DOI: 10.1002/cctc.201300994



# Improved Photocatalytic Performance of the Ultra-small Ag Nanocrystallite-Decorated TiO<sub>2</sub> Hollow Sphere Heterostructures

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The ultra-small Ag nanocrystallite-decorated  $TiO_2$  hollow sphere heterostructures were fabricated by using a two-step hydrothermal method. These heterostructures demonstrated an excellent photodegradation performance of rhodamine B. The photodegradation efficiency could reach up to 100% within 20 min under simulated sunlight irradiation. XRD, field emission SEM, TEM, scanning TEM, high-resolution TEM coupled with energy-dispersive X-ray spectroscopy, UV/Vis absorption and photoluminescence spectroscopy, X-ray photoelectron spectroscopy, Mott–Schottky analysis, and hydroxyl radical measurements were used to correlate the structure, surface property, and energy band alignment of rhodamine B to its photocatalytic activity. In these metal–semiconductor heterostructures, the Ag nanocrystallites were highly crystalline and were distributed evenly on the surface of TiO<sub>2</sub> hollow spheres with compact interfaces. They reduced the recombination rate of charge carriers and favoured the charge transfer across the interfaces. The increased surface adsorbed oxygen facilitated the generation of hydroxyl radicals, and the reduced surface defects increased the lifetime of charge carriers upon Ag loading. The Schottky barriers between Ag and illuminated TiO<sub>2</sub>, the upward shift of the Fermi level, and increased electron density due to Ag coupling contributed to the charge transfer and increase in quantum efficiency. These key factors involved in photocatalysis are of great importance to design functional and effective photocatalysts.

## Introduction

Photocatalysis has been widely studied in environmental remediation.<sup>[1]</sup> TiO<sub>2</sub> has been regarded as the most prominent photocatalyst candidate owing to its high photostability, non-toxicity, low cost, and high efficiency.<sup>[2,3]</sup> However, TiO<sub>2</sub> suffers from limited light absorption owing to its wide band gap and high recombination rate of charge carriers, which restricts its application.<sup>[4]</sup> To overcome these shortcomings, various strategies including nanostructured TiO<sub>2</sub>,<sup>[4–6]</sup> noble metal coupling,<sup>[7–9]</sup> non-metal doping,<sup>[10]</sup> narrow band gap semiconductor composites,<sup>[11]</sup> and surface modification<sup>[12,13]</sup> have been explored.

Of these strategies, the development of functional photocatalysts with nanoscale morphology, such as TiO<sub>2</sub> nanowire,<sup>[5]</sup>

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	Supporting information for this article is available on the WWW under
	http://dx.doi.org/10.1002/cctc.201300994.

nanotube,<sup>[14]</sup> nanobelt,<sup>[6]</sup> and hollow sphere or cup,<sup>[2,4,9,15-17]</sup> has attracted a great deal of interest in photocatalysis owing to large specific surface area, excellent electron transport property, and easy accessibility of organic dye.<sup>[2]</sup> The hollow and porous structures of TiO<sub>2</sub> appeared promising owing to the increase in light absorption through multiple reflections.<sup>[18]</sup> The traditional fabrication methods used to produce hollow structures often employed sacrificial templates such as a SiO<sub>2</sub> sphere<sup>[4,19]</sup> or a carbon sphere.<sup>[9]</sup> The time-consuming nature and high cost of the methods had limited their application on a large scale. Thus, there is a pressing need to develop a facile way for the fabrication of hollow structures.

Furthermore, heterostructures have been used extensively in photocatalysis or photoelectrochemistry by combining the function of individual components in heterostructures.<sup>[1]</sup> A noble metal such as Ag, Au, or Pt was deposited on the surface of the semiconductor to form a metal-semiconductor heterojunction.<sup>[20-22]</sup> Compared with Pt and Au, Ag is less expensive and has a stronger electron storage capacity.<sup>[8]</sup> Some research work has been done to fabricate Aq/TiO<sub>2</sub> (TA) heteroiunctions.<sup>[9,23-28]</sup> However, it is still a challenge to produce small-sized Ag nanocrystallites (2-5 nm) with highly even distribution, which is required for storing electrons.<sup>[8]</sup> The conventional photoreduction method used to produce Ag often leads to low crystallinity of Aq, which retards the separation of charge carriers.<sup>[24]</sup> The thermal decomposition of the AgNO<sub>3</sub> precursor results in the aggregation of Ag nanocrystallites, which tend to become recombination centres.<sup>[29]</sup> The hydrothermal method with ethanol as a reductant has been used to increase the crystallinity and reduce the oxidation of Ag.<sup>[24]</sup> However, the resultant Ag nanocrystallites are relatively large (5-20 nm) and have no even distribution. Thus, an effective method and a suitable reductant should be developed to obtain a higher degree of crystallinity, even distribution, and small-sized Ag nanocrystallites on the surface of TiO<sub>2</sub>. As for the promotional mechanisms of a noble metal-semiconductor heterojunction, no consensus is reached. Su et al.<sup>[30]</sup> attributed the observed visible light-driven photocatalytic activity to the hot electron transported from Ag to TiO<sub>2</sub> owing to surface plasma resonance (SPR); however, Liu et al.<sup>[23]</sup> found that their TA product was inactive under visible light irradiation. Although the evidence of the electron transport from the metal to the semiconductor due to SPR has been presented,<sup>[31]</sup> the increase is small compared with the bulk semiconductor excitation effect.<sup>[8]</sup> Both the Schottky barrier, formed between the metal and the illuminated semiconductor, and the upward shift of the Fermi level due to the electron storage of noble metal favour the charge separation and charge transport.<sup>[21, 32, 33]</sup> Moreover, the smaller size noble metal particles were found to induce a maximum shift of the Fermi level of a noble metal-semiconductor heterojunction.<sup>[8]</sup> Thus, the small noble metal particle would serve as an efficient electron trapper to increase the photocatalytic activity upon excitation of the semiconductor in the noble metal-semiconductor heterojunction.

Herein, we synthesized TA heterostructures, in which the ultra-small Ag nanocrystallties (2 nm) with high crystallinity were distributed evenly on the surface of TiO<sub>2</sub> hollow spheres (THSs). In the synthesis of the hollow structure, the templatefree hydrothermal method was used to avoid the application of the sacrificial template. For the deposition of Ag, DMF was found to be an effective reductant to produce Ag having excellent dispersion with the help of polyvinylpyrrolidone (PVP) by using a short-time (2 h) hydrothermal method. These TA heterostructures demonstrated excellent photodegradation under simulated sunlight irradiation. The degradation efficiency of rhodamine B (RhB) could reach up to 100% within 20 min, which was much better than the results of some reports on TA.<sup>[23, 34]</sup> The high stability of TA heterostructures in our investigated time range made it a promising material for industrial applications.

## **Results and Discussion**

#### Formation of TA heterostructures

Crystal structures, morphology, and configuration were investigated by using XRD, field emission SEM (FE-SEM), TEM, and scanning TEM (STEM) to monitor the evolution process of TA heterostructures. As shown in Figure 1, the TiO<sub>2</sub> bead (TB) prepared through hydrolysis at room temperature demonstrated no XRD peak (bottom curve), and the amorphous phase of the TB was found, as expected. The amorphous TiO<sub>2</sub> sphere transformed to a TiO<sub>2</sub> solid sphere (TS), which consisted of the anatase (JCPDS 21-1272) and brookite (JCPDS 29-1360) phases after the hydrothermal treatment in the absence of NH<sub>4</sub>F, as

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Figure 1. XRD patterns of TB, TS, THS, and TA.

depicted in the TS curve. The anatase phase was dominant, and only a minor peak located at  $2\theta = 30.7^{\circ}$  corresponding to the brookite phase was found. For comparison purposes, the amorphous TB was grown to THS with NH<sub>4</sub>F. No peak corresponding to the brookite phase was observed on the THS curve, which implied that a single anatase phase is present. Thus, the presence of NH<sub>4</sub>F could inhibit the formation of the brookite phase.<sup>[35]</sup> Three diffraction peaks located at  $2\theta = 38.1$ , 44.4, and 64.4° appeared on the TA curve, which should be assigned to Ag nanocrystallites (JCPDS 65-2871). The peak of Ag centred at 38.1° overlapped with the peak of the anatase phase centred at 38.5°. No observable shift or widening of the XRD peak was observed upon decoration of Ag, which suggested that the decoration of Ag had not changed the THS crystal structure. The above analysis demonstrated that TA heterostructures had been obtained by using the two-step hydrothermal method.

To observe the morphology and configuration of TA heterostructures, FE-SEM, TEM, and STEM were used, and the results are illustrated in Figure 2. After a slow hydrolysis of titanium(IV) n-butoxide, the amorphous TB was formed (Figure 2a). These amorphous colloids were evenly distributed with a diameter of approximately 500 nm. In the absence of  $\rm NH_4F,$  the TB had been converted to TS by using the hydrothermal method (Figure 2b). The surface of TS was rougher than that of the TB owing to the crystallization of TiO<sub>2</sub> and the growth of TiO<sub>2</sub> crystallites. A THS with an open gap could be obtained by using the hydrothermal method of TS in the presence of NH<sub>4</sub>F. The presence of F<sup>-</sup> induced a progressive redistribution of mass from the interior to the exterior through highly porous shells; hence, the hollow structure can be fabricated. The panoramic image of THS is shown in Figure 2 c, which indicates that the well-formed hollow structures were obtained on a large scale. A magnified image of THS is shown in Figure 2d, in which the open gap structures can be clearly seen. The decoration of Ag to THS did not change its hollow structure. The typical SEM image of TA is shown in Figure 2e. An open gap structure was retained upon the deposition of

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**Figure 2.** SEM images of a) TB, b) TS, c and d) THS, and e) TA. TEM image of TA is shown in the inset of panel e. f) STEM image of TA with EDX. g) TEM image of TA particles taken from TA heterostructures, and (h) corresponding line-scanning EDX spectra along the red line. i) HRTEM image of the circled region of panel g.

Ag, which was also confirmed by TEM image shown in the inset of Figure 2e. To further confirm the presence of Ag and the three-dimensional configuration of TA, STEM coupled with energy-dispersive X-ray spectroscopy (EDX) was performed. As shown in Figure 2 f, a macrohollow sphere consisting of numerous nanocrystallites and the Ag peak on the EDX spectrum verified that the Ag nanoparticles had been attached to the surface of THS. High-resolution TEM (HRTEM) was used to explore the distribution of Ag nanoparticles on the surface of THS. A component unit of TA obtained by a long-time ultrasonic dispersion of the TA sample is shown in Figure 2g. We conducted a line-scanning EDX spectrum along the red line across a small white spot, and the corresponding element distribution along this red line is shown in Figure 2h. The centre of the red line shows the concentration of Ag, whereas the two sides show a large number of Ti elements. By comparing the position of line-scanning EDX spectrum with that of the marked red line, it was confirmed that the white spot was the Ag nanocrystallite and the tapered block was the TiO<sub>2</sub> nanoparticle. Good dispersion of Ag nanocrystallites on the surface of TiO<sub>2</sub> nanoparticles can be seen in Figure 2g. The HRTEM image corresponding to the circled region of Figure 2g is shown in Figure 2i. The Ag nanocrystallite was approximately 2 nm in diameter, and the fringe spacing of 0.232 nm could be attributed to the (111) plane of Ag. The larger crystal spacing of 0.355 nm should be attributed to the (101) plane of TiO<sub>2</sub>. An intimate and compact interface between the Ag nanocrystallite and the TiO<sub>2</sub> nanoparticle was well formed. The ultrasmall Ag nanocrystallites were deposited on the surface of THS with highly even distribution and compact contact.

By observing the crystal structure, morphology, and configuration changes in TA heterostructures, we summarized their evolution process, as shown in Scheme 1. In the beginning, the amorphous TB formed through slow hydrolysis, which was used as a precursor of THS. If the TB was into contact with the



Scheme 1. Evolution process of TA heterostructures.

 $NH_4F$  solution at the initial stage of the reaction, the outer layer of the TB would be transformed to the crystalline phase thermodynamically once an equilibrium between the surface layer and the surrounding solution was achieved. Thus, the core part of the TB was surrounded by a thin crystalline layer. In comparison to the less solubility of the outer crystalline layer of the TB, the inner amorphous core had a strong tendency to dissolve into the NH<sub>4</sub>F solution.

If the TB solution became supersaturated, it would transfer to the outer layer through highly porous channels and crystallize on the surface layer to reduce the surface energy. Ostwald ripening offered the main driving force for this THS formation.<sup>[35,36]</sup> This process was sensitive to the relative rates of the dissolution and the crystallization of the supersaturated TB solution. In the absence of  $NH_4F$ , the crystallization rate was higher than the dissolution rate; thus, TS was formed by using the hydrothermal process. The presence of F<sup>-</sup> accelerated the dissolution of the TB, and the rates of dissolution and crystallization become similar; thus, THS could be obtained. A THS with a rough surface consisting of numerous small TiO<sub>2</sub> nanoparticles could anchor the AgNO<sub>3</sub> precursor and offer nucleation sites for Ag nanocrystallites; hence, Ag<sup>+</sup> was easily reduced by DMF and the resultant Ag nanocrystallites nucleated and grew on the surface of THS in small size. Finally, the ultrasmall Ag nanocrystallites-decorated THS heterostructures were obtained.

#### **Optical property**

The UV/Vis absorption and photoluminescence (PL) spectra of THS and TA are shown in Figure 3. The decoration of Ag nanocrystallites to THS increased light absorption in the investigated light spectrum range. The increase in light absorption in the visible light range of TA should be attributed to the SPR of Ag,<sup>[24,30,37]</sup> which led to the apparent colour change from white to brown (Figure 3 a, inset). The increased absorption in the UV range of TA could be due to the effective transport of the photo-induced electron from THS to Ag nanocrystallites. This improved UV/Vis light absorption performance of TA is helpful in performing the photocatalytic reaction, which makes the full



Figure 3. a) UV/Vis absorption and b) PL spectra of THS and TA.

use of the incident light. Only increased generation of charge carriers cannot ensure better photocatalytic performance, because the photo-induced charge carriers have to be separated and transported to the surface of the catalysts to initiate the chemical reactions. Thus, the separation rate of photo-induced charge carriers would play a vital role in the photocatalytic reactions.

The PL spectra were often used to measure the separation rate of photo-induced charge carriers. As shown in Figure 3 b, the intensity of the PL peak located at 630–650 nm reduced upon Ag loading. This PL peak was far from its near-band emission; thus, it should be assigned to the surface defects, which often acted as recombination sites.<sup>[38]</sup> The reduced intensity of the PL peak of TA indicated the reduced recombination rate of photo-induced charge carriers owing to the formation of metal–semiconductor heterojunctions. The above analysis demonstrated that the formation of TA heterostructures had increased both light absorption and the separation of charge carriers.

#### Mott-Schottky analysis

The electrochemical impedance measurements of THS and TA were performed in the dark to probe the effect of Ag loading on electronic properties of THS. Both THS and TA demonstrated positive slopes in the Mott–Schottky plots, as expected for the n-type semiconductor (Figure 4.). Notably, TA demonstrated a substantially smaller slope in the Mott–Schottky plot than





Figure 4. Mott-Schottky plots of THS and TA.

THS, which suggested an increase in donor density. The carrier densities of THS and TA were calculated from the slopes of Mott–Schottky plots by using Equation (1):<sup>[39,40]</sup>

$$N_{\rm d} = \left(\frac{2}{e_0 \varepsilon \varepsilon_0}\right) \left[\frac{\rm d}{\rm d} V \left(\frac{1}{C^2}\right)\right]^{-1} \tag{1}$$

in which  $e_0$  is the electronic charge ( $e_0 = 1.6 \times 10^{-19}$  C),  $\varepsilon$  is the dielectric constant of TiO<sub>2</sub> ( $\varepsilon = 170$ ),  $\varepsilon_0$  is the permittivity in vacuum ( $\varepsilon_0 = 8.86 \times 10^{-12}$  F m<sup>-1</sup>),  $N_d$  is the donor density, and V is the applied bias voltage. The calculated electron densities of THS and TA were  $6.78 \times 10^{17}$  and  $4.15 \times 10^{21}$  cm<sup>-3</sup>, respectively. Although the Mott–Schottky plots derived from a flat electrode model could have errors in determining the absolute values of electron densities, the Ag loading induced a significant increase in the carrier density of TA, which was evident from the comparison of the slopes of Mott–Schottky plots of THS and TA. The increased electron density. The increase in electron density would favour the charge transport, which could contribute to the photocatalytic reaction.

#### Surface property

The elemental chemical states on the surface of THS and TA were examined by using X-ray photoelectron spectroscopy (XPS); the results are illustrated in Figure 5. As shown in the survey spectra of THS and TA (Figure 5a), the peak of Ag appeared on the curve of TA upon Ag loading, which further confirmed the presence of Ag. Its concentration on the surface of THS was determined as 2.36 at% through the integration of the element peak area on the XPS spectrum. The comparison of high-resolution spectra of Ti2p of THS and TA is illustrated in Figure 5b. The splitting of Ti2p<sub>1/2</sub> (464.0 eV) and Ti2p<sub>3/2</sub> (458.3 eV) of both THS and TA was 5.7 eV, which suggested that the main state of Ti species was Ti<sup>4+</sup>.<sup>[30]</sup> However, the widening and loss of symmetry of the Ti2p peak of TA compared



**Figure 5.** a) Survey spectra, b) Ti2p spectra of THS and TA, c) Ti2p deconvolution spectra of TA, d) Ag 3d spectrum of TA, e) O1s spectra, and f) VB spectra of THS and TA.

with that of THS, which indicated that more than one Ti species appeared upon Ag loading. Thus, the deconvolution of the Ti2p peak of TA was performed and is presented in Figure 5 c. The peaks located at 458.1 eV (Ti  $2p_{3/2}$ ) and 463.4 eV (Ti  $2p_{1/2}$ ) should be attributed to Ti<sup>3+</sup>, whereas the other two peaks located at 458.6 eV (Ti  $2p_{3/2}$ ) and 464.3 eV (Ti  $2p_{1/2}$ ) should be attributed to Ti4+.[9] The high-resolution spectra of Ag 3d of TA are shown in Figure 5 d. The splitting of  $Ag 3d_{3/2}$ and  $Ag3d_{5/2}$  peaks was approximately 6 eV, which indicated that most of the Ag species was Ag<sup>0</sup>. However, the present Ag 3d XPS peak (373.5 eV for 3d<sub>3/2</sub> and 367.5 eV for 3d<sub>5/2</sub>) shifted to lower binding energy (BE) position compared with bulk Ag (374.3 eV for  $3d_{3/2}$  and 368.2–368.3 eV for  $3d_{5/2}$ ), which suggested that the electron density of Ag was reduced.<sup>[41]</sup> The presence of Ti<sup>3+</sup> and a lower BE shift of the Aq3d peak could be due to the formation of an ohmic contact between Ag and TiO<sub>2</sub> before irradiation. As shown in Scheme 2a, the electrons would flow from Ag ( $E_{\rm fm}$ ) to THS ( $E_{\rm fs}$ ) until they obtained the

(a)  $TiO_2$  Ag (b)  $TiO_2$  Ag  $*E_f$   $*E_f$   $*E_f$   $*E_f$   $E_f$   $E_f$ 

**Scheme 2.** Charge equilibrium of TA a) before and b) under simulated sunlight irradiation.

energy thermodynamic equilibrium level  $(E_f)$  owing to the different work function of Ag (4.26–4.29 eV) and  $TiO_2$  (4.6– 4.7 eV).<sup>[22]</sup> This alignment of the energy band would shift the Fermi level of THS towards a more negative potential, which is similar to that in the Ag/ZnO system.<sup>[41]</sup> The accumulation of electrons on the surface of THS would reduce a small part of  $Ti^{4+}$  to  $Ti^{3+}$  (Figure 5 c). The induced  $Ti^{3+}$  had a promotional effect on photocatalysis because it was involved in the formation of a narrow band gap semiconductor.<sup>[9]</sup> In general, the BE of the zero-valence metal atom is smaller than that of the metal cation. Ag is an exception, because the BE values of Ag<sup>0</sup> and Ag<sup>+</sup> are approximately 368.2 and 367.2 eV, respectively.<sup>[41]</sup> The oxygen atom states of THS and TA are shown in Figure 5 e. The asymmetric profile of the O1s peak indicated that several kinds of oxygen species existed in both THS and TA. As shown in the deconvolution patterns of the O1s spectra, the peak located at 529.4 eV should be attributed to the lattice oxygen in the Ti–O (O<sub> $\alpha$ </sub>) bond whereas the other two peaks located at 530.7 and 532.2 eV should be attributed to surface adsorbed oxygen in the form of hydroxyl radicals (H–O), carboxyl radicals (C-O), or adsorbed oxygen, which was denoted as  $O_{\beta}.^{^{[30,42-44]}}$  The  $O_{\beta}/(O_{\alpha}{+}O_{\beta})$  ratios for THS and TA calculated from the integration area of deconvolution patterns were 37.9 and 48.9%, respectively. The Ag loading increased the adsorbed oxygen originating from hydroxyl radicals, carboxyl radicals, or oxygen on the surface of TA. The hydroxyl radicals and adsorbed oxygen played a pivotal role in the photocatalysis, in which hydroxyl radicals could capture the hole and the adsorbed oxygen would combine with the photo-induced electron to produce highly active hydroxyl radicals. This surface modification of TA due to Ag loading would play a positive role in the following photocatalytic reactions. The valence band (VB) spectra of THS and TA are shown in Figure 5 f. The VB position of THS was determined as 2.43 eV below the Fermi level. The density of states (DOSs) below the Fermi level and above the VB evidently increased upon Ag coupling. As explained in Mott-Schottky plots and Scheme 2a, the Ag coupling led to an upward shift of the Fermi level and the increase in electron density. Thus it was reasonable to observe higher DOS of TA compared with that of THS. This phenomenon also indicated that more energetic electron existed on TA, which would favour the photoexcitation of the semiconductor and the separation of charge carriers.<sup>[8]</sup> The Ag coupling induced a significant surface modification, such as the presence of T<sup>3+</sup>, the lower BE shift of the Ag3d peak, an increase in adsorbed oxygen, and an increase in DOSs, which suggested a strong interaction between Ag and TiO<sub>2</sub>, and would play a vital role in photocatalysis.

#### Photocatalysis

The organic dye RhB was used here as a probe molecule to investigate the photodegradation performance of the as-prepared catalysts. The apparent photodegradation efficiencies of TS, THS, and TA are compared in Figure 6a. To exclude the possible effect of the photo-induced self-degradation of RhB, the control experiment was conducted without catalysts; the

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Figure 6. a) Photocatalytic degradation of RhB over TS, THS, P25, and TA under simulated sunlight irradiation. b) The corresponding kinetic rate constants of TS, THS, P25, and TA.

result is depicted by the top curve in the figure. The nearly flat degradation curve indicated that the self-degradation effect could be negligible herein. The photodegradation efficiencies of TS, THS, and TA increased from 38, 87 to 100%, respectively, within 20 min under simulated sunlight irradiation. TA demonstrated better photocatalytic activity than the commercial P25. The corresponding kinetic rate constants were calculated by using Equation (2):

$$\ln\left(\frac{C}{C_0}\right) = k_a t \tag{2}$$

in which *C* is the concentration of the pollutant (mg L<sup>-1</sup>), *C*<sub>0</sub> is the adsorption equilibrium concentration of the pollutant before irradiation (mg L<sup>-1</sup>), *t* is the reaction time (min), and  $k_a$ is the apparent rate constant (min<sup>-1</sup>). On the basis of the above model, the  $k_a$  values of TS, THS, P25, and TA were determined as 0.0369, 0.1021, 0.1561, and 0.1786 min<sup>-1</sup>, respectively. The turnover number of TA was calculated as 0.015. The formation of hollow structures increased the  $k_a$  of the photocatalytic reaction by 2-fold compared with the formation of solid spheres. The increase in the photocatalytic activity was achieved upon Ag loading. The Ag-decorated THS heterostuctures demonstrated an excellent photodegradation of RhB within 30 min, which was much better than those discussed in previous reports.<sup>[23,34]</sup>

To understand the improved photocatalytic mechanisms of TA under simulated sunlight irradiation in depth, photocatalytic experiments over the same catalysts were conducted under UV and visible light irradiation. As shown in Figure S1, the photocatalytic activity increased with a significant difference in this order: TA > P25 > THS > TS under UV light irradiation, which should be ascribed to the direct semiconductor photoexcitation. In contrast, all the catalysts demonstrated lower photodegradation activity under visible light irradiation, which was due to the indirect dye photosensitization. TS, THS, P25, and TA presented comparable visible light-driven photoactivities. From the above observations, the direct photoexcitation and indirect photosensitization mechanisms coexisted but the direct photoexcitation mechanism played a predominant role under simulated sunlight irradiation. If the TA was photoexcited under simulated sunlight irradiation, the electron in the VB would be excited to the conduction band and then transported to the surface of Ag owing to a higher work function of Ag (4.26-4.29 eV) than the electron affinity of THS (4.2 eV) (Scheme 2 b). $^{[20, 22, 45]}$  The diffusion of the electron from the semiconductor to the metal would lead to a depletion layer at the interface of the semiconductor. The resultant built-in electrical field would cause the drift of the electron in the direction opposite to that of electron diffusion. The space charge zone would finally form once an equilibrium between diffusion and drift of electrons was achieved, which induced the upward bending of the semiconductor band at the interface, which was the Schottky contact. Meanwhile, the Fermi level  $(E_f)$  of THS would shift upward to a new equilibrium position ( $*E_f$ ) owing to the electron storage property of Ag.<sup>[8,21]</sup> This upward shift of the Fermi level would increase the charge separation of the semiconductor by offering more energetic electrons<sup>[8]</sup> as well as at the semiconductor-electrolyte interface by increasing the degree of band bending.<sup>[39]</sup> The separated electrons on the surface of Ag and the holes left on THS would combine with adsorbed oxygen and hydroxyl radicals or water, respectively, to produce hydroxyl radicals, which have a strong oxidation ability to degrade RhB.[38] The concentration of generated hydroxyl radicals was measured to uncover the underlying oxidizing agent in the photocatalytic process.

As shown in Figure 7 a, the generation of hydroxyl radicals increased incrementally, which was consistent with the increase in the photodegradation efficiency of TA within the same time range. The concentration profile of the generated hydroxyl radicals over TS, THS, and TA within 30 min under the same conditions is shown in Figure 7 b. The concentration of hydroxyl radicals increased in the following order: TA > THS > TS, which was also in line with the photocatalytic degradation of RhB. This observation indicated that the correlation between hydroxyl radical generation and photocatalytic activity was established.

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Figure 7. PL spectra of the generated 2-hydroxyterephthalic acid a) over TA at different times and b) over TS, THS, and TA within 30 min.

On the basis of the above analysis, several factors involved in photocatalysis should be emphasized to have a deeper understanding of the increase in the photocatalytic activity of TA. Firstly, THSs with an open gap and a rough surface improved 1) the accessibility of the pollutant by accelerating mass transfer between the pollutant and the photocatalyst and 2) light absorption through multiple reflections. Secondly, the 2 nm Ag nanocrystallites with highly even distribution on the surface of TA increased light absorption and reduced surface defects; hence, the incident photo-conversion efficiency was increased. Thirdly, the upward shift of the Fermi level, the formation of the Schottky barrier under irradiation, and an increased electron density of TA facilitated the charge separation and transport. Finally, the increased adsorbed oxygen and hydroxyl radical concentration contributed substantially to initiate the surface photochemical reaction.

The stability of TA was studied, and the results are illustrated in Figure 8. After five successive runs of photocatalysis, the photodegradation efficiency was still approximately 95%, which suggested a high stability of TA. The slight reduction in photocatalysis efficiency could originate from the reduction of catalysts or the oxidation of Ag nanocrystallites.<sup>[29]</sup>



Figure 8. Stability of TA over five successive runs of photocatalysis under simulated sunlight irradiation.

### Conclusions

The highly crystalline and small-sized Ag nanocrystallites were evenly distributed on the surface of TiO<sub>2</sub> hollow spheres by using a new two-step hydrothermal method. To improve photocatalysis, three aspects should be emphasized. Firstly, the intimate interface of this architecture contributed to the charge transfer across the boundary between Ag and TiO<sub>2</sub>. Secondly, the Schottky barriers between Ag and illuminated TiO<sub>2</sub>, the upward shift of the Fermi level, and the increased electron density of these heterostructures promoted the charge separation and charge transport. Finally, the surface modifications such as increased adsorbed oxygen and reduced surface defects were of great importance to initiate the chemical reaction by increasing the generation of hydroxyl radicals and increasing the lifetime of charge carriers by avoiding the formation of recombination centres. It was vital to consider such important factors involved in photocatalysis to design functional and high-efficiency photocatalysts.

# **Experimental Section**

#### Synthesis of TA heterostructures

All the chemicals used herein were analytical grade and used as received without further purification. The TA heterostructures were fabricated by using a two-step hydrothermal method. The details of experiments are presented as follows. Titanium(IV) n-butoxide (2.5 mL) was added to a pre-mixed solution of ethanol (100 mL) and KCl (0.4 mL, 0.1 m), and the resulting suspension was stirred at RT for approximately 15 min. After keeping the resulting solution in the static state for 24 h, a white precipitate was obtained, which was collected through centrifugation, washed thrice with ethanol and water, and dried at 80 °C. The resulting sample was the amorphous TB. To prepare THS, the as-prepared TB was dispersed into the NH<sub>4</sub>F solution (35 mL) with a Ti/F atomic ratio of 1:1 and then transferred to the 45 mL Teflon-lined stainless steel autoclave for the hydrothermal treatment at 180 °C for 12 h. THS was collected through centrifugation and dried at 80 °C. To deposit Ag particles on THS, we used DMF as a reductant and PVP as a stabilizer. THS (200 mg), AgNO $_3$  (18 mg), and PVP (6 mg) were dispersed into the DMF solution (30 mL) and kept under stirring for 1 h before the resulting solution was transferred to the 45 mL Teflon-lined stainless steel autoclave for the hydrothermal treatment at 160 °C for 2 h. The TA heterostructure was separated through centrifugation and dried at 80 °C. For comparison purposes, TS was also prepared by using the hydrothermal treatment of the TB in the aqueous solution in the absence of  $NH_4F$  at 180 °C for 12 h.

#### Characterizations

The XRD analysis was performed with a Rigaku RU300 X-ray diffractometer with CuK<sub>a</sub> radiation ( $\lambda = 0.1540598$  nm). The surface morphology observation was made with a Quanta F400 field emission scanning electron microscope. The detailed microstructure and chemical composition were investigated by using a transmission electron microscope and a scanning transmission electron microscope (FEG Tecnai F20) equipped with an EDX spectrometer. The UV/Vis absorption spectra were recorded on a Hitachi U-3501 UV/ Vis recording spectrophotometer. The PL spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer with an excitation wavelength of 320 nm. The XPS spectra were collected on PHI Model 5802 with AlK  $_{\!\alpha}$  radiation and calibrated with C1s at 284.8 eV. Mott-Schottky plots were recorded on a CHI660C electrochemical analyzer (CH Instruments Inc., Shanghai, China) operating at 1 kHz in the dark. In this three-electrode electrochemical cell, Pt wire and Ag/AgCl worked as the counter electrode and the reference electrode, respectively, with  $Na_2SO_4$  (0.1 M) as an electrolyte.

#### Photocatalytic reactions

The photocatalytic performance of the samples was evaluated by observing their abilities to degrade the RhB dye in aqueous solutions under simulated sunlight irradiation (320-780 nm) induced by a 300 W Xe lamp (HSX-F300, Beijing NBET Technology Co., Ltd). The visible light-driven photocatalytic experiments were performed with a 420 nm cut-off filter on the same light source. The UV lightdriven photocatalytic experiments were conducted under UV light irradiation (15 W, UVC radiation wavelength: 200-280 nm, Philips). The reaction chamber was placed under the light beam with a distance of 20 cm. In a typical evaluation method, the sample (10 mg) was placed into the RhB solution (30 mL; concentration:  $5 \text{ mg L}^{-1}$ ). The suspension was kept stirring for 60 min in the dark to achieve the adsorption equilibrium between the RhB dye and the sample before simulated sunlight irradiation. At a given time interval, the solution (1.5 mL) was collected and the concentration of RhB was determined by measuring the light absorbance of RhB at 553 nm by using UV/Vis spectroscopy. In this experiment, the RhB concentration obtained right after the adsorption equilibrium in the dark was denoted by  $C_0$ . To confirm the presence of the 'OH groups, PL spectroscopy was used. The approach was similar to that used by Liu et al.,  $^{\mbox{\tiny [46]}}$  who used terephthalic acid molecules as a probe. In the analysis, the catalyst (10 mg) was dispersed into the mixed solution (30 mL) of terephthalic acid (3 mmol L<sup>-1</sup>) and NaOH (10 mmol L<sup>-1</sup>) under stirring in the dark for 60 min before simulated sunlight irradiation. At a given time interval, the sample (2 mL) was collected to monitor the concentration of 'OH groups by measuring the intensity of the PL peak of the generated 2-hydroxyterephthalic acid at 426 nm on a Hitachi F-4500 fluorescence spectrophotometer with an excitation wavelength of 320 nm.

#### Acknowledgements

We thank Dr. Sam Ng for helping us with the XPS measurements.

**Keywords:** Ag  $\cdot$  hollow sphere  $\cdot$  metal-semiconductor  $\cdot$  photocatalysis  $\cdot$  TiO<sub>2</sub>

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Received: November 21, 2013 Revised: January 16, 2014 Published online on March 12, 2014