g-C}_3\text{N}_4, \text{Sr}_2\text{KNb}_5\text{O}_{15} \) or \( \text{Sr}_2\text{KTa}_5\text{O}_{15} \)), the photocatalytic performance of \( \text{g-C}_3\text{N}_4/\text{Sr}_2\text{KNb}_5\text{O}_{15} \) was significantly enhanced while the improvement of \( \text{g-C}_3\text{N}_4/\text{Sr}_2\text{KTa}_5\text{O}_{15} \) was only relatively weak. This can plausibly be explained by the different driving-forces for the electron transfer. Furthermore, by investigation of the preparation of
Summary

g-C$_3$N$_4$/Sr$_2$KNb$_5$O$_{15}$ nanocomposites comparing direct growth method and physical mixture method, the importance of the formation of proper nano-interfaces in the nanocomposites was demonstrated. Thus, a proposed mechanism was associated with a double-role of g-C$_3$N$_4$ as light absorber and sensitizer, and the close cooperation between their components via the nano-interfaces.

In conclusions, the study not only provide a convenient method for designing highly active niobate and tantalate composite photocatalysts with matching band structure for improving the photocatalytic hydrogen production and sheds light on developing efficient composite photocatalyst as a means for conversion of solar energy to chemical energy, but also offer a route to visible light harvesting using a simple and cost-effective approach to sensitize large band-gap niobate and tantalate semiconductor materials for the potential applications of solar energy conversion and environmental remediation.
11. **Outlook**

The study on fabrication of phase-coexisting calcium tantalates composite photocatalysts by adjusting the precursors’ atomic ratio under molten salts medium (Chapter 5) sheds light on developing other multi-component mixed metal oxides system, for example, synthesis of alkali metal and alkaline earth metal niobate and tantalate composites with d⁰ and d¹⁰ electronic configuration. As for the molten salts method, the effect of the synthetic parameters, especially the selection of molten salts, on the morphology, the formation mechanism and the photocatalytic properties of the prepared oxides can be further studied. Moreover, the as-synthesized calcium tantalates composites are only active under ultraviolet light (UV), due to their wide band gaps. Therefore, it is well suitable for band-structure engineering via anion and (or) cation doping technology extending light absorption into the visible region. As introduced in Section 3.1, nitrogen doping may be a very promising and feasible way. During the procedure of nitrogen doping, the effect of doping parameters (such as temperature, time, and flow rate of NH₃, etc) on the nitrogen doping content and oxide to (oxy)nitride transition should be studied in detail.

Similarly, in case of tunnel structure Sr₂KM₅O₁₅ (M= Nb or Ta), it is feasible for the transformation of corner-sharing MO₆ octahedral and cation exchange of three different tunnels (i.e. A₁= Sr, A₂= K, and A₃ is often empty), from viewpoint of the open structure. As described in Chapter 7, the results demonstrated that the Nb cations substituted by Ta has a dramatic effect on the photocatalytic activity for water splitting. For extending the photosensitivity of photocatalytic oxides into the visible-light region, further research can be done through structure modification: on the one hand, partial or full substitution of M sites by Mo, W, or V, etc; on the other hand, the A₁ and A₂ sites can be filled by Na⁺, Ca²⁺, Ba²⁺, Pb²⁺, Bi³⁺ and some rare earth cations. The influence of the exchanges of Sr and K cations in the A₁ and A₂ sites on structure property and photocatalytic behavior can be also investigated.
Outlook

As described in Chapter 8 and 9, the heterostructuring method was employed for synthesis of the visible light-driven g-C₃N₄ sensitized moderate band-gap Sr₂KNb₅O₁₅ and board band-gap Sr₂KTa₅O₁₅ hybrid composite photocatalysts, which can be used as a model to develop novel visible-light-driven heterostructured photocatalyst systems by combination with other narrow band-gap semiconductors. In addition, the obvious difference in photocatalytic performance of g-C₃N₄/Sr₂KNb₅O₁₅ and g-C₃N₄/Sr₂KTa₅O₁₅ has been explained by the different driving-forces for the electron transfer, based on the theoretical calculation of their band levels. Thus, the experimental characterizations of the real band alignment and the lifetime and concentration of electron-hole pairs, etc, should be considered in further research.
Bibliography


Solids 2011, 72, 1319.


Appendix

List of publications


Presentations

Sep. 19\textsuperscript{th}, 2013  4\textsuperscript{th} Junges Chemie Symposium Ruhr, Mülheim/Ruhr, Germany (Poster presentation).

Nov. 21\textsuperscript{th}, 2013  Research Day 2013-RUB Research school, Bochum, Germany (Poster presentation).

Mar. 12-14\textsuperscript{th}, 2014  47\textsuperscript{th} Jahrestreffen Deutscher Katalytiker, Weimar, Germany (Poster presentation).

Apr. 13-16\textsuperscript{th}, 2014  ICCES\textsuperscript{2nd} International Conference on Clean Energy Science, Qingdao, China (Oral presentation).
Curriculum Vitae

Personal Information
Born: May 8th, 1985, in Hunan, China.

Education
09/11-current PhD, Industrial Chemistry, Faculty of Chemistry and Biochemistry, Ruhr-University Bochum (RUB) in Bochum, Germany. (Co-supervisors: 1st-Prof. Dr. Michael Wark and 2nd-Prof. Dr. Martin Muhler).
Title: design and fabrication of niobate and tantalate semiconductor-based photocatalysts for solar energy conversion and environmental remediation.

09/08-07/11 M. Sc., Inorganic Chemistry, East China Normal University (ECNU) in Shanghai, China (Supervisor: Prof. Dr. Yongkui Shan).
Title: magnetic nano-size solid acid materials: synthesis, characterization and their catalytic performance.

09/03-07/07 B. Sc., Study of Applied Chemistry, Hunan Institute of Science and Technology, in Hunan, China.

Award & Honors
09/11-09/14 Doctoral scholarship from China Scholarship Council, China.
02/10-06/11 Top-level scholarship, ECNU, China.
09/08-01/10 Second-level scholarship, ECNU, China.

Other Activities
Associate member of Royal Society of Chemistry (RSC).
Member of Ruhr-University Research School (July, 2013-present).