



Ag⁰-loaded brookite/anatase composite with enhanced photocatalytic performance towards the degradation of methyl orange

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ABSTRACT

Ag⁰-loaded brookite/anatase composite was prepared via an alkaline hydrothermal process. The photocatalytic performance of as-prepared catalysts was evaluated in terms of the degradation of methyl orange (MO). The physical features of the catalysts were measured with XRD, BET and HRTEM techniques. The phase content of brookite and anatase in the TiO₂ can be controlled by fixing the concentration of the electrolyte in the hydrothermal system. The as-formed Ag⁰ clusters have an average diameter of ca. 1.5 nm and intersperse throughout the surface of both anatase nanoparticles and brookite nanorods. Ag⁰ has an optimal loading dosage of 2.0 mol%, with which the photocatalytic degradation of MO are 4.82 and 2.28 times of that with Ag⁰-free composite and P25 TiO₂, respectively. The synergistic effect of hetero-junction in brookite/anatase composite and the schottky barrier at the interface of Ag⁰ and TiO₂ significantly improved the separation of the photogenerated electrons and holes under UV irradiation and thus resulted in a much enhanced photocatalytic reactivity towards the degradation of MO.

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1. Introduction

As a well-known functional material, titanium dioxide has long been investigated for applications in photocatalysis, energy conversion and pollutant degradation due to its inherent properties of superior photoactivity, high chemical stability, low cost and non-toxicity [1–4]. The photocatalytic performance of TiO₂, however, depends upon its physical features [5–8] such as the grain size, morphology, specific surface area, as well as the crystal structure. TiO₂ exists mainly in three crystalline polymorphs: anatase (*I4₁/amd*), rutile (*P4₂/mnm*) and brookite (*Pbca*), which can be modeled as edge and corner-linked structure with Ti cations coordinated octahedrally by oxygen anions [9].

The anatase polymorph is generally reported to exhibit better efficiency for photocatalysis and solar energy conversion because of the low recombination rate of its photogenerated electrons and holes, while the photocatalytic performance of rutile is still indistinct [10,11]. Brookite is the least studied because of the difficulties in synthesizing the pure form [12]. Among the works involves the photocatalytic performance of TiO₂ with its crystal structure, the role of the mixed crystal phases has also been concerned [11,13,14]. Mixed crystal phases, such as anatase/rutile, exhibit better photo-

catalytic performance than pure single crystal phase due to better separation of photogenerated electrons and holes [11,13].

Besides, schottky barrier formed between the deposited noble metal clusters and TiO₂ grains can also act as traps to reduce the recombination of photogenerated electrons and holes, and hence promote the photocatalytic activity of TiO₂ [15,16]. Among the common noble metals such as Pt [17], Pd [18], Au [15] and Ag [16] which have ever been studied in photocatalytic applications, Ag is the cheapest and hence the most frequently studied. Literature works [19,20] show that the role of noble metal clusters depends greatly on their size, of which a suitable cluster size with uniform size distribution is preferred. Further, the effects of chemical states of Ag on the photoelectrochemical properties of Ag–TiO₂ have also been recently studied [21]. It is suggested that Ag⁺ is more effective in promoting the photocatalytic degradation of methylene blue in some cases [21].

Our recent works showed that brookite TiO₂ exhibited higher photocatalytic reactivity than anatase [12], while the crystal phase of the TiO₂ products was precisely controlled from tetrabutyl titanate (TBOT) with an alkaline hydrothermal method [9]. Insight into the formation of TiO₂ in alkaline hydrothermal media showed that TiO₂ is produced from the titanate via a phase transition route, in which cations in the media can be exchanged into the interlayers of titanate and involve in the phase transition process [22]. Photoreduction method is the most frequent route for the preparation of Ag⁰-loaded TiO₂ reported in the literatures [21,23,24]. Unfortunately, the photocatalytic activity improvement of TiO₂ from Ag⁰ clusters is found to be limited [21,23], which is

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ascribed to the fact that photoreduced Ag cannot be highly dispersed on the surface of TiO₂, and thus fails to markedly increase the amount of active sites on the Ag–TiO₂ surface. In this work, AgNO₃ was pre-mixed with titanium precursor before hydrothermal treatment. Noble metal Ag⁰ loaded brookite/anatase composite with enhanced photocatalytic performance is thus prepared via an alkaline hydrothermal process. According to its particular formation process, the Ag⁰ clusters in the composite in this work were formed in situ on the surface defect sites of TiO₂ and thus should have stronger interaction with the photogenerated carriers in the photocatalytic applications of the composite.

2. Experimental

2.1. Reagents and materials

TBOT and NH₃·H₂O (25–28%) were obtained from Ling Feng Chemical Reagent. AgNO₃, NaNO₃ were obtained from Sinopharm Chemical Reagent. Methyl orange (MO) was obtained from Acros. All the reagents were of AR and used as received. Doubly distilled water was used throughout the work.

2.2. Catalyst preparation

The preparation of Ag⁰-loaded TiO₂ was carried out according to the alkaline hydrothermal procedures reported in our previous works [9,22]: a certain amount of NaNO₃ and AgNO₃ was dissolved into aqueous ammonia (NH₃·H₂O). Then 7.8 mL TBOT was directly hydrolyzed in the above solution. The total volume of solution was controlled to 75 mL, and the total cation (Na⁺ and Ag⁺) concentration was controlled to 0.125 mol L⁻¹ unless specified. After stirring for a short time the resulting suspension was transferred to a Teflon-lined autoclave and heated to 180 °C for 24 h. The residual Ag⁺ in the filtrate was detected with KI aqueous solution. The results showed that all the Ag⁺ ions in the system were embedded into the catalyst and dissolved Ag⁺ was below the detection limit. The obtained powders were then washed and dried at 80 °C for 24 h. A series of samples were thus obtained by adjusting the mole percentage of Ag⁺ ions in relation to the TBOT (Ag/Ti ratio) from 0.0% to 5.0% and designated as “x% Ag⁰-TiO₂” (x% is mole percentage ratio of Ag/Ti).

2.3. Catalyst characterization

Samples of Ag⁰-loaded brookite/anatase composites were characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM).

The Crystallographic information of products in this paper was examined by powder XRD. Diffraction patterns of these samples were performed using a powder diffractometer (RIGAKU D/max2550) operating in the reflection mode with a Siemens D5000 diffractometer (Cu-K_α) at a scan rate of 0.02° 2θ s⁻¹. Both TEM and HRTEM were investigated using a JEOL JEM 2100F instrument operated at 200 kV and equipped with an EDX facility as well as with the potential of performing SAED. To prepare the HRTEM specimens, the powder samples were first dispersed ultrasonically in absolute ethanol. One drop of the suspension was placed on a carbon film supported on a copper grid and allowed to dry in air before the specimens were transferred into the microscope.

2.4. Photocatalytic activity

The catalytic activity under UV light was investigated by the photodegradation of MO. UV irradiation was carried out using a 300 W high-pressure mercury lamp, which was surrounded by a

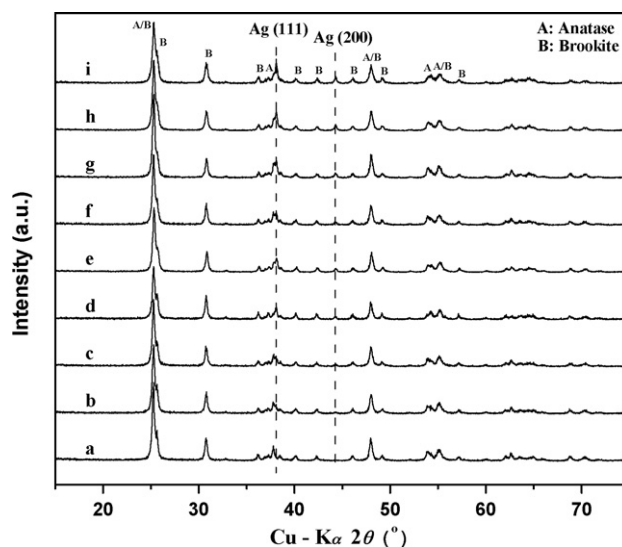


Fig. 1. XRD patterns of the Ag⁰-TiO₂ composites with Ag⁰ mol% of 0.0% (a), 0.5% (b), 1.0% (c), 1.5% (d), 2.0% (e), 2.5% (f), 3.0% (g), 4.0% (h) and 5.0% (i).

quartz jacket to allow for water cooling. Photocatalyst powder (0.10 g) was added into 100 mL aqueous MO solution (10 mg L⁻¹) and magnetically stirred in the dark for 30 min before UV illumination was conducted. The absorbance of MO at 465 nm was monitored by measuring with a UV–vis spectrophotometer (Varian Cary 100).

3. Results and discussion

3.1. Crystal phase and morphology of catalysts

The morphological phase diagram of hydrothermal products of TBOT in aqueous ammonia media has been investigated in our previous work [9,12,22]. The product directly hydrolyzed from TBOT in aqueous ammonia is ammonium dititanate, and Na_{2-x}(NH₄)_xTi₂O₅·H₂O in the presence of Na⁺ ion [9]. Pure anatase can be obtained as a final product after hydrothermal treatment of ammonium dititanate, while brookite phase in a form of nanoflower shape begins to arise in the presence of Na⁺. The content of brookite in the mixture can be controlled by controlling the concentration of Na⁺ in the hydrothermal system. As for the photocatalytic applications, anatase/brookite composite exhibited a relatively better photocatalytic performance towards the degradation of MO, phenol and salicylic acid than that of the pure anatase (obtained from Na⁺ free media) and the pure brookite (obtained in the presence of Na⁺ with concentrations of 0.25 ~ 0.5 M).

Fig. 1 presents the XRD patterns of the photocatalyst samples prepared with the various dosages of Ag⁺. Mixtures of anatase and brookite were observed in all the cases. The phase content of the photocatalysts is calculated according to the following equations [25]:

$$W_A = \frac{k_A A_A}{k_A A_A + k_B A_B}$$

$$W_B = \frac{k_B A_B}{k_A A_A + k_B A_B}$$

A_A refers to the integrity intensity of anatase (101) and A_B refers to the integrity intensity of brookite (121), K_A and K_B are constants of 0.886 and 2.721, respectively. The average grain size

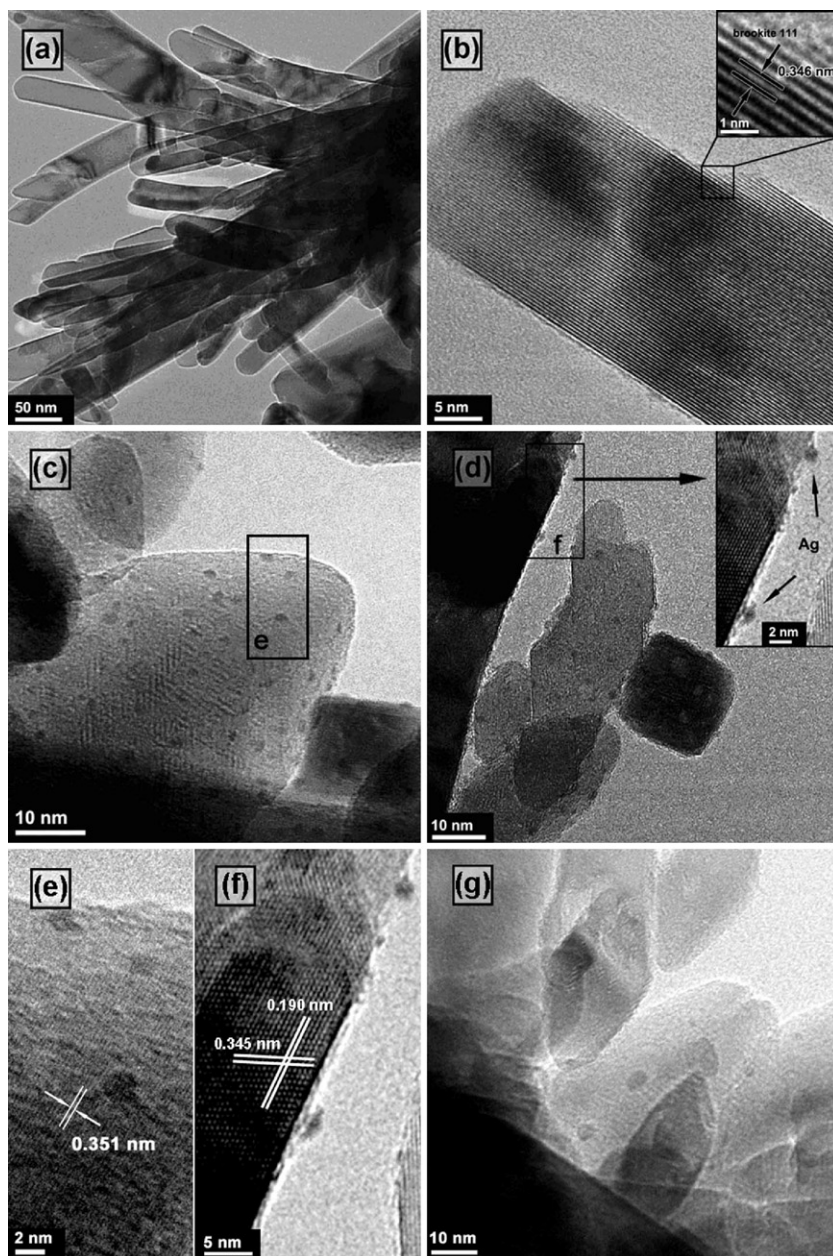


Fig. 2. TEM (a), HRTEM images of 2.0% Ag⁰-TiO₂ (b–f) and K₃[Fe(SCN)₆]/ammonia washed 2.0% Ag⁰-TiO₂ (g).

of the photocatalysts is calculated using the Scherrer equation [15]:

$$D = \frac{K\lambda}{\beta \cos \theta}$$

where β is the half-height width of the diffraction peak of anatase or brookite, $K = 0.89$ is a coefficient, θ is the diffraction angle, and λ is the X-ray wavelength corresponding to the Cu K α radiation. Both the phase content and the average grain size of the photocatalysts as-calculated were listed in Table 1.

The addition of Ag⁺ seemed not to obviously alter the phase compositions and the S_{BET} of TiO₂ products as the total cation concentration of Na⁺ and Ag⁺ was fixed to 0.125 mol L⁻¹ in all cases. The effect of Ag⁺ doping on the phase transformation and grain growth of titania nanoparticle has been studied [26,27]. It is reported that Ag⁺ doping would facilitate the phase transformation and grain growth of oxide such as TiO₂ [26]. However, the calculated grains size of brookite changed little with various

Table 1

The phase compositions, average grain sizes and S_{BET} of the Ag⁰-TiO₂ composites.

Ag ⁰ (mol%)	Phase composition (%)		Average grain sizes (nm)		S _{BET} (m ² /g)
	Anatase	Brookite	Anatase	Brookite	
0%	56.3	43.7	n.c. ^a	46.0	85.6
0.5%	62.9	37.1	n.c. ^a	43.5	–
1.0%	57.8	42.2	n.c. ^a	45.9	83.5
1.5%	63.2	36.8	n.c. ^a	46.7	–
2.0%	63.8	36.2	n.c. ^a	45.5	86.2
2.5%	62.4	37.6	n.c. ^a	43.8	–
3.0%	51.3	48.7	n.c. ^a	46.6	79.7
4.0%	58.5	41.5	n.c. ^a	39.8	–
5.0%	62.7	37.3	n.c. ^a	36.6	85.3
0% ^b	100	0	21.8	–	90.4
2.0% ^b	100	0	32.5	–	57.6

^a Not calculated as the XRD peaks of are overlapped with that of brookite.

^b Catalysts prepared in the absence of Na⁺ ion.

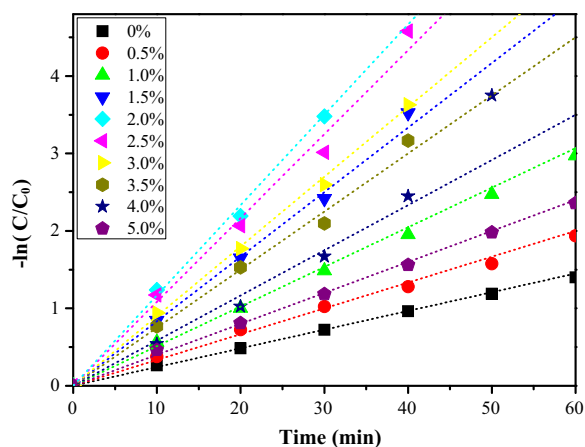


Fig. 3. Photocatalytic degradation of MO with $\text{Ag}^0\text{-TiO}_2$ composite with various Ag^0 mol% under UV irradiation.

Ag^+ dosages. The discrepancy in the observed results here may be ascribed to the presence of Na^+ , as the grain size of the anatase TiO_2 prepared in the Na^+ -free media increased by 50% from Ag^0 -free to 2.0% Ag^0 -loaded TiO_2 (Table 1), which is consistent with the literatures [26]. The characteristic diffraction signals from the Ag^0 (200) planes appeared at 44.3° indicating that Ag^0 clusters were formed in the as-formed catalysts, the intensity of which is enhanced with the increase of Ag^+ dosage in the catalyst preparation. The amount increment of Ag^0 cluster can also be confirmed with another characteristic diffraction signals of Ag^0 (111) at 38.1° , although it overlaps with the (004) diffraction of anatase in the XRD patterns.

The photocatalyst obtained with an Ag mole percentage of 2.0% was further investigated with HRTEM in Fig. 2. The catalyst is mainly composed of nanorods, as well as some nanoparticles as shown in Fig. 2a. Nanorods are of brookite phase according to its lattice features as shown in Fig. 2b and f, while nanoparticles are anatase TiO_2 as shown in Fig. 2c and e. Interplanar lattice spaces of 0.346 nm (0.345 nm) and 0.190 nm in Fig. 2b and f should be assigned to the (111) and (231) lattice planes of brookite, and that of 0.351 nm in Fig. 2e is the (101) lattice plane of anatase. Numerous black dots can be ubiquitously observed both on anatase nanoparticles (Fig. 2c and e) and brookite nanorods (Fig. 2d and f), which should be the Ag^0 clusters and have an average diameter of ca. 1.5 nm. Using 2.0 mM $\text{K}_3[\text{Fe}(\text{SCN})_6]$ as the oxidant and 20 mM ammonia as complexing agent, Ag^0 cluster in Ag-TiO_2 can be washed away as $[\text{Ag}(\text{NH}_3)_2]^+$ [28]. Fig. 2g shows the HRTEM image of as-washed 2.0% Ag^0 -loaded TiO_2 catalyst. The black dots assigned as Ag^0 clusters disappear as expected.

3.2. Photocatalytic performance of catalysts

The photocatalytic performance of as-prepared catalyst was tested by the degradation of MO, which is shown in Fig. 3. The degradation of MO is found to follow the apparent first-order kinetics. Depending on the Ag^0 content in the catalyst, the photocatalytic activity of $\text{Ag}^0\text{-TiO}_2$ initially increases up to 2.0% then decreases at higher content, thus gives an optimal Ag^+ dosage of 2.0%. Nominally, the photocatalytic degradation of MO had a reaction rate constant of 0.1167 min^{-1} for 2.0% $\text{Ag}^0\text{-TiO}_2$, which is 4.82 and 2.28 times of that for Ag^0 -free composite (0.0242 min^{-1} , Fig. 4) and P25 TiO_2 (0.051 min^{-1} , Fig. 4), respectively.

On the other hand, photocatalytic reactivity of composite catalyst also depends on the phase composition of TiO_2 . Alteration of the total cation concentration of electrolytes (Na^+ and Ag^+) in the hydrothermal treatment led to products of different crystal phase.

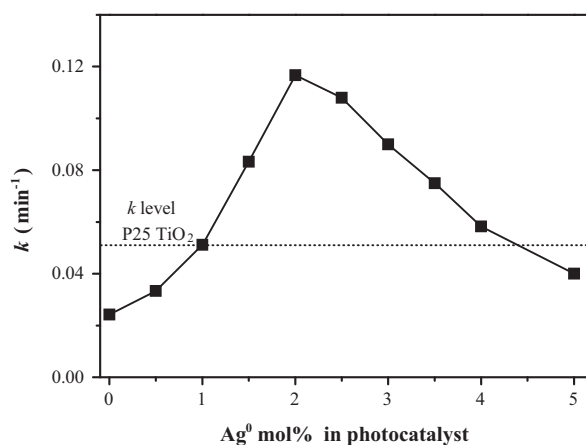


Fig. 4. Reaction rate constant of the photocatalytic degradation of MO vs Ag^0 mol% in the $\text{Ag}^0\text{-TiO}_2$ catalysts under UV irradiation.

More specifically, crystal phases of the TiO_2 product were anatase, brookite/anatase composite and brookite in the presence of 0M NaNO_3 , 0.125 M electrolytes and 0.25 M electrolytes, respectively [9,22]. As shown in Fig. 5, brookite/anatase composite prepared in the presence of 0.125 M electrolytes exhibits the highest photocatalytic reactivity, both for Ag -free and 2.0% $\text{Ag}^0\text{-TiO}_2$ samples. As for the Ag -free samples (Fig. 5a), that is TiO_2 sample, the MO degradation reaction rate constant of the brookite/anatase composite gave a value of 0.0242 min^{-1} , while that of pure anatase

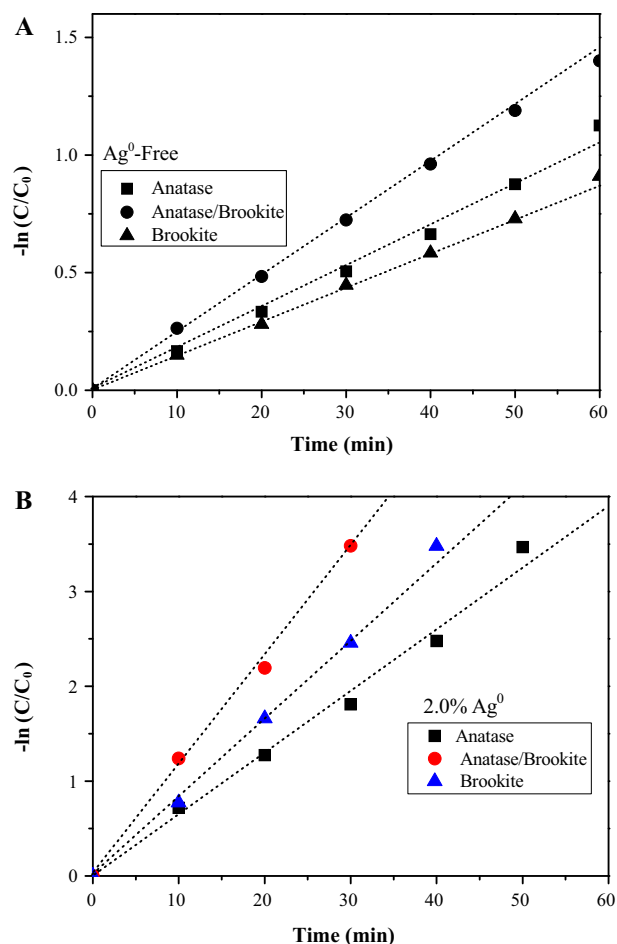


Fig. 5. Photocatalytic degradation of MO with Ag -free (A) and 2.0% Ag^0 -loaded (B) TiO_2 with different crystal phase composition under UV irradiation.

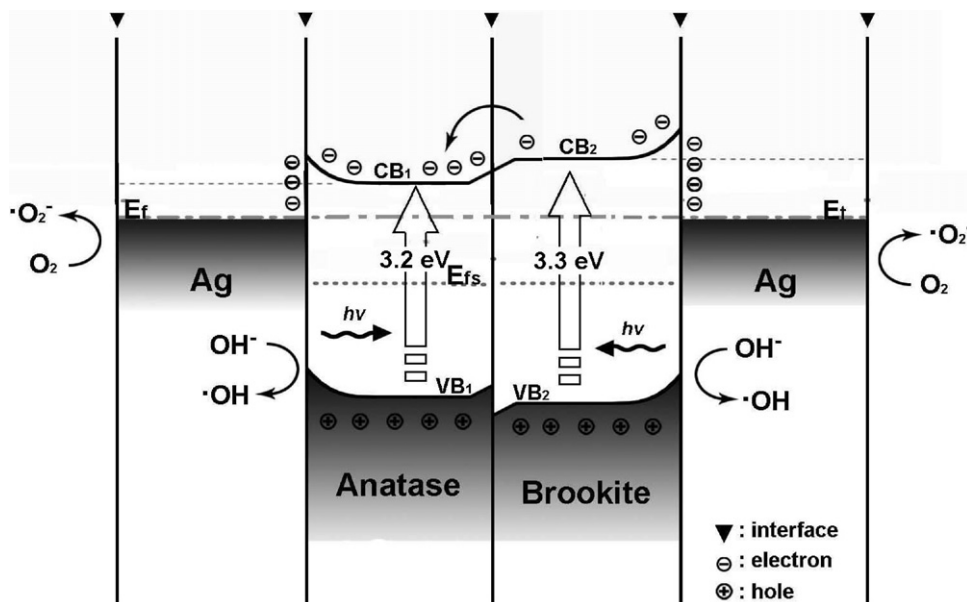


Fig. 6. Proposed mechanism for photogenerated electron transfer in Ag⁰-loaded anatase/brookite composite during the photocatalytic process.

and brookite were 0.0175 min⁻¹ and 0.0144 min⁻¹, respectively. Surface deposition of Ag⁰ further enhanced the reactivity of the catalysts. MO degradation reaction rate constant of the 2.0% Ag⁰-loaded brookite/anatase composite was increased to 0.1167 min⁻¹, while that of 2.0% Ag⁰-loaded pure anatase and brookite were 0.0650 min⁻¹ and 0.0821 min⁻¹, respectively.

3.3. Mechanism explanation for enhanced photocatalytic reactivity of the catalysts

Under the UV irradiation, either brookite or anatase TiO₂ is excited to produce photo-generated electrons and holes, which then carries out interfacial reactions to initiate the photocatalytic procedure. In a hetero-phase catalyst of brookite and anatase, charge transfer between the two phases should be also concerned [11,14]. As the photoelectron has much greater transport rate than that of photohole, the photo-generated electrons would quickly transfer from the conduction band (CB) of brookite to that of anatase and leave the holes behind. One may find that the valence band (VB) of anatase is higher than that of brookite, which means that the active photoholes in brookite also prefer to transport to the CB of anatase and evoke an e⁻-h⁺ recombination in anatase nanoparticles, which is adverse to an effective photocatalyst with high quantum efficiency. Nevertheless, a potential curve cliff, although limited, would play an important role in hindering the holes transfer from brookite to anatase along the potential curve (Fig. 6). Hence, photocatalyst of brookite/anatase composite exhibits a better photocatalytic performance than that of pure brookite and anatase, which is so-called synergistic effect [11] of hetero-junction in brookite/anatase composite.

Noble metals such as Ag⁰ have quite high electron affinities; hence, in the presence of Ag⁰ clusters, the photoelectrons on the CB of either brookite or anatase would spontaneously transfer to the deposited Ag⁰ clusters according to the schottky barrier at the interface of Ag⁰ and TiO₂ [15–18,29]. Consequently, the recombination of photogenerated electrons and holes are hindered more as they are separated into two different phases, TiO₂ and Ag⁰ cluster. Presumably, the electron transfer to Ag⁰ metal from brookite may more efficient than that from anatase to Ag⁰ metal because of its more potential schottky barrier at the interface (Fig. 6). Finally, the photoelectrons react with O₂ to produce superoxide radicals on

the surface of Ag⁰ clusters and the photoholes react with H₂O/OH⁻ to form •OH radicals on the surface of TiO₂. The very small size of Ag⁰ clusters of ca. 1.5 nm resulted from the special preparation method adopted in this work. The feature that highly dispersed Ag⁰ clusters intersperse throughout the entire surface of TiO₂ (Fig. 2c and d) endows high efficiencies of electron transfer from TiO₂ to Ag⁰, which enhances the photocatalytic reactivity of TiO₂ by 2.28 times (Fig. 4), a value higher than that reported in the literatures [12,23,24].

4. Conclusions

Ag⁰-loaded brookite/anatase composite was prepared via an alkaline hydrothermal process, which possesses significantly enhanced photocatalytic reactivity than that of pure TiO₂ and commercial P25 TiO₂. HRTEM analysis shows that as-formed Ag⁰ clusters have an average diameter of ca. 1.5 nm and intersperse throughout the surface of both anatase nanoparticles and brookite nanorods. Ag⁰ has an optimal loading dosage of 2.0 mol%, with which the photocatalytic degradation of MO is 2.28 more than that with P25 TiO₂. The enhanced photocatalytic reactivity of Ag⁰-loaded brookite/anatase composite is attributed to the significant improvement in separation of the photogenerated electrons and holes, which can be ascribed to two aspects: (1) synergistic effect of hetero-junction in brookite/anatase composite, and (2) the schottky barrier at the interface of Ag⁰ and TiO₂.

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References

- [1] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Chem. Rev. 95 (1995) 69–96.
- [2] T.L. Thompson, J.T. Yates, Chem. Rev. 106 (2006) 4428–4453.
- [3] A. Fujishima, T.N. Rao, D.A. Tryk, J. Photochem. Photobiol. C 1 (2000) 1–21.
- [4] M.Y. Xing, J.L. Zhang, F. Chen, B.Z. Tian, Chem. Commun. 47 (2011) 4947–4949.
- [5] F. Amano, T. Yasumoto, T. Shibayama, S. Uchida, B. Ohtani, Appl. Catal. B 89 (2009) 583–589.

- [6] R. Scotti, I.R. Bellobono, C. Canevali, C. Cannas, M. Catti, M. D'Arienzo, A. Musinu, S. Polizzi, M. Sommariva, A. Testino, F. Morazzoni, *Chem. Mater.* 20 (2008) 4051–4061.
- [7] B. Oregan, M. Gratzel, *Nature* 353 (1991) 737–740.
- [8] J.G. Li, T. Ishigaki, X.D. Sun, *J. Phys. Chem. C* 111 (2007) 4969–4976.
- [9] B. Zhao, F. Chen, Y.C. Jiao, J.L. Zhang, *J. Mater. Chem.* 20 (2011) 7990–7997.
- [10] K. Yanagisawa, J. Ovenstone, *J. Phys. Chem. B* 103 (1999) 7781–7787.
- [11] M.C. Yan, F. Chen, J.L. Zhang, M. Anpo, *J. Phys. Chem. B* 109 (2005) 8673–8678.
- [12] B. Zhao, F. Chen, Q.W. Huang, J.L. Zhang, *Chem. Commun.* 34 (2009) 5115–5117.
- [13] J.H. Zhang, X. Xiao, J.M. Nan, *J. Hazard. Mater.* 176 (2010) 617–622.
- [14] J.C. Yu, L. Zhang, J.G. Yu, *Chem. Mater.* 14 (2002) 4647–4653.
- [15] Y.M. Wu, H.B. Liu, J.L. Zhang, F. Chen, *J. Phys. Chem. C* 113 (2009) 14689–14695.
- [16] Y.H. Zheng, C.Q. Chen, Y.Y. Zhan, X.Y. Lin, Q. Zheng, K.M. Wei, J.F. Zhu, *J. Phys. Chem. C* 112 (2008) 10773–10777.
- [17] X.Z. Li, F.B. Li, *Environ. Sci. Technol.* 35 (2001) 2381–2387.
- [18] X.F. You, F. Chen, J.L. Zhang, M. Anpo, *Catal. Lett.* 102 (2005) 247.
- [19] V. Subramanian, E.E. Wolf, P.V. Kamat, *J. Am. Chem. Soc.* 126 (2004) 4943–4950.
- [20] Z.X. Yang, R.Q. Wu, D.W. Goodman, *Phys. Rev. B* 6 (2000) 14066–14071.
- [21] H. Zhang, G. Wang, D. Chen, X.J. Lv, J.H. Li, *Chem. Mater.* 20 (2008) 6543–6549.
- [22] Y.C. Jiao, B. Zhao, F. Chen, J.L. Zhang, *CrystEngComm* 13 (2011) 4167–4173.
- [23] V. Vamathevan, R. Amal, D. Beydoun, G. Low, S. McEvoy, *J. Photochem. Photobiol. A* 148 (2002) 233–245.
- [24] J.X. Li, J.H. Xu, W.L. Dai, K.N. Fan, *J. Phys. Chem. C* 113 (2009) 8343–8349.
- [25] H.Z. Zhang, J.F. Banfield, *J. Phys. Chem. B* 104 (2000) 3481–3487.
- [26] H.E. Chao, Y.U. Yun, H.U. Xingfang, A. Larbot, *J. Eur. Ceram. Soc.* 23 (2003) 1457–1464.
- [27] J. García-Serrano, E. Gómez-Hernández, M. Ocampo-Fernández, U. Palc, *Curr. Appl. Phys.* 9 (2009) 1097–1105.
- [28] Wash-off process for Ag^0 cluster in catalysts: $\text{K}_3[\text{Fe}(\text{SCN})_6]$ of 0.1 g was dissolved into 50 mL water. Ag_0 -loaded catalyst of 0.5 g was dispersed into another 50 mL water under stirring. Then the as-prepared $\text{K}_3[\text{Fe}(\text{SCN})_6]$ solution was added into the catalyst suspension. After an interval of 30 min, 1.5 mL aqueous ammonia was added into the suspension under stirring. Kept stirring for ca. 1.5 h, the suspension was then filtered and carefully washed with water to obtain the final Ag^0 -free powder and dried at 80 °C for 24 h.
- [29] A. Sclafani, M.N. Mozzanege, J.M. Herrmann, *J. Catal.* 168 (1997) 117.