Hierarchical Ag/AgCl-TiO₂ hollow spheres with enhanced visible-light photocatalytic activity

Xu Long Wang^a, Hao Yong Yin^a, Qiu Lin Nie^{a,*}, Wei Wei Wu^a, Yang Zhang^b, Qiu LiYuan^b

^a College of Materials Environment Engineering, Hangzhou Dianzi University, Hangzhou 310018, PR China

^b College of Science, Hangzhou Dianzi University, Hangzhou 310018, PR China

Abstract

The hierarchical Ag/AgCl-TiO₂ hollow spheres were synthesized by depositing Ag/AgCl nanoparticles on TiO₂ hollow spheres via a precipitation photoreduction method, and they were further characterized using TGA, SEM, TEM, XRD, XPS, UV-vis DRS and photoelectric chemical analysis. The analysis showed that the hierarchical Ag/AgCl-TiO₂ hollow spheres exhibited the highest photocatalytic activity, which was approximately 13 times higher than that of TiO₂ hollow spheres. The high photocatalytic activity of the composites is due to efficient electron-hole pairs separation at the photocatalyst interfaces, and localized surface plasmon resonance of Ag nanoparticles formed on AgCl particles in the degradation reaction.

Key words:

Semiconductors ; Sol-gel growth ; Plasma deposition ; Visible and ultraviolet spectra

Introduction

Visible light driven photocatalysis for hydrogen production and degradation of pollutants has arose more and more attentions over the past decades because it can directly use the sunlight to deal with the energy source and environmental problems [1]. Among various semiconductors, titanium dioxide is generally recognized as the most promising photocatalyst due to its biological and chemical inertness, strong oxidizing power, cost effectiveness, long term stability, and environmentally friendliness [2]. However, the performance of titanium dioxide needs further enhancement for practical application, due to its low quantum efficiency, and many efforts have been directed towards it. It is well known that the morphology is an important factor influencing the activity of the photocatalysts, which resulted in the material's shape dependency [3]. This observation led to the extensive investigation of nano-titanium dioxides with varying morphology,

*Corresponding author: Tel.: +8657186915125; fax: +86571771713538;
E-mail address: niequlin@hdu.edu.cn (Q.L.Nie)

including nanoribbons[4,5], nanotubes[6,7], hierarchical flower-like nanostructures[8,9], mesostructured spheres[10] core shell structures[11,12]. In particular, titanium dioxide hollow spheres have attracted enormous attention because of their low density, large surface area, good surface permeability as well as high light harvesting efficiency[13]. Yin et al.[14] reported the preparation of hollow TiO_2 by a template implantation route using SiO_2 as template. The product displayed efficient photocatalytic activity outperforming the commercial P25- TiO_2 in the photocatalytic decomposition of organic dye molecules. Tseng et al.[15] also reported the synthesis of hollow TiO_2 by a template implantation route in heptane solvent, which showed the improved photodegradation of aqueous methylene blue (MB) dye under UV exposure. However, it still remains a great challenge to develop a new type of TiO_2 hollow structures with efficient visible light photocatalytic performance.

Recently, localized surface plasmonic resonance (LSPR) of noble metals (mainly silver and gold) showed significant promise in enlarging the absorption scope of TiO_2 [16,17]. The resonant photon wavelength varies for different metals. For example, silver[18,19], gold[1,7,20] and platinum[21,22] nanostructures exhibit resonant behaviour when interacting with visible range photons. Unlike the traditional noble metal/semiconductor plasmonic systems, silver halide materials (AgX , $\text{X} = \text{Cl}$, Br and I) exhibit good stability because they remain stable after the preliminary decomposition into Ag^0 species under irradiation [23] and are, therefore, found to be one of the most promising plasmonic photocatalysts[24]. As reported, many attempts have been made to organize AgX -based TiO_2 nanomaterials[25-28]. Wang et al.[27] reported the synthesis of $\text{Ag}/\text{AgCl}/\text{chiral TiO}_2$ nanofibers which showed highly efficient and stable visible light photocatalytic activities for the degradation of 17- β -ethinylestradiol. Guo et al.[28] demonstrated one-pot synthesis of the plasmonic photocatalyst $\text{Ag}/\text{AgCl}/\text{TiO}_2$ which showed enhanced photocatalytic degradation of 4-CP and photoreduction of Cr(VI) under visible light irradiation, due to the LSPR of Ag and the coexistence of Ag and AgCl. Although the SPR effect of silver and silver halide makes it feasible to synthesize a new type of active, stable photocatalyst by combining the advantages of silver and silver halide nanoparticles with TiO_2 , very little work has been done on the fabrication of TiO_2 hollow spheres and Ag/AgCl nanoparticles based nanocomposite and their photocatalytic activities. The combination may bring to the synergistic

effect of SPR and hollow structure which will improve the visible light induced photocatalytic performance. Moreover, understanding the plasmonic photocatalysis mechanism is still a challenging task, and more experimental evidence is required for a clear understanding of SPR effect enhanced photocatalysis. Therefore, in present work, the TiO_2 hollow spheres were firstly prepared using carbon spheres as templates. Then, the Ag/AgCl-decorated TiO_2 hollow spheres were obtained via a precipitation–photoreduction method. The hierarchical Ag/AgCl- TiO_2 hollow spheres photocatalysts displayed enhanced photocatalytic activities in the degradation of RhB under visible-light irradiation. The photocatalytic mechanism of the hierarchical Ag/AgCl- TiO_2 hollow spheres under visible light irradiation is discussed in the paper.

2. Experimental

2.1 Preparation of photocatalyst

Preparation of carbon sphere templates: 13.6g glucose was dissolved in 80mL deionized water under stirring for 30min using the 100mL round bottom flask. The solution was transferred to a 100mL teflon-lined stainless steel autoclave and treated under 180°C for 12h. After the procedure, the precipitate was washed with water and ethanol absolute(A.R.), dried, and ground to carbon sphere nanoparticles.

Preparation of hollow TiO_2 : 5mL tetrabutyl titanate(C.P.) and 25mL ethanol absolute were mixed to obtain solution A, while 5mL acetate and 5mL ethanol absolute were mixed to obtain solution B. Under magnetic stirring conditions, solution B was dropwise added to solution A to form a sol. Then, 0.5g carbon spheres were added into the sol until it reconstituted into a gel. The above mixture was transferred into a ceramic bowl and calcined for 180 min at 500°C in the air to gain TiO_2 hollow sphere, which were denoted as (h) TiO_2 .

Preparation of Ag/AgCl-(h) TiO_2 : Ag/AgCl nanoparticles were deposited on the as-prepared (h) TiO_2 samples by a precipitation–photoreduction reaction. Typically, the synthesized (h) TiO_2 samples were dispersed in 30mL deionized water and sonicated for 10min. Then 1mmol AgNO_3 was added into the (h) TiO_2 suspension and sonicated for 10min. After stirring magnetically for 20min, 20mL of 0.1mol/L HCl aqueous solution was added, sonicated for 10min and stirred magnetically for 20min. Subsequently, the resulting suspension was irradiated by a 250W High

press Hg lamp for 30min to reduce a part of Ag^+ ions in the AgCl particles to the Ag^0 species by photochemical decomposition of AgCl. The whole reaction process was kept at room temperature. Finally, the dark yellow samples were collected, washed for 3 times, filtered and dried at 80°C in oven for 12 h. The samples were denoted as Ag/AgCl-(h)TiO₂.

2.2 Characterization

Thermogravimetric analysis(TGA) was carried out to track the changes during the heat treatment by a simultaneous thermal analyzer(NETZSCH STA 449F3 Jupiter). Morphological analysis was performed by scanning electron microscopy(SEM) and high resolution transmission electron microscopy (HRTEM) using JEOL JSM-6380LV and a JEOL 200CX microscope operating at 200 kV respectively. The X-ray diffraction(XRD) patterns were obtained on a Rigaku Ultima III X-ray diffractometer (Japan) using $\text{CuK}\alpha$ radiation. X-ray photoelectron spectroscopy(XPS) measurements were done on a PHI-5400 spectrometer. UV-vis Diffuse reflectance spectra (UV-vis DRS) were recorded on the Shimadzu recording Spectrophotometer UV-3600.

2.3 Electrochemical measurements

The doctor blade method was employed to make the photoelectrode. In a typical process, 100mg of catalysts were added into 10mL ethanol to form a uniform suspension. As in a standard doctor blade method process, the ethanol suspension was dropped onto a piece of FTO (fluorine tin oxide) glass, while scraping the unnecessary suspension off the FTO. The film was then allowed to dry at room temperature. Finally, the film was annealed by heating in the air at 80°C for 180min. The photoelectrochemical measurements were carried out using a conventional three-electrode, single-compartment glass cell fitted with a synthesized quartz window. The quartz electrolytic cell was filled with 0.1M NaOH aqueous. The fabricated electrode served as the working electrode. The illuminated area of the working electrode is 0.5cm^2 . A 300W Xe lamp was used as the light source. A cutoff filter of 420nm was employed for the visible light irradiation. The counter and reference electrodes were a platinum plate and saturated Ag/AgCl electrode, respectively. The photoelectrochemical experiment was performed using an electrochemical system (CHI-660D). Photocurrent density of the catalyst at 0.4V was measured in 0.1M NaOH solution under visible light irradiation. Electrochemical impedance spectroscopy (EIS) was performed using Zahner

electrochemical system at similar conditions as described above for photoelectrochemical tests. The magnitude of the sinusoidal voltage was 5mV and the examined frequency range was from 1 Hz to 100 kHz.

2.4 Photocatalytic activity evaluation

The photocatalytic activity of the as-prepared sample for the degradation of RhB in solution was evaluated under the simulative visible light. The 300W xenon lamp (LSH-X5000, Zolix Instruments Co. Ltd., Beijing), combined with a 420 nm cutoff filter was used to provide visible light irradiation. In every experiment, 50mg of the photocatalysts were added into 100mL RhB solution (5mg L^{-1}). The temperature was kept at 20°C by circulating cool water. At definite time intervals, 10mL of the sample solution was collected and separated by centrifugation (4000rpm, 10min). The UV-vis spectrophotometer was used for the determination of absorbance at 550nm.

3. Results and discussion

The TG/DSC results of TiO_2 and (h) TiO_2 precursors are shown in Fig.1. The TGA curves of both samples reveal that the obvious weight loss occurs over three temperature ranges of 50-150, 150-300 and $300\text{--}450^{\circ}\text{C}$ with their corresponding exothermic peaks. The initial weight loss of 3% for two samples is due to the elimination of a small amount of the physically adsorbed water. The second distinct weight loss of 14% for TiO_2 and 15% for (h) TiO_2 respond to the oxidation of tetrabutyl titanate and CH_3COOH . The third weight loss of 10% for TiO_2 may be due to the further combustion of remaining organic residues. However, beyond 300°C , (h) TiO_2 shows a significant weight loss (16% for (h) TiO_2 versus 10% for TiO_2) indicating the decomposition of the carbon template[29]. A plateau region from 450°C to 700°C was observed for (h) TiO_2 . The TG curves suggesting that no further weight loss was observed. This result implies that the temperature above 450°C is sufficient to remove the carbon templates and convert the precursors into (h) TiO_2 . According to the TG/DSC results, the (h) TiO_2 precursors were calcined at 500°C in the air to remove the carbon sphere templates.

Fig.2 displays the morphologies of the as-prepared (h) TiO_2 and Ag/AgCl-(h) TiO_2 photocatalysts. As shown in Fig.2a, the synthesized (h) TiO_2 photocatalyst is formed by semispherical particles with diameters ranging from 700 to 1100nm. The enlarged (h) TiO_2 pattern (Fig.2b) shows that the

sample is composed of thousands of nanograins with diameter about 30nm. The hollow structure can be observed from the cracked (h)TiO₂ (Fig.2c) which show the thickness of the wall is about 30nm. After deposition and photoreduction process, there are no distinct changes on the morphologies of the hollow sphere TiO₂ photocatalysts except a little rougher surface observed on the Ag/AgCl-(h)TiO₂ surface (Fig.2d). The microstructure and interfacial region of the prepared (h)TiO₂ and Ag/AgCl-(h)TiO₂ photocatalysts were further examined using HRTEM. Figs.3a and 3b exhibit that this sample was highly crystallized, as evidenced by well defined lattice fringes. The interplanar spacing of 0.352nm matches the [101] interplanar spacing of anatase TiO₂. Additionally, as shown in Fig. 3b, the lattice fringes with interplanar spacing of 0.235nm and 0.196nm were observed on the sample edge, corresponding to the [111] plane of metal Ag and the [220] plane of AgCl[30], respectively. All of these results confirm that Ag and AgCl particles were formed on the surface of (h)TiO₂ photocatalysts.

As-prepared samples were characterized by XRD. As shown in Fig.4, all the diffraction peaks of (h)TiO₂ photocatalysts can be attributed to the anatase phase of TiO₂ (JCPDS no. 21-1272), suggesting the high phase purity. In addition to (h)TiO₂ photocatalysts diffraction peaks, there are some weak peaks observed in the XRD patterns of Ag/AgCl-(h)TiO₂ photocatalysts at about $2\theta = 27.91, 32.21, 46.21, 57.51,$ and 67.4 which can be indexed to the pattern of AgCl (JCPDS no. 85-1355). It is similar to the result reported by Cui et al[31]. However, no distinct diffraction peaks of metallic Ag could be found, probably due to its low content, high dispersity or small crystallite size. As confirmed by the analysis of corresponding diffraction peak area, AgCl was successfully deposited onto (h)TiO₂ photocatalysts.

EDS was carried out to determine the chemical composition of the prepared species. The EDS spectrum shown in Fig.5 indicates that the Ag/AgCl-(h)TiO₂ photocatalyst has no impurity except weak amount of copper, typical contamination from instrument background. The samples contain Ti, O and Ag element, but the Cl signal was not observed. It is clear that, in the Ag/AgCl-(h)TiO₂ photocatalysts, the Ag amount is much higher than that of Cl.

The XPS measurements were carried out to determine the chemical composition and the element valence states of the prepared species. The survey XPS spectra shown in Fig.6a reveal the presence of Ti, Ag, O, Cl and C. No other impurity peaks were detected, evidencing the high

purity of the resulting sample. The high-resolution XPS spectra in Fig.2b–e show the characteristic peaks of Ti 2p, O 1s, Ag 3d and Cl 2p of the Ag/AgCl-(h)TiO₂ photocatalysts. The spin–orbit components 2p_{3/2} and 2p_{1/2} of the Ti 2p peaks of Ag/AgCl-(h)TiO₂ photocatalysts are well corresponding to 458.3 and 464.1eV (Fig.6b). Moreover, the O1s peak is observed at around 529.5eV(Fig.6c). It is well known that, for dielectric samples, it is topical to use the binding energy difference for the metal ion valence characterization. The binding energy difference calculated for titanium is $BE(O1s) - BE(Ti2p_{3/2}) = 529.5 - 458.3 = 71.2$ eV. Thus, the Ti⁴⁺ valence state is observed in this sample. In addition, the value of 71.2 eV is very close to the value reported for TiO₂[32,33] In Fig.6d, the Ag 3d spectra consists of two individual peaks approximately at 373 and 367eV, which are due to Ag 3d_{3/2} and Ag 3d_{5/2} binding energy, respectively. Furthermore, the peaks of Ag 3d_{5/2} and Ag 3d_{3/2} could be further divided into different peaks at 373.43 and 374.3eV, and 367.41 and 368.1eV, respectively[27]. The peaks at 374.3 and 368.1eV could be ascribed to the peaks of Ag 3d_{5/2} and Ag 3d_{3/2} of metallic silver, whereas the peaks at 367.41 and 373.43eV could be attributed to the peaks of Ag 3d inside AgCl[34]. As shown in Fig.6e, the peaks centered at 197.6 and 199.25eV are consistent with the peaks of Cl 2p_{1/2} and 2p_{3/2}, respectively[35]. Compared the peak strength of Ag and Cl XPS, it can be inferred that the surface atomic ratio of silver to chlorine was much higher than the stoichiometric ratio in AgCl (1:1), indicating the existence of excessive Ag on the surface of Ag-RTiO₂HS. Considering the fact that there was metallic silver in the as-prepared Ag/AgCl-(h)TiO₂ sample from the HRTEM and XPS results, this implied that the excessive amount of silver might have been produced from the photo-reduction of AgCl on the surface.

RhB was chosen as the target pollutant to trace the photocatalytic activity of Ag/AgCl-(h)TiO₂ photocatalysts under the visible-light irradiation. The (h)TiO₂ and Ag/AgCl-(h)TiO₂ photocatalytic activity is shown in Fig.7a. As can be seen that the effect of photolysis and absorption of catalyst on the decomposition of RhB was negligible during the test period. The degradation efficiency of RhB solution over (h)TiO₂ photocatalysts was about 38% in 4h. However, the degradation efficiency was significantly improved under the same condition after loaded by Ag/AgCl nanoparticles. The Ag/AgCl-(h)TiO₂ photocatalysts possessed the higher degradation efficiency, and almost 100% RhB was degraded after 4h. To have a better understanding of the reaction

kinetics of the RhB degradation catalyzed by various samples, Fig.7b shows the relationships between $\ln(C/C_0)$ and the irradiation time for RhB degradation. As the relationships were linear, the photocatalytic degradation curves fit well with first-order reaction. Ag/AgCl-TiO₂ hollow spheres exhibited the higher rate constant in the degradation reaction of RhB, which was approximately 13 times larger than that of TiO₂ hollow spheres. The variation of UV-visible absorption spectra of RhB degraded over Ag/AgCl-(h)TiO₂ photocatalysts is shown in Fig.8. Under visible light illumination, the color of RhB solution changed from an initial red to light red and then disappeared during the reaction. The peak intensity of the UV-visible absorption related to RhB decreased apparently, accompanied by a slight shift of this peak towards shorter wavelength. This phenomenon indicates that the complete mineralization of RhB over Ag/AgCl-(h)TiO₂ photocatalysts generally goes through a two steps process, the formation of N-de-ethylated intermediates in a step wise manner followed by the destruction of the conjugated structure into CO₂ and H₂O[36].

In order to examine the stability of the photocatalyst, the photocatalysis process was repeated four times with the same photocatalyst. The Ag/AgCl-(h)TiO₂ photocatalysts were easily recycled by centrifugation without any treatment in these experiments. After four recycles for the photodegradation of RhB, the Ag/AgCl-(h)TiO₂ photocatalysts did not exhibit any significant loss of activity, as shown by Fig.9, which confirms the excellent stability of the photocatalysts.

The UV-vis diffuse reflectance of the Ag/AgCl-(h)TiO₂ photocatalysts showed strong absorption in the ultraviolet and visible-light regions (Fig.10). The stronger absorption of Ag/AgCl-(h)TiO₂ photocatalysts over 200-350nm, as compared to that of (h)TiO₂ photocatalyst, can be attributed to the characteristic absorption of the AgCl semiconductor. Besides, Ag nanoparticles can absorb photons from an area much larger than their geometric cross section. Resonance energy transfer (RET, the transfer of energy from a plasmon to a nearby semiconductor) enhances the electric field intensity thereby increasing the optical absorption. In contrast, the increased response in the visible light region (400-700 nm) results from the creation of LSPR[37]. This sample could be excluded..

Fig.11 shows the photoinduced current as a function of time (i-t) at (h)TiO₂ and Ag/AgCl-(h)TiO₂ optical electrodes under visible light irradiation. Under visible light irradiation, almost no

photocurrent responded from the (h)TiO₂ optical electrode. The Ag/AgCl-(h)TiO₂ photocatalyst light electrode held a little lower dark current than that of (h)TiO₂. This is due to the fact that Ag⁺ with 0V(vs. Ag/AgCl) bias underwent reduction reaction on AgCl surface[38]. It can be observed that the raw current value of Ag/AgCl-(h)TiO₂ was a little lower than that of (h)TiO₂ photocatalyst, which may indicate that the light induced electron underwent reduction reaction on the surface of Ag/AgCl-(h)TiO₂ photoelectrode and the corresponding photogenerated hole oxidation reaction occurred on the Pt electrode. The related studies have shown that, in the Ag/AgCl photocatalytic materials system, electrons generated thorough Ag LSPR can be quickly transferred to AgCl and cause the electron hole separation.

EIS provides a powerful method for the study of charge transfer and recombined processes at the interfaces of semiconductor electrolytes [39, 40]. A typical Nyquist plot for the Ag/AgCl-(h)TiO₂ photocatalysts and (h)TiO₂ photocatalysts are shown in Fig.12. The EIS arc of Ag/AgCl-(h)TiO₂ photocatalysts electrode becomes smaller than (h)TiO₂ photocatalysts at the same potential. It is well known that the smaller size of the semicircle arc diameter indicates a more effective separation of the photogenerated electron hole pair and/or a faster interfacial charge transfer to the electron donor acceptor [39]. It is clear that metallic Ag act as a sink of electrons and Ag/AgCl nanostructures are characterized by their strong interaction with resonant photons through an excitation of LSPR. Hence, by injecting electrons from conduction band of TiO₂ to fermi level of Ag, the separation of the electron–hole pairs can effectively takes place.

To deeper understanding of the charge transport properties of (h)TiO₂ and Ag/AgCl-(h)TiO₂ photocatalysts, the electron recombination kinetics of (h)TiO₂ and Ag/AgCl-(h)TiO₂ photocatalysts was investigated, and the results are shown in Fig.13. The electron recombination kinetics was investigated by monitoring the transient Voc as a function of time upon turning off the illumination. Under irradiation conditions, electrons accumulate within the nanostructure semiconductor films following visible light irradiation and shifting the apparent Fermi level to negative potentials. The Ag/AgCl-(h)TiO₂ photocatalysts electrode light electrode holds 0.1235V in illuminated state, and the voltage value was generated by light in the opposite direction to that of TiO₂. A negative Voc signal means that photoinduced electrons transfer to the irradiated sample side, and a positive Voc signal suggests photoinduced holes movement to the irradiated sample

side[40]. Once the illumination is switched off, the accumulated electrons are slowly discharged because they are scavenged by redox species in the Ag/AgCl-(h)TiO₂ photocatalysts electrolyte. The electron density in the conduction band decays slowly due to charge recombination, and the Voc decay rate is directly determined by the recombination rate[41]. This result also reveals that the Voc decay time benefits from LSPR[42]. This phenomenon is in good agreement with the longer carrier lifetime, as mentioned previously, and the decreased saturation current density.

Plasmonic enhancements and facile charge transfer resulting from the assistance of metallic Ag are proposed to explain the high photocatalytic activity of the Ag/AgCl/TiO₂ photocatalysts. Previous studies demonstrated that the LSPR effect of Ag nanoparticles plays a very important role in producing high visible light photocatalytic activity due to the oscillation of surface electrons[26, 27, 28]. Additionally, the rich conduction band (CB) electrons of noble metals can enhance the reducibility of hybrids, resulting in a decreased recombination opportunity of electrons and holes[43]. In particular, the excellent conductivity of Ag nanoparticles greatly promotes interfacial charge transfer kinetics among Ag, AgCl, and TiO₂. The proposed charge-transfer mechanism for the Ag/AgCl-(h)TiO₂ photocatalysts is illustrated in Fig14. For reference, the CB and VB energy levels of AgCl were calculated to be -0.95 and +2.3eV [44], and the CB and VB of TiO₂ were about -0.53 and 2.67[5], respectively. Under visible light irradiation, due to the LSPR character of metallic Ag, metallic Ag could absorb visible light, and the absorbed photon would be efficiently separated to electron and hole. The AgCl in our system also acted as a hole acceptor[44]. The holes generated were then be transferred to the AgCl surface, thereby resulting in the oxidation of Cl⁻ ions to Cl⁰ atoms[45]. The Cl⁰ atoms, in turn, acted as reactive species for the oxidation of dye molecules. Meanwhile, more holes with strong oxidation power in the VB could be trapped by OH⁻ to form hydroxyl radicals, which caused the RhB degradation to N-de-ethylated. The plasmon induced electrons of Ag nanoparticles were transported to the CB of TiO₂[46]. As a result, the photogenerated electrons were thought to be trapped by absorbed O₂ to produce O₂⁻, which was the active species in the reaction with Ag/AgCl-(h)TiO₂ photocatalysts, leading to the continuous formation of O₂⁻ on the surface of Ag/AgCl-(h)TiO₂ photocatalysts, which could oxidize RhB and result in a high photocatalytic degradation rate. Furthermore, Ag/AgCl nanoparticles loaded on the TiO₂ could also act independently as superior visible light driven

photocatalysts for degrading organic contaminants, further enhancing the photocatalytic activity of the Ag/AgCl-(h)TiO₂ photocatalysts.

4. Conclusions

In summary, the hierarchical Ag/AgCl-TiO₂ hollow spheres were synthesized through a precipitation–photoreduction method. The prepared sample had spherical structures which were composed of thousands of nanoparticles with diameter about 30 nm, forming over all diameters ranging from 700 nm to 1100 nm. The thickness of the spherical wall was about 30nm. The hierarchical Ag/AgCl-TiO₂ hollow spheres exhibited a higher rate constant in the degradation reaction of RhB, approximately 13 times larger than that of TiO₂ hollow spheres. The high photocatalytic activity of the Ag/AgCl-TiO₂ compound is the result of efficient electron-hole pairs separation at the interfaces and role of localized surface plasmon resonance of Ag nanoparticles formed on AgCl particles in the degradation reaction.

Acknowledgements

This work was supported in part by the National Science Foundation (No. 41271249) and Key Laboratory of Advanced Textile Materials and Manufacturing Technology (Zhejiang Sci-Tech University), Ministry of Education (No. 2013008) of China.

References

- [1] Cao-Thang Dinh, Hoang Yen, Freddy Kleitz, and Trong-On Do, Three-Dimensional Ordered Assembly of Thin-Shell Au/TiO₂ Hollow Nanospheres for Enhanced Visible-Light-Driven Photocatalysis, *Angew. Chem. Int. Ed.*, 53(2014) 6618 –6623;
- [2] Jenny Schneider, Masaya Matsuoka, Masato Takeuchi, Jinlong Zhang, Yu Horiuchi, Masakazu Anpo, Detlef W. Bahnemann, Understanding TiO₂ Photocatalysis: Mechanisms and Materials, *Chem. Rev.*, 114(2014) 9919–9986;
- [3] Jian Zhu, Shao-Hua Wang, Zhen-Feng Bian, Chen-Ling Cai, He-Xing Li, A facile synthesis of hierarchical flower-like TiO₂ with enhanced photocatalytic activity, *Res Chem Intermed*, 35(2009)769–777;
- [4] S. Thennarasu, K. Rajasekar, K. Balkis Ameen, Hydrothermal temperature as a morphological control factor: Preparation, characterization and photocatalytic activity of titanate nanotubes and nanoribbons, *Journal of Molecular Structure*, 1049 (2013) 446–457;
- [5] Zhigang Xiong, Xiu Song Zhao, Nitrogen-Doped Titanate-Anatase Core–Shell Nanobelts with Exposed {101} Anatase Facets and Enhanced Visible Light Photocatalytic Activity, *J. Am. Chem. Soc.*, 134(2012)5754 – 5757;
- [6] Su Il In, Yidong Hou, Billie L. Abrams, Peter C. K. Vesborg, Ib Chorkendorff, Controlled Directional Growth of TiO₂ Nanotubes, *Journal of The Electrochemical Society*, 157(2010)E69-E74;
- [7] Kiyoun Lee, Robert Hahn, Marco Altomare, Elena Selli, Patrik Schmuki, Intrinsic Au

Decoration of Growing TiO₂ Nanotubes and Formation of a High Efficiency Photocatalyst for H₂ Production, *Adv.Mater.*, 25(2013)6133–6137;

[8] Zhijiao Wu, Qian Wu, Lixia Du, Chao Jiang, Lingyu Piao, Progress in the synthesis and applications of hierarchical flower-like TiO₂ nanostructures, *Particuology*, 15(2014) 61–70;

[9] Yufeng Tang, Li Yang, Jizhang Chen, and Zheng Qiu, Facile Fabrication of Hierarchical Hollow Microspheres Assembled by Titanate Nanotubes, *Langmuir*, 26(2010)10111–10114;

[10] I.B. Troitskaia, T.A. Gavrilova, V.V. Atuchin, Structure and micromorphology of titanium dioxide nanoporous microspheres formed in water solution, *Physics Procedia*, 23(2012)65–68;

[11] Wenjiao Wang, Jinlong Zhang, Feng Chen, Dannong He, Masakazu Anpo, Preparation and photocatalytic properties of Fe³⁺-doped Ag@TiO₂ core–shell nanoparticles, *Journal of Colloid and Interface Science*, 323(2008)182–186;

[12] Fei He, Chao Zhang, Di Zhou, Ling Cheng, Tao Li, Guangxing Li, Mesoporous core–shell TiO₂ walnuts for photocatalysts and photodetectors with improved performances, *Dalton Trans.*, 43(2014)7599–7607;

[13] Jingjing Xu, Mindong Chen, Degang Fu, Study on highly visible light active Bi-doped TiO₂ composite hollow sphere, *Applied Surface Science*, 257(2011)7381–7386;

[14] Ji Bong Joo, Ilkeun Lee, Michael Dahl, Geon Dae Moon, Francisco Zaera, Yadong Yin, Controllable Synthesis of Mesoporous TiO₂ Hollow Shells: Toward an Efficient Photocatalyst, *Adv. Funct. Mater.*, 23(2013)4246–4254;

[15] Wenjea J. Tseng, Po-Sung Chao, Synthesis and photocatalysis of TiO₂ hollow spheres by a facile template-implantation route, *Ceramics International*, 39 (2013)3779–3787;

[16] Ruibin Jiang, Benxia Li, Caihong Fang, Jianfang Wang, Metal/Semiconductor Hybrid Nanostructures for Plasmon-Enhanced Applications, *Advanced Materials.*, 26(2014)5274–5309;

[17] Suljo Linic, Phillip Christopher, David B. Ingram, Plasmonic-metal nanostructures for efficient conversion of solar to chemical energy, *Nature materials*, 10(2011)911–921;

[18] Koichi Awazu, Makoto Fujimaki, Carsten Rockstuhl, Junji Tominaga, Hirotaka Murakami, Yoshimichi Ohki, Naoya Yoshida, Toshiya Watanabe, A Plasmonic Photocatalyst Consisting of Silver Nanoparticles Embedded in Titanium Dioxide, *J. Am. Chem. Soc.*, 130(2008)1676–1680;

[19] Jianchao Zhan, Hui Zhang, Guoqing Zhu, Magnetic photocatalysts of cenospheres coated with Fe₃O₄/TiO₂ core/shell nanoparticles decorated with Ag nanoparticles, *Ceramics International*, 40 (2014) 8547 – 8559;

[20] Qiao Zhang, Diana Q. Lima, Ilkeun Lee, Francisco Zaera, Miaofang Chi, Yadong Yin, A Highly Active Titanium Dioxide Based Visible-Light Photocatalyst with Nonmetal Doping and Plasmonic Metal Decoration, *Angew. Chem.Int.Ed.*, 50(2011)7088–7092;

[21] Alberto Naldoni, Massimiliano D'Arienzo, Marco Altomare, Marcello Marelli, Roberto Scotti, Franca Morazzoni, Elena Selli, Vladimiro Dal Santo, Pt and Au/TiO₂ photocatalysts for methanol reforming: Role of metal nanoparticles in tuning charge trapping properties and photo efficiency, *Applied Catalysis B: Environmental*, 130–131(2013)239–248;

[22] Lanbo Di, Xiuling Zhang, Zhijian Xu, Kai Wang, Atmospheric-Pressure Cold Plasma for Preparation of High Performance Pt/TiO₂ Photocatalyst and Its Mechanism, *Plasma Chem Plasma Process*, 34(2014)301–31;

[23] Wentao Liu, Deliang Chen, Seung Hwa Yoo, Sung Oh Cho, Hierarchical visible-light-response Ag/AgCl@TiO₂ plasmonic photocatalysts for organic dye degradation, *Nanotechnology*, 24(2013)405706–405712;

- [24] Bin Cai, Jing Wang, Shiyu Gan, Dongxue Han, Zhijian Wu, Li Niu, A distinctive red Ag/AgCl photocatalyst with efficient photocatalytic oxidative and reductive activities, *J. Mater. Chem. A*, 2(2014)5280–5286;
- [25] Wenjuan Liao, Yanrong Zhang, Mi Zhang, Muthu Murugananthan, Sachio Yoshihara, Photoelectrocatalytic degradation of microcystin-LR using Ag/AgCl/TiO₂ nanotube arrays electrode under visible light irradiation, *Chemical Engineering Journal*, 231(2013)455–463;
- [26] Lifang Qi, Jiaguo Yu, Gang Liu, Po Keung Wong, Synthesis and photocatalytic activity of plasmonic Ag@AgCl composite immobilized on titanate nanowire films, *Catalysis Today*, 224(2014)193–199;
- [27] Dawei Wang, Yi Li, Gianluca Li Puma, Chao Wang, Peifang Wang, Wenlong Zhang, Qing Wang, Ag/AgCl@helical chiral TiO₂ nanofibers as a visible-light driven plasmon photocatalyst, *Chem. Commun.*, 49(2013)10367–10369;
- [28] Jianfeng Guo, Bowen Ma, Anyuan Yin, Kangnian Fan, Weilin Dai, Highly stable and efficient Ag/AgCl@TiO₂ photocatalyst: Preparation, characterization, and application in the treatment of aqueous hazardous pollutants, *Journal of Hazardous Materials*, 211–212(2012)77–82;
- [29] C.K. Ngaw, Q. Xu, T.T.Y. Tan, P. Hu, S. Cao, J.S.C. Loo, A strategy for in-situ synthesis of well-defined core-shell Au@TiO₂ hollow spheres for enhanced photocatalytic hydrogen evolution, *Chemical Engineering Journal*, 257 (2014) 112–121;
- [30] Rui Guo, Gaoke Zhang, Jiu Liu, Preparation of Ag/AgCl/BiMg₂VO₆ composite and its visible-light photocatalytic activity, *Materials Research Bulletin*, 48(2013)1857–1863;
- [31] Wenquan Cui, Huan Wang, Li Liu, Yinghua Liang, Joanne Gamage McEvoy, Plasmonic Ag@AgCl-intercalated K₄Nb₆O₁₇ composite for enhanced photocatalytic degradation of Rhodamine B under visible light, *Applied Surface Science*, 283 (2013) 820–827;
- [32] V.V. Atuchin, V.G. Kesler, N.V. Pervukhina, Z. Zhang, Ti 2p and O 1s core levels and chemical bonding in titanium-bearing oxides, *Journal of Electron Spectroscopy and Related Phenomena*, 152(2006) 18–24;
- [33] Victor V. Atuchin, Ludmila I. Isaenko, Valery G. Kesler, Lei Kang, Zheshuai Lin, Maxim S. Molokeev, Alexander P. Yeliseyev, Sergey A. Zhurkov, Structural, Spectroscopic, and Electronic Properties of Cubic G0-Rb₂KTiOF₅ Oxyfluoride, *J. Phys. Chem. C*, 117(2013) 7269–7278;
- [34] Joanne Gamage McEvoy, Wenquan Cui, Zisheng Zhang, Synthesis and characterization of Ag/AgCl-activated carbon composites for enhanced visible light photocatalysis, *Applied Catalysis B: Environmental*, 144 (2014) 702–712;
- [35] Lei Han, Zhikun Xu, Ping Wang and Shaojun Dong, Facile synthesis of a free-standing Ag@AgCl film for a high performance photocatalyst and photodetector, *Chem. Commun.*, 49(2013)4953–4955;
- [36] Lei Shi, Lin Liang, Jun Ma, Yanan Meng, Shifa Zhong, Fangxiao Wang, Jianmin Sun, Highly efficient visible light-driven Ag/AgBr/ZnO composite photocatalyst for degrading Rhodamine B, *Ceramics International*, 40(2014)3495–3502;
- [37] Deyong Wu, Lianzhi Wang, Xinjian Song, Yuanbin Tan, Enhancing the visible-light-induced photocatalytic activity of the self-cleaning TiO₂-coated cotton by loading Ag/AgCl nanoparticles, *Thin Solid Films*, 540(2013)36–40;
- [38] Weibing Li, Fangxia Hua, Jiguang Yue, Jiwei Li, Ag@AgCl plasmon-induced sensitized ZnO particle for high-efficiency photocatalytic property under visible light, *Applied Surface Science*, 285P(2013)490–49;

- [39] H. Nouri, A. Habibi Yangjeh, M. Azadi, Preparation of Ag/ZnMgO nanocomposites as novel highly efficient photocatalysts by one-pot method under microwave irradiation, *Journal of Photochemistry and Photobiology A: Chemistry*, 281 (2014) 59–67;
- [40] Haimei Fan, Tengfei Jiang, Haiyan Li, Dejun Wang, Lingling Wang, Jiali Zhai, Dongqing He, Ping Wang, Tengfeng Xie, Effect of BiVO₄ Crystalline Phases on the Photoinduced Carriers Behavior and Photocatalytic Activity, *J. Phys. Chem. C*, 1162(2012)2425–2430;
- [41] Huanping Zhou, Qi Chen, Gang Li, Song Luo, Tze-bing Song, Hsin-Sheng Duan, Ziruo Hong, Jingbi You, Yongsheng Liu, Yang Yang, Interface engineering of highly efficient perovskite solar cells, *Science*, 345(2014)542-546;
- [42] Qing Kang, Junyu Cao, Yuanjian Zhang, Lequan Liu, Hua Xu, Jinhua Ye, Reduced TiO₂ nanotube arrays for photoelectrochemical water splitting, *J. Mater. Chem. A*, 1(2013)5766–5774;
- [43] Minh-Hao Pham, Cao-Thang Dinh, Gia-Thanh Vuong, Ngoc-Don Ta, Trong-On Do, Visible light induced hydrogen generation using a hollow photocatalyst with two cocatalysts separated on two surface sides, *Phys. Chem. Chem. Phys.*, 16(2014)5937-5941;
- [44] Xiaxi Yao, Xiaoheng Liu, One-pot synthesis of Ag/AgCl@SiO₂ core-shell plasmonic photocatalyst in natural geothermal water for efficient photocatalysis under visible light, *Journal of Molecular Catalysis A: Chemical*, 393(2014)30–38;
- [45] Wenquan Cui, Huan Wang, Li Liu, Yinghua Liang, Joanne Gamage McEvoy, Plasmonic Ag@AgCl-intercalated K₄Nb₆O₁₇ composite for enhanced photocatalytic degradation of Rhodamine B under visible light, *Applied Surface Science*, 283 (2013) 820– 827;
- [46] Yinghua Liang, Shuanglong Lin, Jinshan Hu, Li Liu, Joanne Gamage McEvoy, Wenquan Cui, Facile hydrothermal synthesis of nanocomposite Ag@AgCl/K₂Ti₄O₉ and photocatalytic degradation under visible light irradiation, *Journal of Molecular Catalysis A: Chemical*, 383–384(2014)231–238.

Figures and Captions

Fig.1 TG-DTA of TiO_2 (a) and (h) TiO_2 (b).

Fig.2 SEM images of the (h) TiO_2 (a and c) and Ag/AgCl-(h) TiO_2 photocatalysts (b and d).

Fig.3 TRTEM images of the (h) TiO_2 (a) and Ag/AgCl-(h) TiO_2 (b) photocatalysts.

Fig.4 XRD patterns of the TiO_2 , (h) TiO_2 and Ag/AgCl-(h) TiO_2 photocatalysts.

Fig.5 EDS patterns of the Ag/AgCl-(h) TiO_2 photocatalysts.

Fig.6 Survey-scan XPS spectra of (h) TiO_2 and Ag/AgCl-(h) TiO_2 photocatalysts over a wide energy range(a), the corresponding high resolution XPS spectrum of Ti 2p(b), O 1s(c), Ag 3d(d) and Cl 2p(e).

Fig.7 Photocatalytic activity for the degradation of RhB solution by using (h) TiO_2 and Ag/AgCl-(h) TiO_2 photocatalysts under visible light irradiation(a); the first-order kinetics of RhB solution degradation with (h) TiO_2 and Ag/AgCl-(h) TiO_2 photocatalysts under visible light irradiation(b).

Fig.8 Absorption spectra of the RhB molecules at different times under visible light illumination by Ag/AgCl-(h) TiO_2 photocatalysts.

Fig.9 Cycle runs in the photocatalytic degradation of RhB in the presence of Ag/AgCl-(h) TiO_2 photocatalysts under visible light irradiation for 20 min.

Fig.10 UV-vis diffuse reflectance of (h) TiO_2 and Ag/AgCl-(h) TiO_2 photocatalysts.

Fig.11 Photocurrent response of (h) TiO_2 and Ag/AgCl-(h) TiO_2 photocatalysts under visible irradiation.

Fig.12 EIS profile of (h) TiO_2 and Ag/AgCl-(h) TiO_2 photocatalysts.

Fig.13 Open circuit potential of (h) TiO_2 and Ag/AgCl-(h) TiO_2 photocatalysts under visible light irradiation.

Fig.14 Photocatalytic mechanism scheme of Ag/AgCl-(h) TiO_2 samples under visible light irradiation.

Fig.1TG-DTA of $\text{TiO}_2(\text{a})$ and $(\text{h})\text{TiO}_2$ (b).

Fig.2 SEM images of the (h)TiO₂ (a and c) and Ag/AgCl-(h)TiO₂ photocatalysts (b and d).

Fig.3 HRTEM images of the (h)TiO₂ (a) and Ag/AgCl-(h)TiO₂(b)

Fig.4 XRD patterns of the TiO_2 , $(\text{h})\text{TiO}_2$ and $\text{Ag}/\text{AgCl}/(\text{h})\text{TiO}_2$ photocatalysts.

Fig.5 EDS patterns of Ag/AgCl-(h)TiO₂ photocatalysts.

Fig.6 Survey-scan XPS spectra of (h)TiO₂ and Ag/AgCl-(h)TiO₂ photocatalysts over a wide energy range(a), the corresponding high resolution XPS spectrum of Ti 2p(b), O 1s(c), Ag 3d(d) and Cl 2p(e).

Fig.7 Photocatalytic activity for the degradation of RhB solution by using (h)TiO₂ and Ag/AgCl-(h)TiO₂ photocatalysts under visible light irradiation(a); the first-order kinetics of RhB solution degradation with (h)TiO₂ and Ag/AgCl-(h)TiO₂ photocatalysts under visible light irradiation(b).

Fig.8 Absorption spectra of the RhB molecules at different times under visible light illumination by Ag/AgCl-(h)TiO₂ photocatalysts.

Fig.9 Cycle runs in the photocatalytic degradation of RhB in the presence of Ag/AgCl/(h)TiO₂ photocatalysts under visible light irradiation for 20 min.

Fig.10 The UV-vis diffuse reflectance of $(\text{h})\text{TiO}_2$ and $\text{Ag}/\text{AgCl}-(\text{h})\text{TiO}_2$ photocatalysts.

Fig.11 Photocurrent response of $(h)TiO_2$ and $Ag/AgCl-(h)TiO_2$ photocatalysts under visible irradiation.

Fig.12 EIS profile of $(h)\text{TiO}_2$ and $\text{Ag/AgCl-}(h)\text{TiO}_2$ photocatalysts.

Fig.13 Open circuit potential of (h)TiO₂ and Ag/AgCl-(h)TiO₂ photocatalysts under visible light irradiation

Fig.14 Photocatalytic mechanism scheme of Ag/AgCl-(h)TiO₂ samples under visible light irradiation.