Enhanced photocatalytic activity in Ag-nanoparticle-dispersed BaTiO₃ composite thin films: Role of charge transfer

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Abstract: Optical absorption and photocatalytic activity can be enhanced by surface plasmon resonance (SPR) effect, but the charge transfer (CT) mechanism between the dispersed noble metal nanoparticles (NPs) and the semiconductor matrix has been ignored. Herein, we adduce a direct and strong evidence in Ag-nanoparticle-dispersed BaTiO₃ (Ag/BTO) composite films through X-ray photoelectron and photoluminescence spectra which reveals the CT from BTO trapped by Ag NPs under UV light and from Ag NPs to BTO under visible light. Owing to the broadened optical absorption and efficient CT from Ag NPs to BTO, the Ag₂₅/BTO film manifests the optimal photocatalytic activity under the irradiation of visible light rather than UV–Vis light. Our work provides a helpful insight to design highly efficient plasmonic photocatalyst through considering the synergetic effect of the CT between metal and semiconductor on the enhanced photocatalytic activity.

Keywords: charge transfer (CT); composite films; photocatalytic activity; surface plasmon resonance (SPR)

1 Introduction

Semiconductor photocatalysis, which provides a relatively simple and environment-friendly route for directly converting and harvesting sunlight into chemical energy, has received considerable attention to tackle the environmental pollution issues [1–3]. However, a number of intertwined factors limit the efficiency of photocatalysts. One bottleneck in photocatalysis is the low charge transfer (CT) rate and/or high recombination rate of electron–hole (e[−]–h⁺) pairs, resulting in low quantum yield [4]. In addition, on account of the broad band gap (E_g) of commonly used

semiconductors, e.g., TiO₂ (3.26 eV) [5], ZnO (3.2 eV) [6], and ZnS (3.66 eV) [7], the absorption in visible wavelength range is confined, which seriously weakens the photocatalytic efficiency.

Tremendous studies have been carried out to improve the photocatalytic activity, including ion doping [2,8], metal oxide complexes [9], and dispersion of noble metals [10–12], etc. Among these methods, dispersing metal (e.g., Au, Ag, and Pt) nanoparticles (NPs) has been proven as an effective way to improve the photocatalytic efficiency of semiconductor [13,14]. Two main mechanisms can be responsible for the enhanced photocatalytic property of semiconductor dispersed with metal NPs. On the one hand, the metal NPs can behave as an e[−] trap to facilitate the CT from semiconductor to metal in such heterojunction system

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[15–17]. On the other hand, it has also been discovered that surface plasmon resonance (SPR) effect of metal NPs could broaden the absorption of semiconductor to the visible light region, and promote the CT from metal to semiconductor leading to the increased separation efficiency of e^-h^+ pairs [4,5,18,19]. Although the effective influence of the CT on the enhanced photocatalytic performance has been confirmed, the detailed CT mechanism between metal and semiconductor remains a matter of debate throughout the field, and direct experimental evidence needs to be disclosed.

BaTiO₃ (BTO) has attracted much attention with respect to its high dielectric constant and refractive index [20,21], chemical stability, environmental benignity, and excellent optical property [22]. However, the photocatalytic activity of BTO is also suffered by its wide E_g (~3.18 eV) [23], which has response only to UV light. To date, further study about BTO has not ceased, and a few studies reveal that there are possibilities to improve the photocatalytic property of BTO via dispersing Ag NPs. For instance, Liu *et al.* [24] prepared flower-like BTO nanotube arrays by a hydrothermal method, and concluded that the photocatalytic performance of BTO nanotube arrays can be improved by dispersing Ag NPs. A recent study on Ag-modified BTO NPs [25] has investigated the effects of the ferroelectricity and loading of Ag on the photocatalytic property of BTO, and demonstrated that the photocatalytic efficiency could be significantly enhanced by attaching Ag onto the surface of ferroelectric BTO. Despite of a few emerging published works, the detailed effect of CT between Ag NPs and BTO on the photocatalytic activity has not been addressed up to now. This motivated us to explore the possibility of using BTO thin films dispersed with Ag NPs for understanding the detailed CT mechanism in such a system and for further developing highly efficient photocatalysts.

Herein, Ag/BTO thin films were prepared by a sol-gel and spin-coating method. The effect of Ag loading on the structure, optical absorption property, along with the photocatalytic property of the thin films was investigated systematically. The considerably enhanced optical absorption property and improved photocatalytic efficiency compared with the monolithic BTO were obtained in the Ag/BTO thin films due to the SPR effect. Furthermore, by systematically comparing the photocatalytic performance of the Ag/BTO system under UV, visible, and UV-Vis light, we provided a

comprehensive understanding of the SPR effect of the Ag NPs on the photocatalytic activity and the CT mechanism between Ag and BTO in the composite films, which is indispensable in designing highly efficient photocatalysts.

2 Experimental

2.1 Preparation

The Ag/BTO thin films with different Ag/(Ag+BTO) ratios (abbreviated as Ag_x/BTO, $x = 0, 5, 10, 15, 20, 25, 30$, where x is the mole percent (mol%) of Ag) were prepared by a sol-gel and spin-coating method starting with barium acetate (Ba(CH₃COO)₂, 99.0%), tetrabutyl titanate (Ti(C₄H₉O)₄, 98.0%), and silver nitrate (AgNO₃, 99.8%) as raw materials, as well as acetic acid (CH₃COOH, 99.5%), deionized water (H₂O), and glycerol (C₃H₈O₃, 99.0%) as solvents. Firstly, 1 mol of Ba(CH₃COO)₂ was dissolved in the mixed solution of CH₃COOH (5 mL), H₂O (5 mL), and C₃H₈O₃ (5 mL). After stirring for 2 h, 1 mol of Ti(C₄H₉O)₄ was added to the solution, followed by stirring for another 2 h. Several drops of nitric acid were added before stirring as hydrolysis catalysis for adjusting the pH value of the solution between 2 and 3. Then, a mixed solution of C₃H₈O₃ and AgNO₃ was added into the above mentioned precursor solution with a designed chemical composition of Ag_x/BTO. To form the Ag_x/BTO films, the ultimate solution was spin-coated onto glass substrate with size of 2 cm × 2 cm at 500 rpm for 5 s and subsequently 3000 rpm for 15 s. Finally, the thin films were dried at 150 °C for 30 s and successively heated to 500 °C for 1 h. These sequences of coating and pyrolysis treatments were repeated for 10 times.

2.2 Characterization methods

The phase and crystal structure of all samples were investigated by X-ray diffraction (XRD, DMAX-RB, Rigaku Inc., Japan) with Cu K α radiation ($\lambda = 1.5406$ Å) filtered through an Ni foil. The microstructure was observed by transmission electron microscopy (TEM, JEM-100CXII, JEOL, Japan). The chemical binding state of the constitution elements of the prepared films was characterized by X-ray photoelectron spectroscopy (XPS, PHI-5300, PHI, USA) using Al K α radiation ($h\nu = 1486.6$ eV) as an X-ray source. The energies of all spectra were adjusted by normalizing with respect to the C 1s peak at 284.8 eV. The Ag 3d, Ba 3d, Ti 2p, and

O 1s spectra were fitted using the XPS data which were determined by deconvolution with the program of XPS Peak 4.0. The absorption spectra were obtained by UV–Vis spectrophotometer (UV-2800, UNICO Instruments Co., Ltd., China). Steady state photoluminescence (PL) spectra of the thin films were measured using F-4500 FL spectrophotometer with an excitation wavelength of 335 nm at room temperature.

2.3 Photocatalytic activity assessment

The photocatalytic activity was evaluated by degradation of Rhodamine B (RhB) under UV, visible, and UV–Vis light. A 20 W UV light with emission wavelength of 365 ± 5 nm was used as the UV light source, and a 500 W xenon lamp (Beijing Institute of Electrical Light Sources, China) was used as UV–Vis and visible light source (with a 420 nm optical filter). 20 mM RhB solution was spin-coated onto the surface of the thin films. The reaction temperature was kept at room temperature to prevent any thermal catalytic effect. The films with RhB layer were statically placed in the dark to reach the adsorption/desorption equilibrium between the photocatalyst and RhB before illumination. The degradation rate was monitored by the intensity of absorption peak of RhB (580 nm) relative to its initial intensity under various illumination times.

3 Results and discussion

3.1 Phase structure and morphology

Figure 1 shows the XRD patterns of the Ag_x/BTO thin films. The standard diffraction peaks of Ag (PDF No. 04-0783) are indicated by vertical lines for comparison. A broad diffraction peak for all the samples was observed around 25° , corresponding to the amorphous

Fig. 1 XRD patterns of the Ag_x/BTO thin films.

BTO matrix and/or the glass substrate [26]. The absent peak of crystallized BTO after annealing indicates that the matrix is amorphous up to 500°C . Besides, the diffraction peaks at 2θ values of 38.1° , 44.3° , 64.4° , and 77.5° correspond to (111), (200), (220), and (311) crystal planes of the fcc Ag phase, respectively, whose peak intensity increases as x increasing, suggesting an improved crystallinity and grown grain.

To determine the dispersion and size of the Ag NPs inside the films, TEM analysis was performed for the $\text{Ag}_{25}/\text{BTO}$ thin film as shown in Fig. 2. The in-plane TEM image in Fig. 2(a) reveals that most of the Ag NPs are in spherical structure and uniformly dispersed in the amorphous BTO matrix, apart from some aggregations. The corresponding selected area electron diffraction (SAED) pattern in Fig. 2(b) shows the characteristic diffraction rings of cubic structure Ag (111), (200), (220), (311), and (222) (from inner to outer), which match well with the XRD results (Fig. 1). The Ag NPs in the $\text{Ag}_{25}/\text{BTO}$ thin film have a wide range of size distribution from 20 to 110 nm with a mean size of ca. 52 nm as shown in distribution histogram (Fig. 2(c)), which may be due to the partial aggregation of the Ag NPs. Further energy dispersive spectroscopy (EDS) analysis in Fig. 2(d) shows the co-existence of film-related Ag, O, Ba, and Ti emission peaks in addition to the Cu emission peak which is attributed to copper microgrid.

3.2 Chemical binding state and interaction of the involved elements

To further investigate the chemical binding state of the

Fig. 2 (a) Bright field TEM micrograph, (b) SAED pattern, (c) particle size distribution histogram, and (d) EDS spectrum of the $\text{Ag}_{25}/\text{BTO}$ thin film.

constitution elements and the interaction of the involved elements in the composite thin films, XPS characterization was carried out for the Ag₂₅/BTO sample. XPS survey scan in Fig. 3 reveals the co-existence of Ag, Ba, Ti, and O elements in the film. The appearance of Na peaks is due to the diffusion of Na atoms onto the surface from the glass substrate after annealing, the Si peak results from the SiO₂ substrate, and the carbon peak arises from an overlying contaminant hydrocarbon layer which is unavoidable for the XPS analysis. High-resolution XPS spectra of Ag 3d, Ba 3d, Ti 2p, and O 1s peaks of the Ag₂₅/BTO thin film are displayed in Fig. 4. We show that the spectrum of Ag 3d (Fig. 4(a)) is made up of two characteristic peaks, Ag⁰ 3d_{5/2} at 367.5 eV and Ag⁰ 3d_{3/2} at 373.5 eV. The spin-orbit splitting of 3d doublet is 6.0 eV [27,28]. This spectrum is consistent with the XPS result obtained for metallic Ag, confirming that Ag in the film is in metallic form. Moreover, the binding energy (BE) of Ag⁰ 3d_{5/2} and Ag⁰ 3d_{3/2} for the Ag/BTO sample shifts to lower BE compared to the corresponding value of the synthesized pure metallic Ag (BE values of Ag⁰ are about 368.3 and 374.3 eV, respectively) [27]. The high-resolution spectrum of Ba 3d (Fig. 4(b)) exhibits two peaks at 779.2 (Ba²⁺ 3d_{5/2}) and 794.4 eV (Ba²⁺ 3d_{3/2}), which are consistent with those at 779.0 and 794.2 eV detected in BTO powders [29] respectively. The BE of 458.0 and 463.7 eV in Fig. 4(c), ascribed to Ti⁴⁺ 2p_{3/2} and Ti⁴⁺ 2p_{1/2} respectively, are approximate to the values as reported

at 457.9 and 463.6 eV by Yang *et al.* [30] in single crystal BTO nanotube arrays, and 457.8 and 463.6 eV by Chakraborty *et al.* [31] in Fe-doped BTO single crystal. The asymmetric profile of the O 1s spectrum in Fig. 4(d) indicates that more than one kind of oxygen species exist. Spectral deconvolution yields two peaks, with one centered at 529.4 eV resulting from O in the BTO lattice (529.5 eV in polycrystalline BTO by Kumar *et al.* [32]), while the other at 531.7 eV could be attributed to surface hydroxyls or strongly chemisorbed H₂O [32]. Table 1 lists the characteristic peak position of observed Ag⁰, Ba²⁺, Ti⁴⁺, and O²⁻ ions in the Ag₂₅/BTO system in our present study as well as previously reported values mentioned above. From the decreased BE of Ag, we could infer that there is a CT process from BTO to Ag (named CT_{trap}), which will be interpreted in the following discussions.

Fig. 3 XPS survey scan spectra of the Ag₂₅/BTO thin film.

Fig. 4 High-resolution XPS spectra of the Ag₂₅/BTO thin film: (a) Ag 3d, (b) Ba 3d, (c) Ti 2p, and (d) O 1s.

Table 1 XPS data (binding energy) of the Ag₂₅/BTO sample compared with reported values

Material	Binding energy (eV)							Ref.
	Ag ⁰ 3d _{5/2}	Ag ⁰ 3d _{3/2}	Ba ²⁺ 3d _{5/2}	Ba ²⁺ 3d _{3/2}	Ti ⁴⁺ 2p _{3/2}	Ti ⁴⁺ 2p _{1/2}	O ²⁻ 1s	
Ag	368.3	374.3	—	—	—	—	—	[27]
BTO	—	—	779.0	794.2	—	—	—	[29]
	—	—	—	—	457.9	463.6	—	[30]
	—	—	—	—	457.8	463.6	—	[31]
	—	—	—	—	—	—	529.5 531.4	[32]
Ag ₂₅ /BTO	367.5	373.5	779.2	794.4	458.0	463.7	529.4 531.7	This work

3.3 Optical properties and band energy

The optical absorption spectra of the Ag_x/BTO thin films except for the monolithic BTO in Fig. 5 exhibit an absorption peak in the wavelength region of 450–600 nm, which results from the SPR effect of the Ag NPs under visible light. On the one hand, the SPR peak becomes stronger as x increases from 5 to 30, which is explained generally by Mie and relevant “Mie-like” theories [33–35]. In this study, the major factors affecting the intensity of SPR peak are the amount and size distribution of the Ag NPs along with a varied x from 5 to 30. The Ag NPs are almost uniformly dispersed in the BTO matrix when $x \leq 30$ (a series of TEM micrographs with different x are not given herein), resulting in an upward SPR peak intensity. On the other hand, the broadened SPR peak may be due to the mean free path effect as well as the influence of conduction electron collisions with particle surfaces [36].

Apart from the variation of SPR peak intensity in Fig. 5, another feature is the shift of SPR peak position (named λ_{SPR}), which shows a slightly red shift trend from 517 to 523 nm as x increasing from 5 to 25 while an obvious blue shift to 498 nm as x further increasing to 30, as listed in Table 2. It is well known that the shift of λ_{SPR} for small free Au NPs as increasing particle size is due to the quantum size effect (QSE) [33]. In the present study, the Ag_x/BTO thin films may follow the similar behavior. Herein, it is possible that, the QSE

becomes stronger due to grown particle amount and size when x increases from 0 to 25, which leads to a red shift of λ_{SPR} ; while that weakening may be due to the oversize Ag NPs with x further increasing to 30, resulting in a blue shift of λ_{SPR} although the SPR effect increases with an upward SPR intensity; thereby, $x = 25$ is the dispersion threshold.

To further understand the optical absorption behavior of the nanocomposite thin films, E_g was estimated by the Tauc's equation [37]:

$$\alpha = A \frac{(h\nu - E_g)^m}{h\nu}$$

where α , A , and $h\nu$ are the absorption coefficient, the constant, and the incident photon energy, respectively. The exponent m is an index which determines the type of optical transition (m is 2 and 1/2 corresponding to indirectly allowed and directly allowed transitions, respectively [38]). The dependence of $(\alpha h\nu)^2$ in Fig. 6(a) as a function of photon energy $h\nu$ indicates that all samples are the directly allowed nature of band-to-band transition. Figure 6(b) shows the E_g determined by extrapolating the linear region of the curve to the $h\nu$ axis when $(\alpha h\nu)^2 = 0$, is 2.75, 1.92, 1.90, 1.87, 1.80, 1.70, and 1.76 eV for the Ag_x/BTO composite films with $x = 0, 5, 10, 15, 20, 25$, and 30, respectively. E_g is

Fig. 5 Optical absorption spectra of the Ag_x/BTO thin films. **Fig. 6** Relationship between $(\alpha h\nu)^2$ and $h\nu$ for the Ag_x/BTO thin films.

gradually narrowed as x increasing up to 25 leading to the red shift, and then widened as x increasing from 25 to 30 resulting in the blue shift of λ_{SPR} , which is in well agreement with the optical absorption spectra mentioned above.

3.4 Photocatalytic activity

The photocatalytic activity in Fig. 7 indicates that the self-degradation of RhB is extremely weak under UV–Vis light at the absence of the catalyst, and only 2% of RhB is degraded after 5 h irradiation, while ca. 12% of RhB could be photodegraded by the monolithic BTO. The Ag_x/BTO films with SPR effect show an enhanced photocatalytic property, whose degradation rates are ca. 19%, 24%, 31%, 36%, 43%, and 40% as $x = 5, 10, 15, 20, 25$, and 30, respectively. The highest photodegradation rate of RhB solution arrives in 43% as $x = 25$. The optimized photocatalytic property in $\text{Au}/\text{Co}_3\text{O}_4$ [33] system was achieved in the sample with the strongest SPR peak intensity due to the more intensified electric field existed between metal and semiconductor. However, different from the $\text{Au}/\text{Co}_3\text{O}_4$ system, the photodegradation rate of RhB solution for the present Ag/BTO system in Fig. 7 reaches the peak value of 43% at $x = 25$ instead of $x = 30$ which has the strongest SPR peak intensity. This might be due to the fact that the present $\text{Ag}_{25}/\text{BTO}$ film possesses smaller E_g (1.70 eV) than the $\text{Ag}_{30}/\text{BTO}$ (1.76 eV), since smaller E_g indicates a possibility of utilizing more visible light for semiconductor photocatalyst, thus generating larger amount of $e^- - h^+$ pairs [39].

3.5 CT mechanism for the enhanced photocatalytic activity

To get further understanding of the SPR effect on the

Fig. 7 Degradation rate of RhB using the Ag_x/BTO thin films under UV–Vis light.

photocatalytic activity and the CT mechanism, we carried out PL measurement with an excitation wavelength of 335 nm at room temperature to probe the charge separation behavior in the Ag/BTO system using the sample of $\text{Ag}_{25}/\text{BTO}$, which shows the highest photocatalytic efficiency, as well as the monolithic BTO film for comparison. Both of the spectra in Fig. 8 are composed of two emission peaks regardless of the Ag NPs dispersion. The UV-range emission at 387 nm is a radiative recombination due to the recombination between e^- in the conduction band (CB) and h^+ in the valence band (VB). The visible-range emission around 424 nm, called nonradiative recombination, occurs possibly due to the recombination between e^- in a defect level and h^+ in the VB. Similar behavior has been reported in noble metal/ ZnO system [40]. The emission intensity of the $\text{Ag}_{25}/\text{BTO}$ increases compared to that of the monolithic BTO film, suggesting the occurrence of CT from Ag NPs to BTO (named CT_{SPR}) under visible light. Similar phenomena were also observed in the Au/ZnO system [41], which showed a significantly increased intensity of emission in PL spectra compared to that of the monolithic ZnO film, demonstrating the existence of CT_{SPR} from Au NPs to ZnO .

Our present work indicates that the SPR effect of the Ag NPs could enhance the photocatalytic activity in the Ag/BTO system under UV–Vis light in Fig. 7. However, the photocatalytic performance and CT mechanism of the Ag/BTO system under UV and/or visible light have not been investigated so far. To determine which CT process between CT_{trap} and CT_{SPR} contributes more to the enhanced reaction rate of photocatalysis, we studied the photodegradation of RhB for the $\text{Ag}_{25}/\text{BTO}$ thin film under UV, visible, and UV–Vis light, as shown in

Fig. 8 PL spectra of the monolithic BTO and $\text{Ag}_{25}/\text{BTO}$ thin films with an excitation wavelength of 335 nm at room temperature.

Fig. 9, along with the monolithic BTO under UV and UV–Vis light for comparison. An approximate photocatalytic property for the monolithic BTO under UV and UV–Vis light is observed. The photocatalytic activity of the Ag₂₅/BTO is identical to the monolithic BTO under UV light, which indicates that the CT_{trap} from BTO to Ag NPs is very poor for the Ag₂₅/BTO system. Surprisingly, the sample of Ag₂₅/BTO shows the fastest degradation rate (ca. 62%) under visible light where the CT_{SPR} from Ag NPs to BTO is existed, much better than that (ca. 43%) under UV–Vis light where the CT_{trap} from BTO to Ag NPs and the CT_{SPR} from Ag NPs to BTO are co-existed. This indicates that the CT_{SPR} from Ag NPs to BTO plays a dominant role on the photocatalytic reaction of the Ag/BTO, along with an opposite role caused by the CT_{trap} from BTO to Ag NPs, when employing UV–Vis light, which will be discussed later. For better explaining the CT mechanism in the Ag/BTO system, the band structure is constructed as illustrated in Fig. 10. Since the $E_{f(Ag)}$ (−4.3 eV [42]) is more positive than $E_{f(BTO)}$ (−5.3 eV [43]), when they come into contact, the e^- of Ag will diffuse to BTO at the lower energy level to build up an equilibrium state $E_{f(balance)}$ between $E_{f(Ag)}$ and $E_{f(BTO)}$.

Under UV light in Fig. 10(a), when the photocatalyst is irradiated by photons with energy ($h\nu$) equal to or higher than the E_g of BTO, the photoexcited e^- in the VB are elevated to the CB with simultaneous generation of the same amount of h^+ left in the VB. As the CB bottom level of BTO is higher than the $E_{f(balance)}$, the CT_{trap} from BTO to Ag NPs as indicated by a green arrow would occur actuated by the above potential energy, which can promote the separation and minimize the recombination of e^-h^+ pairs of BTO to some extent. It has been reported that the enhanced photocatalytic

Fig. 9 Degradation rate of RhB using the Ag₂₅/BTO thin film under UV, visible, and UV–Vis light, and the monolithic BTO under UV and UV–Vis light.

Fig. 10 Mechanism of CT for the Ag/BTO system under different light sources with approximate energy levels on the vacuum level: (a) UV light, (b) visible light, and (c) UV–Vis light.

activity of semiconductor dispersed with metal NPs could be ascribed to the possible reason that nanostructured metal (in our case Ag) can act as e^- trap, leading to the efficient separation of e^-h^+ pairs, and in turn to enhance the photocatalytic property [44]. Such CT_{trap} from BTO to Ag NPs behavior in the present work demonstrated by the XPS result (Fig. 4) helps to minimize the e^-h^+ recombination. Similar CT behavior has previously been reported in the Au/TiO₂ system [45], which is however irrelevant to the SPR effect.

It is well known that no e^-h^+ pairs are generated in the monolithic BTO under visible light because of the lower energy of irradiated photons than the E_g of BTO. As a result, there is no photocatalytic performance for the monolithic BTO under visible light. After dispersing Ag NPs in the BTO matrix, the Ag/BTO shows the excitation of the Ag NPs SPR effect under visible light (Fig. 5) and enhanced visible photocatalytic activity

(Fig. 9), which could be ascribed to several possible reasons. Firstly, noble metal NPs, such as Ag and Au, can broaden the optical absorption over a wider visible light wavelength range through the SPR effect [46]. Secondly, the SPR effect could also play an important role in enhancing the rate of photocatalytic reaction, through injecting hot e^- from metal NPs to semiconductor, that is, the CT_{SPR} from Ag NPs to BTO in our case as demonstrated by the PL spectra in Fig. 8. The excited SPR effect under visible light induces the efficient CT_{SPR} from Ag NPs to BTO as indicated by blue arrows in Fig. 10(b), which is an opposite direction to the CT_{trap} from BTO to Ag NPs happened under UV light. Such CT_{SPR} from Ag NPs to BTO can enhance the generation of active $\bullet O_2^-$ radicals on the BTO surface, while the h^+ retained in the Ag NPs can be used for the generation of active $\bullet OH$ radicals [47], both of which contribute to the degradation of RhB. Furthermore, the SPR effect could be intensified with the increase of x , resulting in a larger amount of the CT_{SPR} from Ag NPs to BTO. Moreover, the work of Cushing *et al.* [48,49] pointed out that the SPR effect can also excite e^-h^+ pairs in semiconductor by transferring the plasmonic energy from metal to semiconductor, and more photoexcited charge carriers will participate in the process of photocatalysis, resulting in the enhanced photocatalytic property.

In the last case, under the irradiation of UV–Vis light (Fig. 10(c)), the CT mechanism for the monolithic BTO is consistent with that under UV light (Fig. 10(a)), leading to the approximate photocatalytic activity of the monolithic BTO under UV and UV–Vis light (Fig. 9). However, both of the CT_{trap} from BTO to Ag NPs and the CT_{SPR} from Ag NPs to BTO under UV–Vis light would occur after dispersing Ag NPs; that is, the photogenerated e^- in the BTO induced by UV light will transfer to the Ag NPs, and the Ag NPs can inject hot e^- to BTO due to the SPR effect induced by visible light simultaneously. On the other hand, the Ag NPs and BTO can respectively inject the trapped e^- back into the BTO and Ag NPs under UV–Vis light; hence, the time that the e^- resides in the Ag NPs and BTO under UV–Vis light is shortened in comparison to that under UV or visible light alone. These two processes will promote the recombination of e^-h^+ pairs to a certain extent and impair the photocatalytic activity [50]. Meanwhile, collisions would possibly occur in the process of e^- transferring from one to another between Ag NPs and BTO in different directions, whereby the

migration rate will decrease to some extent. Hence, above pros and cons exist simultaneously in the photocatalytic reaction of the Ag/BTO when employing UV–Vis light, consequently leading to the lower photocatalytic activity of Ag_x/BTO under UV–Vis light compared to that under visible light (Fig. 9). A similar phenomenon was observed in the UV–Vis light irradiated Au/TiO₂ photocatalysis system although the authors mainly focused on the pros and cons of localized SPR [50].

Table 2 lists the potential energy ($1240/\lambda_{SPR}$) of the hot e^- (named $h\nu_{hot e^-}$) of the Ag_x/BTO thin films through the λ_{SPR} of the absorption spectra (Fig. 5) which is induced by the SPR effect of metal NPs escaping from metal to semiconductor [51]. As long as the hot e^- has higher energy than the CB level bottom of the BTO, the CT_{SPR} from Ag NPs to BTO could occur. Here, we introduce the concept of ΔE determined by the difference between the SPR state and the CB of BTO, i.e., $\Delta E = h\nu_{hot e^-} - E_{CB}$, as shown in Table 2. From the standpoint of energy, e^- can more easily transfer between two more closely matched energy levels, implying that the smaller ΔE is more beneficial to the CT_{SPR} from Ag NPs to BTO. We have shown that the Ag_{25}/BTO film which has the lowest ΔE possesses the best photocatalytic activity (Fig. 7). These interesting phenomena only observed herein would provide a useful guidance for further designing highly efficient plasmonic photocatalysts.

4 Conclusions

Ag_x/BTO ($0 \leq x \leq 30$) composite thin films are prepared using a sol–gel and spin-coating method. The approximately spherical Ag NPs are dispersed in the amorphous BTO matrix. All the Ag_x/BTO thin films except for the monolithic BTO exhibit an absorption peak in the visible wavelength region of 450–600 nm resulting from the SPR effect of the Ag NPs; the SPR

Table 2 Summary of λ_{SPR} , E_g , $h\nu_{hot e^-}$, and ΔE of the Ag_x/BTO thin films

x (mol%)	λ_{SPR} (nm)	E_g (eV)	$h\nu_{hot e^-}$ (eV)	ΔE (eV)
5	517	1.92	2.40	6.20
10	519	1.90	2.39	6.19
15	520	1.87	2.38	6.18
20	521	1.80	2.38	6.18
25	523	1.70	2.37	6.17
30	499	1.76	2.48	6.28

peaks generally exhibit a red shift with the increase of x from 5 to 25, while a blue shift as x further increasing to 30. The XPS and PL results provide a direct and strong evidence about the synergetic effect between the CT_{trap} from BTO to Ag NPs under UV light and the CT_{SPR} from Ag NPs to BTO under visible light. Owing to the broadened optical absorption and the efficient CT_{SPR} from Ag NPs to BTO, an optimal photocatalytic activity for the degradation of RhB achieves in the Ag_{25}/BTO film. This study provides helpful insights to explore highly efficient visible-light-sensitive plasmonic photocatalyst.

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References

- [1] Fujishima A, Honda K. Electrochemical photolysis of water at a semiconductor electrode. *Nature* 1972, **238**: 37–38.
- [2] Asahi R, Morikawa T, Ohwaki T, *et al.* Visible-light photocatalysis in nitrogen-doped titanium oxides. *Science* 2001, **293**: 269–271.
- [3] Hoffmann MR, Martin ST, Choi W, *et al.* Environmental applications of semiconductor photocatalysis. *Chem Rev* 1995, **95**: 69–96.
- [4] Zhao W, Feng LL, Yang R, *et al.* Synthesis, characterization, and photocatalytic properties of Ag modified hollow SiO_2/TiO_2 hybrid microspheres. *Appl Catal B: Environ* 2011, **103**: 181–189.
- [5] Awazu K, Fujimaki M, Rockstuhl C, *et al.* A plasmonic photocatalyst consisting of silver nanoparticles embedded in titanium dioxide. *J Am Chem Soc* 2008, **130**: 1676–1680.
- [6] Maeda K, Takata T, Hara M, *et al.* GaN:ZnO solid solution as a photocatalyst for visible-light-driven overall water splitting. *J Am Chem Soc* 2005, **127**: 8286–8287.
- [7] Zhang J, Yu J, Zhang Y, *et al.* Visible light photocatalytic H_2 -production activity of CuS/ZnS porous nanosheets based on photoinduced interfacial charge transfer. *Nano Lett* 2011, **11**: 4774–4779.
- [8] Maeda K. Rhodium-doped barium titanate perovskite as a stable p-type semiconductor photocatalyst for hydrogen evolution under visible light. *ACS Appl Mater Interfaces* 2014, **6**: 2167–2173.
- [9] Li L, Salvador PA, Rohrer GS. Photocatalysts with internal electric fields. *Nanoscale* 2014, **6**: 24–42.
- [10] Subramanian V, Wolf EE, Kamat PV. Catalysis with TiO_2 /gold nanocomposites. Effect of metal particle size on the fermi level equilibration. *J Am Chem Soc* 2004, **126**: 4943–4950.
- [11] Rupa AV, Manikandan D, Divakar D, *et al.* Effect of deposition of Ag on TiO_2 nanoparticles on the photodegradation of Reactive Yellow-17. *J Hazard Mater* 2007, **147**: 906–913.
- [12] Height MJ, Pratsinis SE, Mekasuwandumrong O, *et al.* Ag–ZnO catalysts for UV-photodegradation of methylene blue. *Appl Catal B: Environ* 2006, **63**: 305–312.
- [13] Zhang X, Chen YL, Liu R-S, *et al.* Plasmonic photocatalysis. *Rep Prog Phys* 2013, **76**: 046401.
- [14] Wold A. Photocatalytic properties of titanium dioxide (TiO_2). *Chem Mater* 1993, **5**: 280–283.
- [15] Lai Y, Meng M, Yu Y. One-step synthesis, characterizations and mechanistic study of nanosheets-constructed fluffy ZnO and Ag/ZnO spheres used for Rhodamine B photodegradation. *Appl Catal B: Environ* 2010, **100**: 491–501.
- [16] Ren C, Yang B, Wu M, *et al.* Synthesis of Ag/ZnO nanorods array with enhanced photocatalytic performance. *J Hazard Mater* 2010, **182**: 123–129.
- [17] Lu W, Gao S, Wang J. One-pot synthesis of Ag/ZnO self-assembled 3D hollow microspheres with enhanced photocatalytic performance. *J Phys Chem C* 2008, **112**: 16792–16800.
- [18] Bian ZF, Tachikawa T, Zhang P, *et al.* Au/ TiO_2 superstructure-based plasmonic photocatalysts exhibiting efficient charge separation and unprecedented activity. *J Am Chem Soc* 2014, **136**: 458–465.
- [19] Ingram DB, Linic S. Water splitting on composite plasmonic-metal/semiconductor photoelectrodes: Evidence for selective plasmon-induced formation of charge carriers near the semiconductor surface. *J Am Chem Soc* 2011, **133**: 5202–5205.
- [20] Yang Y, Shi J, Huang W, *et al.* Preparation and optical properties of gold nanoparticles embedded in barium titanate thin films. *J Mater Sci* 2003, **38**: 1243–1248.
- [21] Zhang SW, Zhang BP, Li S, *et al.* SPR enhanced photocatalytic properties of Au-dispersed amorphous $BaTiO_3$ nanocomposite thin films. *J Alloys Compd* 2016, **654**: 112–119.
- [22] Masaki Y, Koutzarov IP, Ruda HE, *et al.* Gold-particle-enhanced crystallite growth of thin films of barium titanate prepared by the sol–gel process. *J Am Ceram Soc* 1998, **81**: 1074–1076.
- [23] Fan H, Li H, Liu B, *et al.* Photoinduced charge transfer properties and photocatalytic activity in $Bi_2O_3/BaTiO_3$ composite photocatalyst. *ACS Appl Mater Interfaces* 2012, **4**: 4853–4857.
- [24] Liu J, Sun Y, Li Z. Ag loaded flower-like $BaTiO_3$ nanotube arrays: Fabrication and enhanced photocatalytic property. *CrystEngComm* 2012, **14**: 1473–1478.
- [25] Su R, Shen YJ, Li L, *et al.* Silver-modified nanosized ferroelectrics as a novel photocatalyst. *Small* 2015, **11**: 202–207.
- [26] Li Y, Zhang B-P, Zhao C-H, *et al.* Structure transition, formation, and optical absorption property study of Ag/ SiO_2 nanofilm by sol–gel method. *J Mater Res* 2012, **27**: 3141–3146.

- [27] Moulder JF, Chastain J, King RC. *Handbook of X-ray Photoelectron Spectroscopy: A Reference Book of Standard Spectra for Identification and Interpretation of XPS Data*. Perkin-Elmer Eden Prairie, 1992.
- [28] Cui Y, Briscoe J, Dunn S. Effect of ferroelectricity on solar-light-driven photocatalytic activity of BaTiO₃—Influence on the carrier separation and stern layer formation. *Chem Mater* 2013, **25**: 4215–4223.
- [29] López MDCB, Fourlaris G, Rand B, *et al.* Characterization of barium titanate powders: Barium carbonate identification. *J Am Ceram Soc* 1999, **82**: 1777–1786.
- [30] Yang Y, Wang X, Sun C, *et al.* Structure study of single crystal BaTiO₃ nanotube arrays produced by the hydrothermal method. *Nanotechnology* 2009, **20**: 055709.
- [31] Chakraborty T, Ray S, Itoh M. Defect-induced magnetism: Test of dilute magnetism in Fe-doped hexagonal BaTiO₃ single crystals. *Phys Rev B* 2011, **83**: 144407.
- [32] Kumar S, Raju VS, Kutty TRN. Investigations on the chemical states of sintered barium titanate by X-ray photoelectron spectroscopy. *Appl Surf Sci* 2003, **206**: 250–261.
- [33] Wang S, Zhang B. SPR propelled visible-active photocatalysis on Au-dispersed Co₃O₄ films. *Appl Catal A: Gen* 2013, **467**: 585–592.
- [34] Hövel H, Fritz S, Hilger A, *et al.* Width of cluster plasmon resonances: Bulk dielectric functions and chemical interface damping. *Phys Rev B* 1993, **48**: 18178.
- [35] Lermé J, Palpant B, Prével B, *et al.* Quenching of the size effects in free and matrix-embedded silver clusters. *Phys Rev Lett* 1998, **80**: 5105.
- [36] Kreibig U, Fragstein Cv. The limitation of electron mean free path in small silver particles. *Z Physik* 1969, **224**: 307–323.
- [37] Davis EA, Mott NF. Conduction in non-crystalline system V. Conductivity, optical absorption and photoconductivity in amorphous semiconductors. *Philos Mag* 1970, **22**: 903–922.
- [38] Pankove JJ. *Optical Processes in Semiconductors*. Courier Corporation, 2012.
- [39] Gao F, Chen XY, Yin KB, *et al.* Visible-light photocatalytic properties of weak magnetic BiFeO₃ nanoparticles. *Adv Mater* 2007, **19**: 2889–2892.
- [40] Lee M-K, Kim TG, Kim W, *et al.* Surface plasmon resonance (SPR) electron and energy transfer in noble metal-zinc oxide composite nanocrystals. *J Phys Chem C* 2008, **112**: 10079–10082.
- [41] Li X, Zhang Y, Ren X. Effects of localized surface plasmons on the photoluminescence properties of Au-coated ZnO films. *Opt Express* 2009, **17**: 8735–8740.
- [42] Michaelson HB. The work function of the elements and its periodicity. *J Appl Phys* 1977, **48**: 4729–4733.
- [43] Schulmeyer T, Paniagua SA, Veneman PA, *et al.* Modification of BaTiO₃ thin films: Adjustment of the effective surface work function. *J Mater Chem* 2007, **17**: 4563–4570.
- [44] Zhou H, Qu Y, Zeid T, *et al.* Towards highly efficient photocatalysts using semiconductor nanoarchitectures. *Energy Environ Sci* 2012, **5**: 6732–6743.
- [45] Xu Z, Quintanilla M, Vetrone F, *et al.* Harvesting lost photons: Plasmon and upconversion enhanced broadband photocatalytic activity in core@shell microspheres based on lanthanide-doped NaYF₄, TiO₂, and Au. *Adv Funct Mater* 2015, **25**: 2950–2960.
- [46] Linic S, Christopher P, Ingram DB. Plasmonic-metal nanostructures for efficient conversion of solar to chemical energy. *Nat Mater* 2011, **10**: 911–921.
- [47] Linic S, Christopher P, Xin H, *et al.* Catalytic and photocatalytic transformations on metal nanoparticles with targeted geometric and plasmonic properties. *Acc Chem Res* 2013, **46**: 1890–1899.
- [48] Cushing SK, Li J, Meng F, *et al.* Photocatalytic activity enhanced by plasmonic resonant energy transfer from metal to semiconductor. *J Am Chem Soc* 2012, **134**: 15033–15041.
- [49] Cushing SK, Wu N. Plasmon-enhanced solar energy harvesting. *Electrochem Soc Interface Summer* 2013, **22**: 63–67.
- [50] Lin Z, Wang X, Liu J, *et al.* On the role of localized surface plasmon resonance in UV–Vis light irradiated Au/TiO₂ photocatalysis systems: Pros and cons. *Nanoscale* 2015, **7**: 4114–4123.
- [51] Bai S, Jiang J, Zhang Q, *et al.* Steering charge kinetics in photocatalysis: Intersection of materials syntheses, characterization techniques and theoretical simulations. *Chem Soc Rev* 2015, **44**: 2893–2939.

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