Rational design of semiconductor crystal for efficient photocatalytic chemical conversion

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2016

Bu, J. (2016). Rational design of semiconductor crystal for efficient photocatalytic chemical conversion. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/65912>

<https://doi.org/10.32657/10356/65912>

NANYANG
TECHNOLOGICAL
UNIVERSITY

Rational Design of Semiconductor Crystal
for Efficient Photocatalytic Chemical
Conversion

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2015

Rational Design of Semiconductor Crystal for Efficient Photocatalytic Chemical Conversion

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A thesis submitted to the Nanyang Technological University in
partial fulfilment of the requirement for the degree of Doctor of
Philosophy

2015

Acknowledgement

It is great honor to present my appreciation to those who kindly offered his/her assistance and guidance during my PhD study.

First of all I would like to express my gratitude to my supervisor Prof. Chen Xiaodong for the opportunity to work in this distinguished group. Also I'd like to say thanks for his selfless support, guidance and sharing of knowledge. Without his support, this project cannot be finished and present in this thesis.

Secondly I want to thank Miss Leow Wanru, Dr. Lang Xianjun, Dr. Zhang Yanyan and Miss Bevita Kallupalathinkal Chandran for photocatalytic application measurement and discussion, Mr. Srikanth Pedireddy for XPS testing from SPMS and Dr. Xu Lin for TEM measurement. My heartfelt gratitude goes to my group members, Dianpeng, Fanben, Lili, Kaihong, Shao Qi, Xuebo, Yuxin, Zhiqiang for their sharing of knowledge, encouragement and assistance during my study. Also I would like to thank my friends Lisha, Shaowen, Wang Zheng, Yusen, Yupeng, Gu Quan, Zaizhu and Zhenyi for their help and support through my PhD study.

Finally I would like to thank my family for their patience, support, understanding and love, especially my husband, Dr. Fang Jun. Only with his love and support I can finish my project through the 4 years.

Abstract

Semiconductor based energy conversion from solar energy to chemical energy is one of the most possible solution for the severe worldwide energy crisis and followed environmental issues. However due to the low efficiency, the commercial application of semiconductor based energy conversion is still limited and further modification for better performance is required. Hence this thesis tries to improve the photocatalytic property of semiconductor by several kinds of modifications including control synthesis of TiO_2 with 3D hierarchical structure, loaded Pt nanoclusters with discrete energy levels and combination of TiO_2 and Cu_2O with different exposed crystal planes.

Nano-flower like rutile TiO_2 hierarchical structures have been synthesized by a solvent-thermal method. The structure of the nano-flowers was carefully characterized via various techniques, such as XRD, Raman spectra, UV-Vis diffuse reflectance spectra, XPS et al. we found that the building blocks of such nano-flower structures are single-crystalline rutile TiO_2 nanorods with their growth along [001] axis and exposed (110) facet on nanarods' side walls. Owing to this hierarchical nanostructure, this rutile TiO_2 showed enhanced photocatalytic activity for the selective oxidation from Benzylamine to N-BIBL. This suggests the great potential of this 3D highly ordered hierarchical structure in many other photocatalytic applications, such as PEC or DSSCs.

It is well accepted that Pt is the best cocatalyst for photocatalytic H_2 generation from water splitting. However, most consumed Pt is nanoparticles but not Pt nanoclusters with discrete energy levels which show totally different properties due to quantum size effect. In this thesis Pt nanoclusters protected by

L-glutathione reduced (GSH) are deposited on the surface of anatase TiO_2 with enhanced photocatalytic activity and stability. It is suggested that the synergistic effect of TiO_2 and Pt nanoclusters is crucial for the improved photocatalytic performance. And the size of prepared Pt nanoclusters shows great influence on the photocatalytic performance. Pt nanoclusters open a door for better modification of TiO_2 by tuning property of co-catalyst atom by atom.

Besides the controlled modification to obtain fancy morphology of TiO_2 or decorated TiO_2 with suitable cocatalysts, facet controlled combination of TiO_2 with other semiconductor (Cu_2O) is achieved. TiO_2 is successfully deposited on the surface of Cu_2O with different morphologies which exposed different crystal planes. The combination enhances the photocatalytic activity of the nanocomposites and improves the stability of the TiO_2 hybrid Cu_2O photocatalysts.

In conclusion, we developed different modification strategies for pristine TiO_2 to obtain improved photocatalytic activity. These researches on the modification strategies and their positive influence on the photocatalytic performance of the modified TiO_2 based photocatalysts suggests the rational design for the nano-structures of these catalysts is very crucial for the acquisition of desired catalytic properties of these catalysts. And this thesis show the promising prospect of the rational designed complex ordered nanostructures and their diverse applications in photocatalysis.

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Chapter 1: Introduction

1.1 Renewable energy for increasing energy crisis

Ever since early 19th century the requirement of energy for human society had greatly increased. Especially when time goes into 20th century after World War II today almost 80% of the consumed energies are fossil fuels

Fig 1.1 World energy consumption since 1820. The data is from the blog of Gail Tverberg

Take U.S.A as example, the annual data for energy consumption of 2011 shows that 36% of consumed energy comes from petroleum, 25% of consumed energy comes from natural gas while 20% of consumed energy comes from coal. Only 8% of consumed energy comes from nuclear technology which is alternative but not renewable energy. Renewable energy only supplies quite small amount for about 9%.

Fig 1.2 Energy source distribution in USA. The data is from U.S. Energy Information Administration, Monthly energy review.

However the economy growth and worldwide increasing population bring in great pressure on energy supply and demand. It is estimated that additional 10 terawatts (TW) of energy will be required for human life's maintaining compared with current 13TW for 6.5 billion people in the world (1). But the global oil reserve will almost exhaust due to the increased demand which will lead to high price for oil consumption. If new energy supply is not built up, huge energy crisis will devastate modern industry and human society.

Besides the tremendous contradiction between energy supply and demand, the consumption of fossil fuel energy leads to serious environmental problems like greenhouse gas emission, ocean acidification, land degradation among which greenhouse gas emission followed with global warming has significant

influence on the climate all over the world. According to Intergovernmental Panel on Climate Change (2) report, three main kinds of greenhouse gases emission significantly increased after 19th century which is consistent with the trend of energy consumption. The accumulated emission of greenhouse gases will lead to global warming. By the end of 21st century, it is estimated that the temperature will increase 4.8 °C for the highest reported by IPCC which will lead to melting arctic ice.

Fig 1.3 Global concentration of three kinds of greenhouse gases in air.

To reduce the negative influence of energy consumption and satisfy the increased energy demand, it is necessary to develop renewable and environmental benign energy for sustainable development of human society.

Among known renewable energies, solar energy shows special advantages due to the property of wide distribution, infinite amount of energy and free transportation. Nowadays the main applications of solar energy are photovoltaic cells and solar heat collector. Applying solar energy for chemical energy conversion like fuel production, water treatment et.al is still under research. Moreover only quite small amount of absorbed solar energy is consumed. The efficiency of solar energy utilization also requires enhancement. Employment of semiconductor based photocatalysts might be the approach to solve the problems in the future.

1.2 TiO₂ based photocatalytic applications

Over past several decades the interests in the research of semiconductor based photocatalysts increased dramatically. Semiconductor based photocatalysts were widely applied in degradation of pollutants, H₂ generation, CO₂ reduction, reduction of heavy metal ions and anti-bacteria driven by solar energy(3,4). Since the report of photoelectron water splitting on TiO₂ electrode, TiO₂ known for nontoxicity, earth abundance, high stability and activity has been well accepted and researched for promising photocatalytic application (107). Generally, take photocatalytic H₂ generation as example, the mechanism of photocatalytic reaction is shown in Fig 1.4 (5).

Fig 1.4 Fundamental mechanism of photocatalytic H₂ generation. Reprinted with permission from ref 5.

To achieve water splitting, standard Gibbs free energy change of 237 kJ/mol or potential of 1.23V must be fulfilled as shown in eq 1. So the band gap of semiconductor for water splitting must larger than 1.23eV. To make full utilization of photoexcited charges, the potential of valence band and conduction band of semiconductor is important. The more positive of the top level of conduction band, the more active oxidation. The more negative of the bottom level of valence band, the more active reduction. For full water splitting, the conduction band must be more positive than the oxidation potential of O₂/H₂O and the valence band must be negative than the reduction potential of H⁺/H₂O.

When TiO₂ is irradiated by light with wavelength with energy larger than the band gap energy, electrons in the valence band are excited to the conduction

band. After the photoexcitation of electron-hole pairs, there are several possible ways for the charge transfers. One is the bulk recombination which consumes great part of photoexcited electrons and holes. Some excited electron-hole pairs will move to the surface of the catalysts and recombine there which is called surface recombination. Besides bulk recombination and surface recombination charge separation also occurs which lead to electron trap and hole trap. When the excited electrons and holes migrate to the surface, reduction and oxidation processes are achieved.

Fig 1.5 Mechanism of photocatalytic reaction. Reprinted with permission from ref 5.

The processes of charge separation and recombination are competitive processes for the efficiency of photocatalytic reaction. The process that consumes excited electrons must be suppressed and the process that generates electrons should be enhanced.

However the band gap energy of TiO_2 is 3.2 eV for anatase phase and 3.0 eV for rutile phase both of which have no visible light response. As only about 5% of incoming solar light is UV light, to improve the efficiency of photocatalytic reaction the light response should be extended for TiO_2 .

Besides, the fast charge recombination rate on the surface of TiO_2 leads to low efficiency of H_2 generation. Different modification methods are applied to reduce the charge separation and enhance the charge transfer for improving the photocatalytic efficiency of TiO_2 (6).

1.3 Modification of TiO_2 photocatalysts.

1.3.1 Light absorbance enhancement

With wide band gap TiO_2 can only absorb UV light which restrict the utilizations of incoming solar energy. There has been much work about the extension of light absorbance based on TiO_2 . One is to dope TiO_2 with other elements for the alignment of band structure for visible light absorbance. Another strategy is to combine TiO_2 with other photosensitive molecules together to improve the light response.

1.3.1.1 Band gap modification

Doping of cations

Typically in the semiconductor crystals highest occupied molecular orbitals (HOMO) build up the valence band while the conduction band is composed of lowest unoccupied molecular orbitals (LUMO). For TiO_2 localized O 2p orbitals contribute to HOMO while Ti 3d, 4s, 4p orbitals form LUMO. When TiO_2 absorb light with energy larger than the band gap energy,

electrons in conduction band will be excited to valence band which leave holes in conduction band. With the photoexcitation O^{2-} in conduction band is transferred to O^- as photogenerated holes and Ti^{4+} in valence band is transferred to Ti^{3+} as photogenerated electrons. The band gap between the bottom level of conduction band and the top level of valence band is forbidden band in which electrons can't move freely.

By cation doping the introduced defects in TiO_2 crystal structure or the changes of crystallinity will bring in extended photoresponse and enhance the photoexcited charge carrier separation for improved photocatalytic activity. Additional energy level will be introduced into the forbidden band as capture center for visible light response. Capture center for electrons will be introduced when TiO_2 is doped with cations with higher valent state while holes are captured when TiO_2 is doped with cations with lower valent state.

Fig 1.6 Acceptor level and donor level achieved by cation doping. Reprint with permission from ref 5.

As early as in 1982 visible light driven water splitting achieved by Cr^{3+} doped TiO_2 was reported by Borgarello et al (7). The visible light response was

mainly achieved by the electron transition from Cr to CB (conduction band) of TiO_2 . Since then, great amount of researches have focused on cation doping of TiO_2 .

Overall water splitting under visible light irradiation was also achieved by doping Fe^{3+} to TiO_2 by hydrothermal method (8). With improved synthesis method Pt, Ir, Or Co doping into TiO_2 nanotube for visible light driven full water splitting was also reported (9,10). Due to different trapping property of Fe and Cr modified catalysts show different performances in charge separation and Fe doped TiO_2 show higher photocatalytic activity towards H_2 generation than Cr doped TiO_2 (11). Besides Fe, Cu and Mn doping can also introduce trapping of both electrons and holes for improved photocatalytic performance (12).

Co-doping of two cations shows better performance than single cation doping does. The absorption of visible light can be significantly enhanced by co-doping of Ni^{2+} and Nb^{5+} into TiO_2 (13). Similar phenomenon was observed by co-doping of Fe and Ni into TiO_2 with enhanced visible light driven activity which can be attributed to the efficient charge separation (14). But there is also report pointed out that the enhanced visible light driven activity is not always attributed to cations doping by improved light absorption (15-20).

Doping of anions

Besides cation doping, anion doping also improves the visible light response. The enhancement of photocatalytic performance by anion doping is usually achieved by adjusting VB (valence band) of TiO_2 which leads to narrowed band gap.

Asahi reported that narrowed band gap of TiO_2 was observed in N doped TiO_2 (21). But some report also demonstrated that the introduction of local states and oxygen vacancies responsible for the enhanced photocatalytic performance of N doped TiO_2 (22).

Besides N doping, C and P doping are also efficient for extended visible light absorption (23). And S doped TiO_2 even shows superior activity compared with N doped TiO_2 (24).

Co-doping of cations and anions

The combination of cation doping and anion doping can also bring in extended visible light absorption. It is reported that the VB edge of Mo-C co-doped TiO_2 is raised with almost unchanged CB edge which means narrowed band gap for extended visible light response (25). In and N co-doped TiO_2 also shows similar performance towards H_2 generation (26). 20 times higher activity is achieved by Ce and N co-doping (27).

1.3.1.2 Surface sensitization

Enhanced visible light absorption could also be achieved by modification of dye sensitization to TiO_2 . Generally dye sensitization is to adsorb dye molecules on the surface of TiO_2 by either chemical or physical adsorptions. When the dye sensitized TiO_2 is irradiated by light the dye molecules will absorb photons and inject excited electrons into CB of TiO_2 which would be collected by electrode or combined with adsorbed O_2 on the surface of TiO_2 for the formation of O^{2-} , H_2O_2 , $\bullet\text{OH}$ active radicals. With the introduction of photosensitive dye molecules the absorption of visible light is extended.

Fig 1.7 Basic mechanism of dye sensitized photocatalytic reaction. Reprinted with permission from ref 5.

Transition-metal complex dye sensitization

After the pioneer research of dye sensitization of semiconductor in 1970s, Gräzel et al. conducted a series of researches about dye sensitized photocatalysts including photodecomposing water and dye-sensitized solar cell (28-47). Early in 1980s $Ru(bpy)_3^{2+}$ was applied for visible light driven water splitting(48,49). The other ruthenium-based dye sensitized TiO_2 catalysts were also examined including $Ru(bpy)_3^{2+}$, tris(bipiridine) $Ru(II)(Ru(bpy)_3)$ and porphines-sensitized TiO_2 among which $Ru(bpy)_3^{2+}$ showed the best performance towards photocatalytic H_2 generation under visible light irradiation (50). The enhanced performance might due to the superior ability of photoexcited electron injection from dyes to CB of TiO_2 .

The influences of linking ligands were also carefully examined by Bae and Choi (51). The results illustrated that phosphonate group can be adsorbed on the

surface of TiO_2 more effective than carboxylate group did which is responsible for the better activity. However totally contrast phenomenon was also observed by Peng et al (52). They found out that loose contact will lead to high activity while strong connection only resulted in low activity.

Besides ruthenium-based dye sensitized catalysts, zinc porphyrin complexes and platinum (II) complexes were also studied and showed great ability in visible light driven solar cell and H_2 production (53-60).

Organic dye-sensitization

Despite the high activity, the stability, charge recombination and high cost strongly restrict the application of transition metal dye sensitized catalysts. New catalyst with low cost is required. Still Grätzel developed 8-hydroxyquinoline modified TiO_2 for photocatalytic H_2 generation in 1983 (61).

And whether halogenation or not of xanthenes dyes show great influence on photocatalytic activity towards H_2 generation (62). Also dye sensitization showed superior ability towards photocatalytic activity towards H_2 generation compared with other modification methods including metal doping and CdS loading (63). A series of organic dyes including 1,1'-binaphthalene-2,2'-diol (bn(OH)_2), perylene, and dyes with different hydrophilicity and hydrophobicity were fully examined and all showed visible light response towards photocatalytic application (64-67). It was also revealed that HOMO-LUMO position of the dye could be significantly affected by the anchoring group (68).

From the above review it is clear that the light absorption could be effectively enhanced to visible light region by dye sensitization. But dye

sensitized catalyst suffers from low stability and inefficient charge transfer which limit the photocatalytic activity. Further modification for high stable dye sensitized catalyst is still under study.

1.3.2 Improved charge separation

Even if light absorption is enhanced by other modification methods, the photocatalytic activity towards chemical conversion is still low due to the fast charge recombination rate on the surface of catalysts. So suitable modification methods must be applied to effectively separate the photoexcited electron-hole pairs and transfer to active sites for further chemical conversion on the catalyst surface to achieve high efficiency.

Generally charge generation, transfer and recombination are strongly affected by crystal structure like crystal defects and structure distortions. And the photocatalytic activity is also significantly influenced by crystal surface properties which are mainly related with morphology. So modification of crystal structure and morphology would efficiently enhance the photocatalytic activity.

1.3.2.1 Modified crystal structure

It is well accepted that the photocatalytic performance of TiO_2 is significantly affected by crystal structure (69-74). Moreover as photoexcited electrons are trapped by oxygen vacancies in anatase TiO_2 and intrinsic defects in rutile TiO_2 ; the photocatalytic performance of anatase TiO_2 is better than rutile TiO_2 (70, 75). But if the two phases are mixed together, the photocatalytic activity is strongly improved due to the phase junction what facilitates charge

separation and transfer hence leads to better activity compared with what pure phase does.

Fig 1.8 Two possible pathway of charge transfer between anatase and rutile TiO₂. Reprinted with permission from ref 4.

First it is revealed that the photocatalytic activity is irrelevant with specific surface area of TiO₂ with mixed phase structures by Li et al (76,77). But even if only depositing small particles of anatase TiO₂ on the surface of rutile TiO₂, the photocatalytic activity is enhanced remarkably with increased amount of deposited anatase TiO₂ particles which indicates the relationship between improved photocatalytic activity and formed phase junction on the interface of anatase and rutile TiO₂. And Kho et al. concluded that the enhancement is introduced by efficient charge separation due to the phase junction (78). However the detailed mechanism of improved activity by phase junction is still under discussion. One possible route is that electrons transfer from rutile to anatase due to the trapping sites in anatase TiO₂ which is 0.8 eV lower than CB edge of anatase and even lower than CB edge of rutile (79). The controversial route is that electrons transfer from anatase to rutile due to the lower CB edge of rutile compared with the CB edge of anatase (80, 81). Although there is no

clear mechanism of charge transfer in the phase junction of anatase and rutile TiO_2 , the enhancement of photocatalytic activity due to efficient charge separation driving by phase junction is confirmed.

Fig 1.9 Three types of heterojunction of TiO_2 combined with other semiconductors. Reprinted with permission from ref 4.

Besides phase junction formed by the two phase of rutile and anatase TiO_2 , heterojunction composed of two semiconductors also effectively improves charge separation.

As shown in Fig 1.9 electrons can be injected from the material with more negative CB position to the one with more positive CB position. Holes are attracted from VB with much more positive position.

Fig 1.10 Energy level of CdS/ TiO_2 heterojunction. Reprinted with permission from ref 4.

CdS is one of the most popular semiconductors that combined with TiO_2 for heterojunctions. No matter how the composites of TiO_2 and CdS are synthesized the heterojunction between the two semiconductors facilitates the charge separation and transfer followed with enhanced photocatalytic performance (4). The introduction of Pt particles further confirms that the electrons transfer from CdS to TiO_2 (82).

Besides CdS carbon-based materials are often applied to combine with TiO_2 for the formations of heterojunctions. Usually carbon-based materials exhibit high mobility of charge carriers what facilitates charge transfer and suppression of charge recombination for better photocatalytic performance (83-

85). No matter what kinds of carbon materials, multiwalled carbon nanotube (86-89), graphene sheets (90-91) and reduced graphene oxide (92-94), combined with TiO_2 , the composites all show superior photocatalytic performance due to the fast charge carrier transfer and suppressed charge recombination. However there is still no direct evidence of the improvement introduced by enhanced charge separation and suppressed charge recombination on the heterojunction of semiconductors. More efforts are required for the detailed research for the mechanism of the enhanced performance.

1.3.2.2 Modified crystal morphology

It is well known that not only the crystal structure affects the photocatalytic performance, the physical properties like size, surface area and surface active sites related to morphology also have great influence on the photocatalytic activity of TiO_2 . Typically smaller particle size will result in higher efficiency which is controlled by the quantum confinement effect of small particle size (95-101). Smaller particle size means less charge carrier transfer length which leads to less recombination hence high efficiency.

Also uniform morphology results in controllable exposed crystal facets which strongly affect the atomic composition and bonding environment on the surfaces of catalysts. Hence photocatalytic activity is also influenced by crystal morphology.

Pan's work revealed that TiO_2 with different exposed facets varies for the photocatalytic reaction (102). Qi's report also confirmed TiO_2 nanosheets with exposed {001} facets and modified by CdS and Pt show significant influence on photocatalytic H_2 generation (103). Similar enhancement was also observed

for layered titanate nanosheets modified with CdS quantum dots (104). To reduce the charge recombination 1D nanostructure is employed for photocatalytic application in which the mobility of charge carriers and defect density are improved. So higher photocatalytic performance of 1D nanostructure can be expected (105). To combine fast charge carrier transfer with large surface area together, 3D branched nanostructure is applied for photocatalytic application. And the prepared 3D branched nanostructure does demonstrate perfect property of charge carrier transfer (105). But the direct evidence of improvement introduced by crystal morphology is still unrevealed.

1.4 Co-catalyst loading

As mentioned before pure TiO_2 usually shows low efficiency towards photocatalytic reaction due to the fast charge recombinations and deficient active sites on the surface. To overcome the drawback co-catalyst loading is employed. Generally loaded co-catalyst can reduce the activation energy, enhance charge separation and consume undesired electrons and holes for improved stability.

1.4.1 Noble metal co-catalyst

When noble metal contacts with semiconductor, due to the different Fermi level, electrons will transfer from the high Fermi level to the low Fermi level. Generally the work function of noble metals especially platinum is larger than semiconductors. So the loading of noble metal on the surface of semiconductor will result in the charge transfer from semiconductor to noble metal. And with the lowest activation energy for proton reduction platinum is believed to be the most active co-catalyst for photocatalytic H_2 generation (106). Many research

have been conducted on the photocatalytic H_2 generation catalyzed by Pt loaded TiO_2 (108-111).

Fig 1.11 Charge transfer between Pt and TiO_2 . Reprinted with permission from ref 5.

The loading methods also affect the photocatalytic activity of Pt loaded TiO_2 . It is reported that the activity of Au/TiO_2 strongly depends on the preparation methods compared with Pt/TiO_2 (112). And cold plasma method shows the advantage in leading effective contact of Pt and TiO_2 compared with impregnation method (113). Also the mesoporous structure of TiO_2 could effective minimize loading amount of Pt (114).

Besides Pt other noble metals are also carefully examined like Au (115-120), Ru (121-125), Pd (126-129), Ag (130-134) and Rh (135-138). Photocatalytic activity towards H_2 yield is obviously enhanced by loading of

fine gold nanoparticles which can bring in more active sites and improved charge separation (139). The particle sizes of loaded Au particles show specific influence on the photocatalytic activity and the optimal size of Au nanoparticles is suggested for less than 10 nm (140). Moreover the plasmonic effect of Au/TiO₂ demonstrates different behavior as co-catalyst (141,142). However due to cost effective consideration non-noble metal co-catalysts also draw great attentions.

1.4.2 Metal oxide/sulfide/hydroxide co-catalyst

Besides metal co-catalyst metal oxide/sulfide also show advantages on improving photocatalytic activity for example NiO(143,144)and RuO₂ (145-148). Similar to gold nanoparticle NiO also shows activity dependence of preparation method (149).

As NiO is p-type semiconductor while TiO₂ is n-type semiconductor, p-n junction what can significantly promotes charge separation on the interface of NiO and TiO₂ might be responsible for the improvement of photocatalytic activity (150). Ni/NiO composite and Ni(OH) also lead to advanced photocatalytic activity for H₂ generation (151,152). Cu(OH) clusters is also reported as effective co-catalyst for photocatalytic H₂ generation with high quantum efficiency (153).

A synergistic effect of RuO₂ and Pt for enhancing photocatalytic activity is observed when RuO₂ and Pt are co-doped (154-156). Also RuO₂ nanoclusters show great ability of improving the photocatalytic activity for full water splitting (157).

Although metal sulfides are widely applied to sulfide or oxysulfide semiconductor, they also show improvement on photocatalytic activity towards H_2 generation when loaded on TiO_2 . Both NiS and MoS all significantly enhance the photocatalytic performance on H_2 generation (158,159). But metal sulfides suffer from stability problems.

1.5 Summary

In general increasing energy crisis and environmental issues might be solved by transfer of solar energy to chemical energy catalyzed by semiconductor. TiO_2 has been proved to be efficient and cost effective photocatalysts. However due to the wide band gap (>3.2 eV) the light absorption of TiO_2 is limited for UV light. As only about 5% of incoming solar light is UV light, the utilization efficiency of light absorption of TiO_2 is still low. Besides, the fast charge recombination on the surface of TiO_2 also limits the efficiency of photocatalytic conversion. So many kinds of modifications are applied on TiO_2 to improve the photocatalytic performance.

The photocatalytic performance of TiO_2 can be significantly improved by different modification methods either from adjusting crystal structure and morphologies or combining with other materials. Enhanced light absorption and efficient charge carrier transfer and charge separation all contribute to improve photocatalytic activity.

However despite of numerous researches on modification of TiO_2 the photocatalytic efficiency is still not high enough for commercial applications. And the detailed mechanism of modification is still unrevealed. There are even

some controversial discussions about the enhancement on photocatalytic activity achieved by modification on TiO_2 .

So TiO_2 based cost effective, stable and highly efficient photocatalysts and detailed mechanism of modification are still waiting for further research.

1.6 Project scope and objective

Based on previous introduction we try to focus on the modification of TiO_2 morphology and detect the detailed influence of co-catalyst.

Firstly the influence of morphology towards photocatalytic reaction is examined by preparing TiO_2 with specific hierarchical structure. The advantage of hierarchical structure was revealed by specific photocatalytic reaction.

Secondly although Pt has been widely examined as co-catalyst for photocatalytic H_2 generation, majority of loaded Pt are nanoparticles. Since nanoclusters show total different property with Pt nanoparticles and can be adjusted atom by atom, it is ideal model material for the mechanism research of modification on TiO_2 . The reduced charge separation and influence of size effect is revealed.

Last combination of TiO_2 and Cu_2O with different exposed crystal planes is achieved. The facet controlled modification of TiO_2 from crystal structure by combining with other semiconductor might bring in some understanding on the photocatalytic behavior of TiO_2 .

The objectives are shown below.

1. To develop TiO_2 nanoparticles with hierarchical structure for efficient charge separation with superior photocatalytic activity.
2. To evaluate the specific influence of special co-catalyst for enhanced visible driven photocatalytic reaction.
3. To examine the effect of heterostructure based on facet controlled growth

1.7. Construction of this thesis

This thesis is composed of five parts. Chapter 1 provides the description of current energy crisis and environment issues which require renewable and alternative energy as solution among which utilization of solar energy by semiconductors show great potentials. It also introduces the background, challenges and potential solutions of improvement of TiO_2 for better photocatalytic activity. Chapter 2 introduces the rational design and synthesis of rutile TiO_2 nano-flower for photocatalytic application. Chapter 3 presents the visible light induced photocatalytic H_2 generation by TiO_2 modified with Pt nanoclusters. Chapter 4 demonstrates facet controlled photocatalytic H_2 generation based on Pt nanoparticle modified $\text{Cu}_2\text{O-TiO}_2$ nanocomposites. Finally conclusion and future recommendations are given in chapter 5.

Chapter 2: Rational design and synthesis of rutile TiO₂ nanoflower for photocatalytic application.

2.1 Introduction

Usually pure TiO₂ shows low efficiency towards photocatalytic conversion due to the fast charge carrier recombination. Many attempts have been devoted to the improvement of charge separation among which special 3D morphology might be one potential approach as 3D hierarchical structure can provide both rapid charge transfer pathway and more active sites (105, 160,161).

Wang's work demonstrates that TiO₂ with flower-like structure shows superior photocatalytic activity. The better performance is attributed to the combination of structure and exposed {001} facet which shows stronger ability towards dissociative adsorption compared with {101} facets (162-167). Urchin-like structure prepared by etching process also shows superior photocatalytic performance (168).

Fig 2.1 Diagram of principle of multi-reflection in piping geometry. Reprinted with permission from ref 169.

As illustrated in Fig 2.1 the utilization of nanotube can facilitate the enhancement of light absorption efficiency due to the possible multi-reflections (169). As 3D hierarchical structure already shows the advantage in improving charge transport and separation, 3D flower-like hierarchical structure with fine building block like nanorod with small diameter might show specific enhanced performance due to the combination of improved charge separation and light absorption.

2.2 Experimental section

2.2.1 Materials

Titanium tetrabutoxide was purchased from Sigma Aldrich and used as received. Toluene and Hydrochloric acid fuming were purchased from Merck and used as received. Titanium tetrachloride and cetyltrimethylammonium bromide (CTAB) were purchased from Sinopharm Chemical Reagent Co., Ltd and used as received. Deionized water (resistance over 18M Ω) from Nanopure Diamond water system was used in all experiment.

2.2.2 Synthesis of rutile TiO₂ nanoflowers

Typically, 10 mL of toluene, 1 mL of titanium (IV) tetrabutoxide, 1 mL of titanium tetrachloride dissolved in toluene with concentration of 1M, 1 mL of hydrochloric acid (37%) and cetyltrimethylammonium bromide (CTAB) with given molar ratio towards Ti precursors were added to autoclave separately and stirred for 10 minutes. Then the mixed solution was heated at 180 °C for 2 hours. The temperature was cooled down to room temperature. The obtained precipitates were collected by centrifuging and washed with distilled water and ethanol for several times and dried at 60 °C overnight.

2.2.3 Materials characterization

The XRD patterns of prepared rutile TiO₂ nanoflowers were obtained by Shimadzu powder XRD using Cu K α radiation ($\lambda=1.54178$ Å). FESEM (JEOL-JSM-7600F) was employed to detect the morphology of prepared rutile TiO₂ nanoflowers. Transmission electron microscopy was carried out on JEOL-2010. The UV-vis diffuse reflectance spectra of TiO₂ nanoparticles were obtained by Lambda 750 UV/Vis/NIR spectrophotometer (Perkin Elmer, USA) with barium

sulfate as the reference. Specific surface area and porous information of TiO₂ nanoparticles were detected by ASAP 2020 adsorption apparatus from Micromeritics. Raman spectra were detected by confocal raman spectroscopy (Witec alpha 300 SR).

2.2.4 Photocatalytic oxidation of benzylamine to imine

0.01mmol of benzylamine was dissolved in 5 mL of acetonitrile in a Pyrex vessel. 25 mg of catalyst was applied for the photocatalytic oxidation of benzylamine. An Asahi Spectra MAX-303 300 W Xenon lamp was employed for light source with a cut-off filter of 420 nm. Typically the mixed solution with catalyst was first stirred for 30 minutes in dark for adsorption equilibrium. Then the pressure of 0.1 MPa was obtained by O₂ purging. During the reaction the mixed solution was stirred with a rate of 800 rpm at 25 °C. When the reaction ended after removing the catalysts by filtration, the products were detected by gas chromatography (GC) (Agilent 7890A, Agilent Technology 19091J-413 capillary column, FID detector, N₂ carrier gas). Gas chromatography–mass spectrometry (GC–MS) (Shimadzu GC 2010 and GCMS-QP2010 Ultra mass spectrometer) was applied for further confirmation of obtained products' structure by comparing with standard samples.

2.3 Results and discussions

2.3.1 Characterization of rutile TiO₂ nanoflowers

Fig 2.2 Low and high magnification SEM images (1a, 1b) and TEM images (1c, 1d) and SAED patterns of rutile TiO₂ nanoflower hierarchical structures (1e).

With one-step solvo-thermal process rutile TiO₂ nanoflower hierarchical structures were synthesized. The low and high magnification SEM and TEM images of obtained rutile TiO₂ nanoflower hierarchical structures are shown in Fig 2.2.

Clearly flower like nano-structure can be observed composed with basic units of small nanorods. The nanorods firstly combined together for nanobundles and then further formed nanoflowers. The diameter of prepared uniform rutile TiO₂ nanoflower structure is ca. 1.5 μm .

The low and high magnification TEM images further confirm the flower-like structure of rutile TiO₂ composed of small nanorods. The lattice fringe shown in HRTEM image is 0.32 nm corresponding to (110) facet of rutile TiO₂ with growth direction along [001] direction. The SAED pattern of rutile TiO₂ nanoflower structures examined along the [110] zone axis shown in Fig 1e confirms that the obtained TiO₂ nanostructure is single crystalline. This also shows that the [110] axis is perpendicular to the wall of the small nanorod which composed the flower-like structures.

Fig 2.3 XRD patterns of rutile TiO₂ nanoflower structures.

The XRD spectrum also confirms that the prepared nanoflower structure is pure rutile TiO₂ (JCPDS. 21-1276). The peaks locate at 27.5 °, 36.3 °, 39.3 °, 41.5 °, 44.1 °, 54.6 °, 56.7 °, 63.0 °, 64.3 °, 69.1 °, 70.0 ° and 76.7 ° are indexed to the (110), (101), (200), (111), (210), (211), (220), (002), (310), (301), (112) and (202) planes of rutile TiO₂. But the detailed growth mechanism of the prepared rutile TiO₂ nanoflower structure is unrevealed. So a series of control experiments were performed.

The effects of reactant

Fig 2.4 FESEM images and XRD patterns of TiO₂ prepared with ethanol as solvent.

The pure rutile TiO₂ nanoflower structure was prepared by solvo-thermal process with titanium tetrabutoxide and titanium tetrachloride as titanium source and toluene as solvent while hydrochloride acid serves to inhibit the hydrolysis of precursors. So the effects of reactants were examined. First the solvent was changed from toluene, the non-polar solvent, to ethanol which is a polar solvent. The result shown in Fig 2.4 illustrates that the non-polar solvent is crucial for the preparation of TiO₂ nanoflower structure (Fig 4a, 4b). No

small flower-like structure was observed with ethanol solvent but only bulk materials composed of small particles. As described in Grimes' work the interface between non-polar toluene and the small amount of polar water in hydrochloric acid facilitates the nucleus of TiO₂ from Ti precursors followed with oriental growth (170). When the solvent was changed from toluene to water, there is no such interface between solvent and water which will not lead to the oriental formation of TiO₂ nanocrystals. The XRD patterns of samples prepared with ethanol as solvent only show characteristic pattern of anatase TiO₂ but not rutile TiO₂ (Fig 4c).

Fig 2.5 FESEM images of TiO₂ prepared with only titanium tetrabutoxide (5a, 5b) and titanium tetrachloride (5c, 5d).

As the precursors are titanium tetrabutoxide and titanium tetrachloride the detailed effects of the precursors were examined by separate preparation with

only titanium tetrabutoxide or titanium tetrachloride as shown in Fig 2.5. Surprisingly when the samples were prepared only with titanium tetrachloride no flower-like structure was observed but only spindle-like structure composed of small nanorods was formed. This indicates that titanium tetrabutoxide has some specific influence on the formation of flower-like structure. When the samples were synthesized separately with titanium tetrabutoxide, flower-like structure was observed but no more fine rods. Moreover the obtained particles are quite small with only about half diameter of as-prepared rutile TiO₂ nanoflower structures. This result suggests that the introduction of TiCl₄ facilitate the formation of fine nanorods.

Fig 2.6 FESEM images of TiO₂ nanoflowers with different molar ratio of CTAB towards Ti precursors (6a-0.2, 6b-0.4, 6c-0.6, 6d-0.8, 6e-1)

Also the concentration of consumed CTAB was fully examined. The molar ratio of CTAB towards Ti precursors increased from 0.2 to 1. When the molar ratio increased to 1:1 as shown in Fig 2.6, uniform nanoflower structures were prepared. When the molar ratio of CTAB towards Ti precursors is only 0.2:1 only small part of nanoflower structures were formed. Most of prepared particles showed sphere-like structures. When the molar ratio of CTAB

increased the proportion of prepared flower-like structures increased. This controlled preparation illustrates that the amount of consumed CTAB leads to the transformation from sphere-like structure to flower-like structure.

The effects of temperature

Fig 2.7 FESEM images of TiO₂ nanoflowers prepared at different temperatures
(7a-80 °C, 7b-100 °C, 7c-120 °C, 7d-140 °C, 7e-180 °C)

Temperature controlled preparations of TiO₂ nanoparticles were performed to indicate the influence of temperature during the synthesis process. The results are shown in Fig 2.7. It is clear that when the reaction temperature is only 80 °C no flower-like structures were observed but only spindle-like structures without any hierarchical structure. Similar to the effect of consumed amount of CTAB, when the reaction temperature increased, the formation of flower-like structures gradually completed. Based on this temperature controlled experiments, high reaction temperature is crucial to the formation of flower-like structure. When high reaction temperature achieved small amount of water in hydrochloric acid diffused to reduce the surface energy followed with the hydrolysis of Ti precursors on the interfaces of water and toluene.

The effects of time

Time based control experiments were also conducted to reveal the influence of time. It is observed that the formation of flower-like structures almost completed within half hour. Time only affected the size of prepared rutile TiO₂ nanoflower structures. When the reaction time is 0.5 hour, the diameter of prepared rutile TiO₂ nanoflower structures is about 1 μm. When the reaction time increased the diameter of prepared nanoflower structure also increased and finally ended for about 1.5 μm with reaction time of 2 hours. This result illustrates that the reaction time only affects the length of nanorod which further composes the flower-like structure but has no influence on the formation of flower-like structure which might due to the fast hydrolysis of Ti precursor.

Fig 2.8 FESEM images of rutile TiO₂ nanoflower structures with different time
(8a-0.5h, 8b-1h, 8c-2h)

Based on the results above one growth mechanism was proposed. First at high temperature, small amount of water in hydrochloric acid will diffuse away and form the interface with toluene. Then Ti precursors will hydrolyze on the non-polar/polar interface leading to the crystal nucleus. When the small particles were formed, Cl⁻ ion will adsorb on (110) plane of TiO₂ and lead to the growth along [001] direction for the formation of nanorods. Later formed small nanorods will combine together for the formation of nanobundle which will finally form the flower-like structures under protection of CTAB with suitable molar ratio towards Ti precursors. The reaction time only affects the size of prepared nanoflower structures.

The XRD patterns of TiO₂ prepared within controlled experiments show that all the prepared samples are pure rutile TiO₂ except the one prepared with ethanol as solvent. This result suggests that the non-polar/polar interface strongly affect the crystallization which leads to different crystal phases.

Fig 2.9 XRD patterns of TiO₂ nanoparticles prepared with different experiment conditions (a-different surfactant, b-different CTAB concentration, c-different reaction temperature, d-different reaction time).

2.3.2 Photocatalytic oxidation of benzylamine to imine

The photocatalytic activity of prepared rutile TiO₂ nanoflower structures were examined by the aerobic photooxidation of benzylamine to imine which is important in synthesis of fine chemicals or pharmaceuticals. P25 was applied as reference for the control experiment. Benzylamine and N-benzylidenebenzylamine were chosen to be the model compound and the target product for the photooxidation process.

	Conversion (%)	Selectivity (%)	Yield (%)
TiO ₂ nanoflower-2h	75.9	69.8	53.0
TiO ₂ nanoflower-4h	99.9	73.3	73.2
P25-2h	33.0	68.1	22.5
P25-4h	78.1	73.0	57.0
P25-6h	98.7	73.6	72.6

Table 1 Photocatalytic activity of oxidation of benzylamine to imine under visible light by rutile TiO₂ nanoflower structures and P25.

As shown in Table 1 despite the well accepted phase junction what is beneficial of charge separation in P25, prepared rutile TiO₂ nanoflower shows superior high activity towards the conversion of benzylamine to imine compared with P25 nanoparticles. After 4 hours, the conversion of benzylamine to imine achieved 99.9% catalyzed by rutile TiO₂ nanoflower structures but only 78.1% catalyzed by P25 with selectivity of 73.3% and 73.0% separately. So the total yield of imine is 73.2% for rutile TiO₂ nanoflower structures and 57.0% for P25. Only when time extended to 6 hours the conversion reached 98.7% for P25 with selectivity of 73.6% for yield of 72.6% for P25. Clearly

rutile TiO₂ nanoflower structures show advantages towards the photooxidation of benzylamine to imine compared with P25.

Fig 2.10 Raman spectrum of prepared rutile TiO₂ nanoflower structures (10a), Br 3d XPS spectrum (10 b1) and N 1s XPS spectrum (10 b2) of prepared rutile TiO₂ nanoflower structures.

Several characterizations were performed for the detailed mechanism of the advanced activity of prepared rutile TiO₂ nanoflower structures. First Raman spectrum indicates that only pure rutile TiO₂ nanoflower structures were prepared during the solvo-thermal process which is shown in Fig2.10. The two

peaks with Raman shift of 442 cm⁻¹ and 606 cm⁻¹ are all indexed to the scattering mode of rutile TiO₂. The result of Raman spectrum excludes the existence of impurities on the surface of prepared rutile TiO₂ nanoflower structures. Also the Br 3d XPS spectrum and N 1s XPS spectrum of prepared rutile TiO₂ nanoflower structures show no characteristic peaks which confirm that CTAB was completely removed as shown in Fig 2.10.

Fig 2.11 UV-vis diffuse reflectance spectrum (a1), transformed UV-vis diffuse reflectance spectrum (a2), the N₂ adsorption-desorption isotherm (b1) and the size distributions (b2) of prepared rutile TiO₂ nanoflower structures.

The UV-vis diffuse reflectance spectrum of prepared rutile TiO₂ nanoflower structure shows step absorption at about 380 nm unlike typical spectrum of

rutile TiO₂ which shows absorption at about 400 nm. The band gaps calculated from transformed UV-vis diffuse reflectance spectrum are 3.0 eV and 3.5 eV corresponding to the step absorption. The multiple band gaps of rutile TiO₂ nanoflower structure might be attributed to the quantum confinement effect due to the small diameter of nanorods which facilitates the electron transfer along the section direction with short transfer distance.

As shown in Fig 2.11 the shape of the N₂ adsorption/desorption isotherm illustrates the mesoporous structure of rutile TiO₂ nanoflower structures. Typical type of H2 for the hysteresis loop was observed in the isotherm represented the ink-bottle pores of rutile TiO₂ nanoflowers. The Barrett–Joyner–Halenda (BJH) pore size distributions of rutile TiO₂ nanoflowers and P25 are also presented in Fig 2.11. Although specific surface areas of rutiel TiO₂ nanoflowers and P25 are quite similar as shown in Table 2; the pore size distributions are quite different. Generally the average pore size of rutile TiO₂ nanoflowers is quite smaller than the pores of P25 which indicates different pore structure of the two samples.

Samples	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore size (nm)
TiO ₂ -nanoflower	43.9	0.098	7.73
P25	47.6	0.19	14.01

Table 2 BET surface area and pore parameter of rutile TiO₂ nanoflowers and

P25

The above results confirm the advantages of prepared 3D hierarchical structures with more active sites on the surface of rutile TiO₂ nanoflowers. Furthermore the building block of the flower-like structure is nanorod with small diameter. Besides more active sites, the hierarchical structure facilitates the vectorial transfer of photogenerated electrons which further enhance the photocatalytic activity. Also the quantum confinement effect of small nanorod can enhance the separation of photogenerated charge carriers. All these advantages of prepared hierarchical structures bring in improved photocatalytic performance.

2.4 Conclusion

Generally single crystal rutile TiO₂ nanoflower hierarchical structure composed of nanorods with exposed (110) facet on the side wall was synthesized via one-step solvo-thermal process for the first time. The factors that influence the growth of rutile TiO₂ nanoflower hierarchical structure were carefully examined for the proposed growth mechanism. The photocatalytic performance of prepared TiO₂ nanoflower hierarchical structure was detected by photocatalytic aerobic oxidation of benzylamine to imine and the results confirmed the advantages of prepared nanostructures compared with P25. The improved photocatalytic activity might be attributed to the more active sites from 3D hierarchical structure, short charge carriers transfer distance of small diameter of nanorod and the enhanced charge carrier separation.

Chapter 3: Visible light induced photocatalytic H₂ generation by TiO₂ modified with Pt nanoclusters

3.1 Introduction

With almost the highest work function which facilitates the photoexcited electron transfer from semiconductor to metal Pt is considered to be the most effective co-catalyst for photocatalytic H₂ generation (171,172). However almost all the loaded Pt shows morphology of nanoparticles. Currently the interests focused on nanoclusters have increased a lot. It is well accepted that nanoclusters with size smaller than 2 nm shows discrete energy level due to the strong quantum confinement of free electrons (173). Moreover the electronic structure is tunable atom by atom. Even change of several atoms has significant influence on the property of prepared metal clusters (174). Based on these conclusions, metal atoms are ideal model catalysts for mechanism research of catalytic reaction.

The research focused on application of metal nanoclusters to photocatalytic reaction is still elementary. It is reported that loaded Au nanoclusters on the surface of semiconductors can efficiently enhance the charge separation (175-177). It is also pointed out that the residue of protected ligands for Au nanoclusters after the loading process may serve as recombination centre which will suppress the charge separation and reduce the photocatalytic activity (175).

Fig 3.1 Energy levels of Au nanoclusters with different sizes. Reprinted with permission from ref 174

Besides Au nanoclusters, PtO nanoclusters were prepared and loaded to TiO₂ which indicate significant relationship between photocatalytic activity and average size of prepared PtO nanoclusters (178). However the detailed research of the exact role of Pt nanoclusters for photocatalytic conversion is still not clear. Hence we try to deposit Pt nanoclusters onto TiO₂ to fully examine the influence of Pt nanoclusters towards photocatalytic reaction for further rational design of catalyst with desired property.

3.2 Experimental section

3.2.1 Materials

Titanium (IV) Fluoride was purchased from Alfa Aesar and used as received. Ammonium hydroxide solution was purchased from Sinopharm Chemical Reagent Co., Ltd and used as received. Hexachloroplatinic (IV) acid hexahydrate was purchased from Merck and used as received. L-ascorbic acid, L-Glutathione reduced and Sodium Borohydride were purchased from Sigma Aldrich and used as received. Sodium hydroxide was purchased from Schedelco and used as received. Deionized water (resistance over 18 MΩ) from Nanopure Diamond water system was used in all experiment.

3.2.2 Synthesis of TiO₂ nanoparticles

Firstly 3 mmol of titanium (IV) fluoride (TiF₄) powder was dissolved in ethanol (50 mL) and acetonitrile (50 mL) mixed solution with stirring. When TiF₄ was fully dissolved, 0.6 mL of ammonium hydroxide solution (NH₃•H₂O) was slowly added to the mixed solution for approximately 10 minutes with continuous stirring. With the addition of ammonium hydroxide solution white precipitate was formed. After continuous stirring for 48 h at room temperature, the precipitates were obtained by centrifuging and dried at 60 °C for 3 h. Then obtained gel-like precursor was annealed at 500 °C for 2 h with temperature heating rate of 1 °C/min. After annealing process, loosely TiO₂ powder with light yellow color was obtained.

3.2.3 Synthesis of Pt nanoclusters protected by L-glutathione reduced

The Pt nanoclusters were prepared by a mild etching procedure. First aqueous solution of L-glutathione reduced with concentration of 50 mM and aqueous solution of chloroplatinic acid hexahydrate with concentration of 20

mM were prepared. And fresh aqueous solution of sodium borohydride with concentration of 112 mM was prepared with adjusting of aqueous solution of sodium hydroxide with concentration of 1 M. Typically 150 μ L of L-glutathione reduced (GSH) solution, 50 μ L of sodium borohydride solution and 125 μ L of chloroplatinic acid hexahydrate solution were added into 5 mL of deionized water sequentially with continuous stirring. After stirring for 1 h at room temperature, Pt nanoclusters protected by L-glutathione reduced were prepared. To achieve the phase transfer of Pt nanoclusters from aqueous solution to organic phase, first 5 mL of cetyltrimethyl-ammonium bromide (CTAB) in ethanol with concentration of 100 mM was added to Pt nanoclusters aqueous solution and stirred for 20 s. Then 5 mL of toluene and 15 μ L of aqueous solution of NaOH with concentration of 1 M were added separately and stirred for 1 more minute. After incubation in toluene for 24 h, the prepared Pt nanoclusters were completely transferred from aqueous solution to organic phase.

3.2.4 Synthesis of TiO₂ nanoparticles modified with Pt nanoclusters

To prepare TiO₂ nanoparticles modified by Pt nanoclusters with molar ratio of 0.12%, first TiO₂ nanoparticles were treated with L-glutathione reduced to enhance the adsorption of Pt nanoclusters. Typically, 100 mg of TiO₂ and 50 mg of L-glutathione reduced were dissolved in 5 mL of deionized water and stirred for 1 h at room temperature. Then the yellow powder was collected by centrifuging and 3.1 mL of Pt nanocluster solution with molar ratio of 0.12 % was added. The mixed solution was stirred for 1h at room temperature. The precipitate was collected and dried in vacuum oven at room temperature for 3 h. After annealing at 300 °C for 2 h in Ar atmosphere Pt nanocluster modified

TiO₂ nanoparticles were obtained. The other photocatalysts were prepared with the same procedure only changing the given amount of Pt precursor and the prepared samples are denoted as TiO₂-xPt in which x represents the loading molar ratio of Pt nanoclusters towards TiO₂ nanoparticles. As control experiment, Pt nanoclusters modified Al₂O₃ was prepared following the same procedure.

3.2.5 Materials characterization

The XRD patterns of prepared TiO₂ nanoparticles with and without modification of Pt nanoclusters were obtained by Shimazu powder XRD using Cu K α radiation ($\lambda=1.54178$ Å). Morphology of the particles was detected by FESEM (JEOL JSM-7600F). Transmission electron microscopy was carried out on JEOL-2010. The UV-vis spectra of liquor during the preparation and UV-vis diffuse reflectance spectra of Pt nanoclusters modified TiO₂ nanoparticles were obtained by Lambda 750 UV/Vis/NIR spectrophotometer (Perkin Elmer, USA) with barium sulfate as the. Specific surface area and porous information of TiO₂ nanoparticles were detected by ASAP 2020 adsorption apparatus from Micromeritics. Fluorescence spectra of Pt nanoclusters were detected by RF 5301 Spectrofluorophotometer (Shimazu). X-ray photoelectron spectroscopy (XPS) spectra are performed on a Phoibos 100 spectrometer with a monochromatic Mg X-ray radiation source. The calibration was performed by setting C 1s peak at 284.5 eV.

3.2.6 Photocatalytic H₂ generation measurement

The visible light induce H₂ generation was carried out in a Pyrex cell under continuous stirring with top irradiation. Circulating water filter was

applied to remove the thermal effect. The light source was a 500 W Xe lamp. The UV light was blocked by a 422 nm cut-off filter for visible light irradiation. The reaction temperature was maintained at 20 °C by external water circulation. For all photocatalytic tests, 25 mg of photocatalyst was dissolved in aqueous solution of L-ascorbic acid with concentration of 0.1 M with pH adjusted to 4 by aqueous solution of NaOH with concentration of 1 M. Argon was employed with repeated purging process to remove the residual air before testing. Gas chromatograph (GC) (Shimadzu GC-2014; Molecular sieve 5A, TCD detector, Ar carrier gas) was applied to test the amount of generated H₂ with on-line program. After the photocatalytic H₂ generation catalyst was collected by centrifuging and washed by DI water and ethanol. The collected particles were dried at 60 °C for further characterization.

3.3 Results and discussions

3.3.1 Characterization of TiO₂ nanoparticles with and without modification.

Fig 3.2 XRD pattern of prepared TiO₂ nanoparticles.

The XRD pattern of prepared TiO₂ nanoparticles is shown in Fig 3.2 which can be well indexed to anatase TiO₂. The peaks locate at 25.4°, 37.1°, 38.0°, 38.7°, 48.1°, 54.2°, 55.2°, 62.9°, 69.1°, 70.4° and 75.2° correspond to the (101), (103), (004), (112), (200), (105), (211), (204), (116), (220) and (215) planes of anatase TiO₂ (JSPDS no. 71-1167).

To detect the fluorescence spectra of prepared Pt nanoclusters, L-glutathione reduced (GSH) protected Pt nanoclusters were transferred from aqueous solution to organic solution. The transfer was achieved by the

electrostatic interaction between cetyltrimethylammonium bromide (CTAB) which has positive charged cation and GSH on the surface of Pt nanoclusters which has negative charged carboxyl groups. The photoemission spectrum of prepared Pt nanoclusters in organic phase is shown in Fig 3.3 what is consistent with the previous report (173). The fluorescence spectra confirm the existence of discrete energy level of Pt nanoclusters due to the small size effect (179). Based on the prepared TiO₂ nanoparticles and Pt nanoclusters, Pt nanoclusters modified TiO₂ photocatalysts were prepared.

Fig 3.3 Fluorescence spectrum of prepared Pt nanoclusters in organic phase.

Due to the limited loading amount of Pt nanoclusters, there is no evidence of the existence of Pt in the XRD patterns of modified TiO₂ nanoparticles (Fig 3.4). The XRD patterns of modified TiO₂ nanoparticles are well indexed to anatase TiO₂.

Fig 3.4 XRD spectra of TiO₂ nanoparticles with and without modification of Pt nanoclusters.

The Pt nanoclusters were deposited on the surface of TiO₂ nanoparticles by adsorption what is confirmed by UV-vis absorption spectra of liquor after adsorption which is shown in Fig 3.5 (a). Compared with the UV-vis absorption spectra of aqueous solution of as-prepared Pt nanoclusters, there is almost no absorption for the liquor after the adsorption. This demonstrates that all the Pt nanoclusters in the aqueous solution are almost fully adsorbed on the surface of TiO₂ nanoparticles which ensures the loading amount of Pt nanoclusters for further investigation.

Fig 3.5 UV-vis absorption spectra of liquor after the absorption of Pt nanoclusters onto TiO₂ nanoparticles (a) and the aqueous solution of Pt nanoclusters with different concentration (b).

However to calculate the exact loading amount of Pt nanoclusters, the relationship between the intensity of UV-vis absorption spectra and the

concentration of aqueous solution of as-prepared Pt nanoclusters was examined and shown in Fig 3.5 (b). It is clear that only when the concentration downs below 20 % of original solution, the intensity of UV-vis absorption spectra has linear relationship with the concentration of solution of as-prepared Pt nanoclusters. So the residual amount of Pt nanoclusters in liquor after adsorption is calculated. When the molar ratio of Pt nanoclusters towards TiO₂ nanoparticles is less than 0.1 %, all Pt nanoclusters were adsorbed onto the surface of TiO₂ nanoparticles. The exact molar ratios of loaded Pt nanoclusters with theoretical amount of 0.12 % and 0.15 % are calculated according to the linear relationship between the intensity of UV-vis spectra and the concentration to about 0.11 % and 0.14 % separately. However in the following discussion, the samples are still denoted with the theoretical loading amount of Pt nanoclusters.

Fig 3.6 FESEM images of pure TiO₂ nanoparticles (a) and TiO₂ nanoparticles with Pt loading molar ratio of 0.05 % (b), 0.1 % (c), 0.12 % (d) and 0.15 % (e).

The field emission scanning electron microscopy images of pure TiO₂ nanoparticles (Fig 3.6 a) indicate that the prepared TiO₂ nanoparticles show pellet-like morphology. However the size of prepared nanoparticles is not very uniform. And the FESEM images of Pt nanoclusters modified TiO₂ nanoparticles confirm that the process of modification doesn't lead to any significant change to the morphology of TiO₂ nanoparticles no matter what the

loading amount of Pt nanoclusters is. After the loading process, TiO₂ nanoparticles still show pellet-like structures as before.

Fig 3.7 TEM images of pure TiO₂ nanoparticles (a,b) and TiO₂ nanoparticles with Pt loading molar ratio of 0.05% (c), 0.1% (d), 0.12% (e) and 0.15% (f).

The transmission electron microscopy (TEM) images further confirm the pellet-like morphology of prepared TiO₂ nanoparticles (Fig 3.7 a). From the high-resolution TEM images (3.7 b) the lattice fringe distance of 0.35 nm represents the (101) plane of anatase TiO₂. And the TEM images of Pt

nanoclusters modified TiO₂ nanoparticles (Fig 3.7 c-f) confirm the existence of loaded Pt nanoclusters. It is clear that the loaded Pt nanoclusters uniformly dispersed on the surface of TiO₂ nanoparticles with quite small sizes for almost no large than 2 nm.

Fig 3.8 The Pt 4f XPS spectra of Pt nanoclusters modified TiO₂ nanoparticles.

The detailed information of surface composition of Pt nanoclusters modified TiO₂ nanoparticles is detected by XPS spectra. And the Pt 4f XPS spectra are shown in Fig 3.8. The Pt 4f XPS spectra of all the prepared catalysts show the peak with binding energy of 72.7 eV which can be assigned to Pt²⁺ but not Pt⁰ as proposed.

Fig 3.9 The S 2p (a) O 1s (b) XPS spectra of Pt nanoclusters modified TiO₂ nanoparticles.

To ascertain the bonding environment of Pt on the surface of Pt nanoclusters modified TiO₂ nanoparticles the S 2p XPS spectra were detected as Pt nanoclusters are protected and linked to TiO₂ surface by thiol- group in GSH. There are two components in the S 2p XPS spectra with binding energy of 168.4 eV and 161.9 eV. The peak locates at 161.9 eV can be assigned to S²⁻ of thiol- group in GSH. And the one locates at 168.4 eV represents S⁶⁺ which indicates the oxidation of GSH during the annealing process. The S 2p XPS spectra confirm that GSH is partially removed during the annealing process what is consistent with previous report that GSH can't be fully decomposed at 300°C (175). The O 1s XPS spectra show 2 peaks with binding energy of 529.3 eV which represents the lattice oxygen in TiO₂ and 530.1 eV which can be assigned to surface hydroxyl. As Pt nanoclusters are protected by GSH in aqueous solution and there is no significant change of binding energy of O 1s, it is reasonable that the loaded Pt²⁺ nanoclusters are still linked with GSH on the surface of TiO₂ nanoparticles but not PtO.

3.3.2 Photocatalytic H₂ generation induced by modified TiO₂ nanoparticles

The photocatalytic activity of modified TiO₂ nanoparticles is detected by H₂ generation under all wavelength light and visible light illumination. As shown in Fig 3.10, pure prepared TiO₂ nanoparticles don't show photocatalytic activity towards H₂ generation no matter what kind of light is applied. The band gap of anatase TiO₂ is 3.2 eV which leads to the UV light response but no response to visible light. The electron in valence band of anatase TiO₂ can't be excited by visible light. So it's reasonable that pure prepared TiO₂ nanoparticles didn't show any response to visible light.

Fig 3.10 Photocatalytic H₂ generation under all wavelength light (a) and visible light illumination (b).

However when the reaction is performed under UV light illumination, although electron in the valence band is activated by UV light no H₂ is generated with pure prepared TiO₂ nanoparticles. This may due to the fast charge recombination on the surface of TiO₂ nanoparticles (4). To reduce the

charge recombination Pt nanoclusters are loaded onto the surface of TiO₂ nanoparticles.

When Pt nanoclusters are loaded onto the surface of prepared TiO₂ nanoparticles, it is clear that all the modified samples show photocatalytic activities towards H₂ generation under all wavelengths light and visible light. As reported before the work function of Pt is larger than TiO₂ which will induce the electron transfer from TiO₂ to Pt (4). Moreover the Schottky barrier in the interface of Pt and TiO₂ will efficiently suppress the recombination of electron and hole. This indicates that the loading of Pt nanoclusters significantly enhances the electron transfer and reduces the charge separation and leads to photocatalytic activities towards H₂ generation.

Fig 3.11 UV-vis diffuse reflectance spectra of TiO₂ nanoparticles with and without Pt nanoclusters modification.

Due to the size effect, Pt nanoclusters have discrete energy levels which mean that the electrons in Pt nanoclusters can be excited by light (180). So when the reaction is carried out under all wavelength light illumination, not only electrons in TiO₂ can be activated but also electrons in Pt nanoclusters can be excited. As shown in Fig 3.11 even pure TiO₂ has visible light absorbance which may due to fluorine doping confirmed by XPS spectra, however the absorbance mainly occur in the UV region below the wavelength of 400 nm. The light response is enhanced by Pt loading. The edge of light absorption extends with the increasing loading amount of Pt nanoclusters which indicates the enhancement of visible light absorption due to Pt nanoclusters loading. The amount of H₂ generated under visible light illumination slightly decreases compared with the one carried out under all wavelength light illumination.

So here one possible mechanism is proposed. When H₂ generation is performed under all wavelengths light or visible light illumination, both electrons in TiO₂ and Pt nanoclusters are excited. The electrons generated in TiO₂ are transferred to the surface due to the existence of Pt while the electrons generated in Pt also transfers to the surface. The synergistic effect of TiO₂ and Pt improves the charge separation and suppress the charge recombination. So the Pt nanoclusters modified TiO₂ nanoparticles showed all wavelength and visible light induced photocatalytic activities towards H₂ generation.

As 422 nm cut-off filter was applied in the visible light induced photocatalytic reactions, all the light with wavelength smaller than 422 nm was filtered. When the reaction was performed under visible light irradiation TiO₂

only absorbed light with wavelength larger than 422 nm. So the total amount of protons taken part in the reaction illuminated by all wavelengths light is larger than the one illuminated by visible light. Based on this condition, the amount of H₂ generated under all wavelength light illumination is higher than the one under visible light illumination as shown in Fig 3.12.

Fig 3.12 Yield of H₂ for TiO₂ with and without modification and Al₂O₃ with modification after 4 hours photocatalytic reaction.

To confirm the detailed influence of TiO₂ nanoparticles in visible light induced reaction, control experiment was performed. Pt nanoclusters modified Al₂O₃ was chosen for the control experiment as Al₂O₃ is insulator without photocatalytic ability. As shown in Fig 3.12, no H₂ was generated with the reaction catalyzed by Pt nanoclusters modified Al₂O₃. Also no H₂ was generated with the reaction carried out with pure TiO₂ nanoparticles. This result demonstrates that the synergistic effect in the interface of TiO₂ nanoparticles and Pt nanoclusters is crucial for the photocatalytic H₂ generation.

Among the modified catalysts, TiO₂ nanoparticles modified with molar ratio of 0.12% of Pt nanoclusters show the best activity towards photocatalytic H₂ generation with both all wavelength light and visible light illumination as shown in Fig 3.12. This may due to two reasons.

First as shown in Fig 3.11 the sample denoted as TiO₂-0.12Pt shows the best light response which is responsible for the best photocatalytic activity. The light absorption edge is strongly extended to visible light. Second, the TEM images not only confirm the existence of Pt nanoclusters on the surface of TiO₂ nanoparticles but also provide the size distribution of loaded Pt nanoclusters which are shown in Fig 3.13. Due to the small loading amount and size, the size distribution of TiO₂ modified with molar ratio of 0.05 % is not shown here. It is well accepted that the particles with size smaller than 2 nm are clusters which have discrete energy levels due to the quantum confinement effect. The discrete energy levels mean that the electrons in the clusters can be excited by light. The size distributions of Pt nanoclusters on the surface of TiO₂ nanoparticles demonstrate that the size of Pt nanoclusters increases with the increasing loading amount of Pt nanoclusters. All the sizes of nanoclusters are smaller than 2 nm when the loading molar ratio of Pt nanoclusters is less than 0.12%. All the loaded Pt nanoclusters are activated in the photocatalytic reaction. More loaded Pt nanoclusters introduce more photoexcited electrons responsible for enhanced photocatalytic activities. So when the loading molar ratio of Pt nanoclusters is below 0.12 %, the photocatalytic activities increase with the increasing loading amount of Pt nanoclusters shown in Fig 3. 12.

Fig 3.13 Size distribution of Pt nanoclusters on the surface of TiO₂ nanoparticles with different loading molar ratio of Pt nanoclusters.

And when the loading molar ratio of Pt nanoclusters increases to 0.15%, the percentage of nanoclusters with size larger than 2 nm is about 35%. This means that quite amount of Pt on the surface of TiO₂ might not be clusters but nanoparticles with continuous energy level. So the electron can't be activated by light. The total amount of activated electrons is decreased. Moreover the exceeded metal platinum can serves as recombination center for charge carrier which also decreases the photocatalytic activity. The size distribution is consistent with the decreased light response of TiO₂-0.15Pt. Due to the

decreased amount of photoexcited electrons and increased recombination center introduced by metal platinum, the photocatalytic activity towards H₂ generation dropped dramatically of TiO₂-0.15Pt compared with TiO₂-0.12Pt. Also the size distribution confirms the importance of discrete energy level of nanoclusters in the photocatalytic reactions indirectly. Take the photocatalytic performance and the size distribution into consideration together, it is clear that there is an optimal loading amount of Pt nanoclusters for the best photocatalytic performance.

Fig 3.14 The Pt 4f XPS spectra of TiO₂-0.15Pt after photocatalytic H₂ generation (a) and the cycled photocatalytic H₂ generation catalyzed by TiO₂-0.12Pt (b).

After the photocatalytic H₂ generation, XPS testing for recycled catalyst of TiO₂-0.12Pt was performed. The Pt 4f XPS spectra demonstrate that there is no valence change of Pt during the photocatalytic reaction which means great stability of catalysts. Pt nanoclusters were well protected by GSH during the photocatalytic reaction even illuminated by all wavelengths light. The photocatalytic H₂ generation performed with TiO₂-0.12Pt was retained for

several identical cycles to confirm the stability of prepared catalysts. After 12h for 3 cycles no significant decrease of activity was observed.

3.4 Conclusions

In summary, we successfully prepared TiO₂ nanoparticles modified with Pt nanoclusters protected by GSH for the first time. The loading process of Pt nanoclusters doesn't lead to any significant change to the morphology of TiO₂ nanoparticles. Only after modification TiO₂ nanoparticles show photocatalytic activities towards H₂ generation. The introduced photocatalytic activity confirms the enhanced charge separation and suppressed charge recombination attributed to loaded Pt nanoclusters.

The photocatalytic results and characterizations of prepared catalysts suggest that both TiO₂ nanoparticles and Pt nanoclusters are crucial for photocatalytic H₂ generation. Due to the discrete energy level in Pt nanoclusters electrons can be excited by light. The synergistic effect in the interface of TiO₂ nanoparticles and Pt nanoclusters is responsible for the introduced photocatalytic activity. Also the particle sizes of the prepared Pt nanoclusters are quite critical to the photocatalytic activities. The increased particle size brings in vanish of discrete energy level Pt nanoclusters which lead to decreased photoexcited electrons and photocatalytic activity.

However the direct evidence of the proposed mechanism of the introduced photocatalytic activity is still unrevealed. Therefore more characterizations of the photocatalytic process and the catalysts are required together with theoretical research.

Chapter 4: Facet controlled photocatalytic H₂ generation based on Pt nanoparticle modified Cu₂O-TiO₂ nanocomposite.

4.1 Introduction

Besides crystal morphology and loading of co-catalyst, combination of semiconductors for the formation of heterojunction also facilitates charge separation and charge transport which leads to photocatalytic activity improvement. Crystal planes with different electronic structure also have some special influence on the reaction pathway and final photocatalytic activity (8).

Shik C. Tsang et al. examined ZnO with different morphology which exposes different crystal planes (181). The result suggests that different synergistic effects occur on the interface of Cu and ZnO crystal face and finally lead to different performance. Cu₂O nanocrystals exposed with different crystal planes are also detected for CO oxidation (182). The experimental and simulation results consisted well and illustrated that the composition of the different crystal planes varied. The different electronic structure lead to different formation of CuO on the surface of Cu₂O nanocrystal with different exposed crystal planes which is crucial for CO oxidation. Hence the activation energy on the two kinds of crystal planes is quite different and results in total different reaction pathway (182). Also there are some pioneering works focusing on the photocatalytic performance of Cu₂O nanocrystals (184,185).

Fig 4.1 Energy profile of CO oxidation on different Cu₂O crystal planes.

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Cu₂O itself is also semiconductor with narrow band gap energy of about 2.4 eV which can absorb visible light. Whether the combination of TiO₂ with Cu₂O nanocrystal exposed with different crystal planes makes different photocatalytic performances requires further detection.

4.2 Experimental section

4.2.1 Materials

Copper (II) chloride (97%), Polyvinylpyrrolidone (average mol wt 40,000) and L-ascorbic acid (reagent grade, crystalline, ~325mesh) were all purchased from Sigma-Aldrich and used as received. Titanium (IV) Fluoride was purchased from Alfa Aesar and used as received. Methanol was purchased from Merck and used as received. Deionized water (resistance over 18 MΩ) from Nanopure Diamond water system was used in all experiment.

4.2.2 Synthesis of Cu₂O nanocube and nanooctahedron

Typically Cu₂O nanocube was prepared with procedure previously reported (183). First 134.45 mg of CuCl₂ was dissolved in 100 mL of distilled

water for the preparation of solution with concentration of 0.01 M. 10 mL aqueous solution of NaOH with concentration of 2 M was slowly added into the aqueous solution of CuCl₂ with the rate of 2 mL/min and kept stirring at 55 °C for 30 minutes. The light blue transparent aqueous solution of CuCl₂ turned to dark brown suspension. Then 10 mL of aqueous solution of L-ascorbic acid with concentration of 0.6M was added also with the rate of 2 mL/min at 55 °C. The mixed solution was stirred at 55 °C for 3 hours and Cu₂O nanocube crystal was obtained. The prepared Cu₂O nanocube crystal was collected by centrifuging and washed with distilled water and ethanol for several times and dried at 60 °C overnight.

For the preparation of Cu₂O nanooctahedron, given amount of polyvinylpyrrolidone (PVP average mol wt 40,000) was introduced control the morphology of prepared crystals. Firstly CuCl₂ was dissolved with different molar ratio of PVP in 100 mL of distilled water. Then the aqueous solutions of NaOH with concentration of 2 M and L-ascorbic acid with concentration of 0.6M were added followed the procedure of preparation of Cu₂O nanocube nanocrystals. The obtained precipitate was also collected by centrifuging and washed with distilled water and ethanol for several times and dried at 60 °C overnight. The prepared Cu₂O nanocrystals were denoted as Cu₂O-x in which x represent the molar ratio of PVP towards copper. And Cu₂O nanocube and nanooctahedron crystals were denoted as C-Cu₂O and O-Cu₂O separately.

4.2.3 Preparation of Cu₂O-TiO₂ nanocomposite

Cu₂O-TiO₂ nanocomposite was prepared as follows. Typically 60 mg of Cu₂O nanocrystals were dissolved in 60 mL of distilled water. Then 3.6 mL of

aqueous solution of TiF₄ with concentration of 0.02 M was added and stirred for 5 minutes. Then the mixed solution was transferred to autoclave and heated at 180 °C for 30 minutes. The prepared samples were collected by centrifuging and washed with distilled water and ethanol for several times and dried at 60 °C overnight.

4.2.4 Photodeposition of Pt nanoparticles onto the surface of Cu₂O-TiO₂ nanocomposite

Pt nanoparticles were deposited onto the surface of Cu₂O-TiO₂ nanocomposite by photoreduction process. 40 mg of Cu₂O-TiO₂ nanocomposite was dissolved in the mixed solution of distilled water and methanol (4 mL of distilled water and 1 mL of methanol). Then 0.5 mL of aqueous solution of hexachloroplatinic acid (H₂PtCl₆) with concentration of 2.8 mM for the molar ratio of 0.5 % was added to the suspension of Cu₂O-TiO₂ nanocomposite. The mixed suspension was irradiated under UV-visible light (300 W xeon lamp) for 2 hours. Then the particles were collected by centrifuging and washed with distilled water and ethanol for several times and dried at 60 °C overnight.

4.2.5 Materials characterization

The XRD patterns of prepared Cu₂O nanocrystals and Cu₂O-TiO₂ nanocomposites with and without deposited Pt nanoparticles were obtained by Shimazu powder XRD using Cu K α radiation ($\lambda=1.54178$ Å). Morphology and detailed structure of the particles was detected by FESEM (JEOL JSM-7600F) and TEM (JEOL-2010). The EDX attached to FESEM (JEOL JSM-7600F) was employed to analyze the deposited TiO₂ on the surface of Cu₂O nanocrystals and the distribution of Pt nanoparticles on the surface of Cu₂O-TiO₂

nanocomposites. The UV-vis diffuse reflectance spectra of Cu₂O nanocrystals and Cu₂O-TiO₂ nanocomposites were obtained by Lambda 750 UV/Vis/NIR spectrophotometer (Perkin Elmer, USA) with barium sulfate as the reference. X-ray photoelectron spectroscopy (XPS) spectra are performed on a Phoibos 100 spectrometer with a monochromatic Mg X-ray radiation source. The calibration was performed by setting C 1s peak at 284.5 eV.

4.2.6 Photocatalytic H₂ generation measurement

The photocatalytic H₂ generation was performed in a Pyrex cell under continuous stirring with light irradiation from top. The light source was a 500 W Xe lamp. For visible light testing, a 422 nm cut-off filter was applied to block the UV light. External water circulation was employed to remove the infrared (IR) component. For all photocatalytic tests, 25 mg of photocatalyst was dissolved in 80 mL of distilled water and 20 mL of methanol. Residual air was removed by repeatedly evacuation of air and purging of argon before testing. The amount of generated H₂ was tested by gas chromatograph (GC) (Shimadzu GC-2014; Molecular sieve 5A, TCD detector, Ar carrier gas) with on-line program.

4.3 Results and discussions

4.3.1 Characterization of Cu₂O nanocrystals, Cu₂O-TiO₂ nanocomposites with and without photodeposited Pt nanoparticles.

Fig 4.2 XRD patterns of Cu₂O nanocrystals prepared with different molar ratios of PVP.

As reported before (183) the morphology of prepared Cu₂O nanocrystals is controlled by the adding amount of PVP during the synthesis process. So the Cu₂O nanocrystals was prepared with different molar ratio of PVP and fully characterized

The XRD pattern of all prepared Cu₂O nanocrystals with different molar ratio of PVP shown in Fig 4.2 can be indexed to pure Cu₂O without any characteristic peak of CuO. The peaks locate at 29.6 °C, 36.6 °C, 42.5 °C, 61.6

°C, 73.8 °C and 77.7 °C correspond to (110), (111), (200), (220), (311) and (222) planes of Cu₂O (JCPDS 78-2076).

Fig 4.3 FESEM images of Cu₂O nanocrystals prepared with different molar ratio of PVP (2a-0, 2b-10, 2c-30, 2d-60)

From the above SEM images it is clear that the morphologies of synthesized Cu₂O particles were controlled by the molar ratios of PVP to CuCl₂. Pure Cu₂O nanocube crystals were prepared without PVP. When the molar ratio increased to 10 the corner-truncated Cu₂O nanocubes were obtained. When the molar ratio of PVP increased to 30 and above Cu₂O nanooctahedron was prepared. However the increased molar ratio not only brings in the synthesized Cu₂O nanooctahedron crystal but also makes the crystals not uniform any more.

Fig 4.4 Possible mechanism of the controlled synthesis of Cu₂O nanocube and nanooctahedron crystals. Reprinted with permission from ref 183.

According to Zhang et al.'s work PVP prefers to be adsorbed on the (111) planes of Cu₂O particles due to the more active interaction of PVP and the coordination unsaturated Cu. So PVP serves as capping agent and leads to the formation of Cu₂O nanooctahedron crystals with exposed (111) planes. The possible mechanism is shown above (183)

Fig 4.5 The Cu 2p XPS spectra of Cu₂O nanocube crystals.

The surface composition of Cu₂O nanocube crystals were detected and shown in Fig 4.5. The two peaks with binding energy of 931.1 eV and 950.9 eV

which can be assigned to the Cu 2p_{3/2} and 2p_{1/2}. As the Cu 2p XPS spectra for CuO have 4 peaks while the spectra of Cu₂O only have 2 peaks, it is easy to distinguish the spectra of Cu in Cu₂O from that of CuO. This result suggests that the main composition of prepared crystals is Cu₂O.

As discussed before, Cu₂O nanocube crystals with exposed (100) crystal planes and nanooctahedron crystals with exposed (111) crystal planes were successfully synthesized by adjusting the consumed amount of PVP during the preparation process. And the main component of prepared crystals are Cu₂O while surface oxidation lead to bivalent binding energy state of copper.

Fig 4.6 XRD patterns of Cu₂O-TiO₂ nanocomposite

Fig 4.7 FESEM images of prepared C-Cu₂O (6a), C-Cu₂O-TiO₂ (6b), O-Cu₂O (6c) and O-Cu₂O-TiO₂ (6d).

Although there is no characteristic peak of TiO₂ in the XRD patterns of Cu₂O-TiO₂ nanocomposite due to the small loading amount of TiO₂ shown in Fig 4.6. All the XRD patterns can be assigned to pure Cu₂O. The EDX spectra attached to FESEM show characteristic peaks of Ti element which confirms the existence of TiO₂ on the surface (Fig 4.8).

Fig 4.8 EDX data of C-Cu₂O-TiO₂ (a) and O-Cu₂O-TiO₂ (b).

The FESEM and TEM images also confirm the deposition of TiO₂ on the surface of Cu₂O nanocrystals. After the deposition of TiO₂ the morphology of nanocube and nanooctahedron were well maintained. But a rough film of TiO₂ composed of small particles on the surface was formed.

As shown in Fig 4.9 the TEM and HRTEM images confirm that TiO₂ was successfully deposited on the surface of Cu₂O nanocube and nanooctahedron crystals. The fringe lattice distance of deposited TiO₂ is 0.35 nm corresponding to anatase TiO₂.

Fig 4.9 TEM and HRTEM images of C- $\text{Cu}_2\text{O-TiO}_2$ (8a, 8b) and O- $\text{Cu}_2\text{O-TiO}_2$ (8c, 8d)

Due to the fast recombination of photoexcited electrons and holes on the surface of TiO_2 , pure TiO_2 usually show limited efficiency to photocatalytic reaction. Pt was introduced to the complex as co-catalyst for photocatalytic H_2 generation. The EDX data confirms the existence of loaded Pt nanoparticles on the surface of $\text{Cu}_2\text{O-TiO}_2$ nanocomposite.

Fig 4.10 EDX data of Pt loaded C- $\text{Cu}_2\text{O-TiO}_2$ (9a, 9b) and O- $\text{Cu}_2\text{O-TiO}_2$ (9c, 9d) nanocomposites.

From the EDX mapping images shown in Fig 4.10, small amount of Pt elements dispersed uniformly on the surface of both $\text{Cu}_2\text{O-TiO}_2$ nanocube and nanooctahedron composites what is consistent with the small loading amount. It is clear that Pt nanoparticles were successfully deposited on the surface of $\text{Cu}_2\text{O-TiO}_2$ nanocube and nanooctahedron composites.

4.3.2 Photocatalytic H₂ generation catalyzed by Pt nanoparticles modified Cu₂O-TiO₂ nanocomposites.

Fig 4.11 Photocatalytic H₂ generation of C-Cu₂O-TiO₂-Pt and O-Cu₂O-TiO₂-Pt

As shown in Fig 4.11 both Pt nanoparticle modified Cu₂O-TiO₂ nanocrystals show photocatalytic activity towards H₂ generation under all wavelength irradiation. No visible light induced H₂ generation was observed. The yield of H₂ shows linear relationship with reaction time even after 10 hours which indicates the photostability of prepared catalysts. Furthermore the yield of H₂ for 10 hour catalyzed by O-Cu₂O-TiO₂ is almost twice of the one catalyzed by C-Cu₂O-TiO₂. As only exposed crystal plane of Cu₂O nanocrystals varied in the two catalysts, the different yield of H₂ can be attributed to the different facets of prepared catalysts.

As described before in Huang's work (182), the surface composition and restructuring of Cu₂O are well controlled by the exposed crystal plane and

further connected to the activation energy of reaction process which leads to different activity. This result demonstrates the facet control photoactivity towards H₂ generation catalyzed by Pt nanoparticles modified Cu₂O-TiO₂ with different exposed crystal planes. It indicates that the crystal plane of Cu₂O might affect the epitaxial growth of TiO₂ on the surface which leads to different photo response.

4.4 Conclusion

TiO₂ was successfully deposited on the surface of Cu₂O with different exposed crystal planes and further decorated with Pt nanoparticles. The yield of H₂ photocatalyzed by O-Cu₂O-TiO₂-Pt is almost twice compared with the one photocatalyzed by C-Cu₂O-TiO₂-Pt. As TiO₂ was deposited on different crystal planes of Cu₂O, the epitaxial growth was affected by the surface composition and structure of Cu₂O which was proved to have different photocatalytic activity towards H₂ generation. Hence facet controlled preparation of photocatalyst with different activity was achieved. And the influence of crystal plane towards crystal growth and photocatalytic ability was proved. This research develops a new way to rational design of efficient catalyst with desired property.

Chapter 5: Conclusions

Rational design of TiO_2 based efficient photocatalyst with efficient light response; enhanced charge separation and facet control activity are examined. Various kinds of experiment techniques are applied to detect the detailed information of crystal structures, properties and photocatalytic activities to reveal the influence of modification towards the enhancement of photocatalytic performance of TiO_2 .

Firstly, rutile TiO_2 with 3D nanoflower hierarchical structure was synthesized by a facile solvo-thermal process and the advantage of flower-like 3D hierarchical structure was revealed. Secondly, TiO_2 modified with Pt nanoclusters protected by L-glutathione reduced (GSH) was prepared for the first time. The combination of Pt nanoclusters and TiO_2 resulted in suppressed charge recombination and visible light driven H_2 generation which might due to the synergistic effect of TiO_2 and Pt nanoclusters. The sizes of deposited Pt nanoclusters strongly affect the photocatalytic activity. The facet controlled photocatalytic H_2 generation was achieved by depositing TiO_2 on the surface of Cu_2O nanocrystal exposed different crystal planes.

Several conclusions drawn from above work are shown below.

1. To enhance the utilization of photoexcited electrons and suppress the charge recombination, 3D flower-like hierarchical structure of rutile TiO_2 was synthesized by one step facile solvo-thermal process for photooxidation of benzylamine to imine. Normally pure TiO_2 show low efficiency towards photocatalytic reaction and has no visible light

response for anatase TiO_2 . Here visible light driven conversion of benzylamine to imine was achieved with rutile TiO_2 with flower-like 3D hierarchical structures. The 3D hierarchical structure efficiently enhances the charge separation and transfer hence suppresses the charge recombination and posses more active sites compared with P25 thus show better photocatalytic activity.

2. Later TiO_2 modified with Pt nanoclusters protected by L-glutathione reduced (GSH) was successfully prepared for the first time. As ideal model co-catalyst with discrete energy levels, loaded Pt nanoclusters significantly suppress the charge recombination on the surface of TiO_2 and improve photocatalytic performance under visible light. Several techniques are applied for the characterization of modified TiO_2 . XPS spectra confirm the existence of Pt nanoclusters on the surface of TiO_2 and further reveal the valent information of deposited Pt nanoclusters. The synergetic effect of TiO_2 and loaded Pt nanoclusters is crucial for the visible light driven activity towards H_2 generation. The photocatalytic activity varies when loading amount of Pt nanoclusters increased with different particle sizes which bring in different property of deposited Pt nanoclusters. The size differences of Pt nanoclusters in various samples lead to different behavior of photogenerated electrons which confirm the importance of discrete energy levels of Pt nanoclusters for the enhanced photocatalytic activity. So the photocatalytic performance of TiO_2 can be adjusted by the loading of Pt nanoclusters with different size.

3. Besides the modification of morphology of pure TiO_2 and co-catalyst loading, the combination of TiO_2 with other semiconductor with facet controlled property is examined. Take Cu_2O nanocrystal exposed with different crystal planes as substrate, TiO_2 is successfully deposited on the surface of Cu_2O for the formation of $\text{Cu}_2\text{O}/\text{TiO}_2$ nanocomposite with heterojunction at the interface. Pt nanoparticles are employed as co-catalyst for H_2 photogeneration. The yields of H_2 catalyzed by $\text{Cu}_2\text{O}/\text{TiO}_2$ nanocomposite with different structures were distinguished related with the exposed crystal plane of Cu_2O . The results confirm that it is possible to control the photocatalytic property by the exposure of different crystal planes of these nanocomposites.

With understanding of above research, by tuning morphology, choosing suitable co-catalyst and combining with proper semiconductor; rational design of semiconductor for desired property can be expected.

Recommendation for future work

1. Based on the first part of work the detailed examination of photocatalytic reaction for mechanism research is still unclear. The real influence of the flower-like hierarchical structure towards the reaction requires further detection. And for better performance, the fine structure of nanorods which is the building block of the flower-like structure requires improvement. Also modification of prepared rutile TiO_2 nanoflower hierarchical structure with other materials for better performance can be expected.

2. Although the loading of Pt nanoclusters does improve the photocatalytic activity, direct evidence of suppressed charge separation and enhanced light response is still blank. Some time-resolved spectroscopic study can be performed to reveal the mechanism of the modification. Also the control preparation of Pt nanocluster for adjust atom by atom might result in deep understanding of the influence of modification and overcome the huge material gap between model catalyst and real catalyst.
3. As described in chapter 4 a lot of work is required for deep understanding of the real influence between Cu_2O crystal plane and the difference of photocatalytic activity. The real role of Cu_2O in this composite is still unclear. The lateral work on the relationship of crystal plane and the growth of TiO_2 further the photocatalytic activity will help to understand the influence of photocatalyst better.

List of Publications

1. **Bu, J.**; Fang, J.; Leow, W. R.; Zheng, K.; Chen, X.* "Single-crystalline rutile TiO₂ nano-flower hierarchical structures for enhanced photocatalytic selective oxidation from amine to imine" *RSC Adv.*, **2015**, 5, 103895-103900.
2. Cao, X.; Qi, D.; Yin, S.; **Bu, J.**; Li, F.; Goh, C. F.; Zhang, S.; Chen, X.* "Ambient Fabrication of Large-area Graphene Films via a Synchronous Reduction and Assembly Strategy" *Adv. Mater.* **2013**, 25, 2957-2962.

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