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Ag^0-loaded brookite/anatase composite with enhanced photocatalytic performance towards the degradation of methyl orange

Bin Zhao[a,b], Feng Chen[a,*], Yanchao Jiao[a], Hongyun Yang[a], Jinlong Zhang[a]

[a] Laboratory for Advanced Materials and Institute of Fine Chemicals, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, PR China
[b] National Engineering Research Center for Nanotechnology, 28 East Jiangchuan Road, Shanghai 200241, PR China

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ABSTRACT

Ag^0-loaded brookite/anatase composite was prepared via an alkalescent 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 TiO_2 can be controlled by fixing the concentration of the electrolyte in the hydrothermal system. The as-formed Ag^0 clusters have an average diameter of ca. 1.5 nm and intersperse throughout the surface of both anatase nanoparticles and brookite nanorods. Ag^0 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 Ag^0-free composite and P25 TiO_2, respectively. The synergistic effect of hetero-junction in brookite/anatase composite and the schottky barrier at the interface of Ag^0 and TiO_2 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.

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 TiO_2, however, depends upon its physical features [5–8] such as the grain size, morphology, specific surface area, as well as the crystal structure. TiO_2 exists mainly in three crystalline polymorphs: anatase ($I4_1/amd$), rutile ($P4_2/mnm$) 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 TiO_2 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 photocatalytic 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 TiO_2 grains can also act as traps to reduce the recombination of photogenerated electrons and holes, and hence promote the photocatalytic activity of TiO_2 [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–TiO_2 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 TiO_2 exhibited higher photocatalytic reactivity than anatase [12], while the crystal phase of the TiO_2 products was precisely controlled from tetrabutyl titanate (TBOT) with an alkalescent hydrothermal method [9]. Insight into the formation of TiO_2 in alkalescent hydrothermal media showed that TiO_2 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 Ag^0-loaded TiO_2 reported in the literatures [21,23,24]. Unfortunately, the photocatalytic activity improvement of TiO_2 from Ag^0 clusters is found to be limited [21,23], which is

* Corresponding author. Fax: +86 21 64252062.
E-mail addresses: zhaobinwily@163.com (B. Zhao), fengchen@ecust.edu.cn (F. Chen), jiaojj@126.com (Y. Jiao), yanghongyun001@163.com (H. Yang), jlzhang@ecust.edu.cn (J. Zhang).

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ascribed to the fact that photoreduced Ag cannot be highly dispersed on the surface of TiO_2, and thus fails to markedly increase the amount of active sites on the Ag–TiO_2 surface. In this work, $AgNO_3$ was pre-mixed with titanium precursor before hydrothermal treatment. Noble metal Ag^0 loaded brookite/anatase composite with enhanced photocatalytic performance is thus prepared via an alkalescent hydrothermal process. According to its particular formation process, the Ag^0 clusters in the composite in this work were formed in situ on the surface defect sites of TiO_2 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 $NH_3{\cdot}H_2O$ (25–28%) were obtained from Ling Feng Chemical Reagent. $AgNO_3$, $NaNO_3$ 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 Ag^0-loaded TiO_2 was carried out according to the alkalescent hydrothermal procedures reported in our previous works [9,22]: a certain amount of $NaNO_3$ and $AgNO_3$ was dissolved into aqueous ammonia ($NH_3{\cdot}H_2O$). 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*% Ag^0–TiO_2" (*x*% is mole percentage ratio of Ag/Ti).

2.3. Catalyst characterization

Samples of Ag^0-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° $2\theta\,s^{-1}$. 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 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).

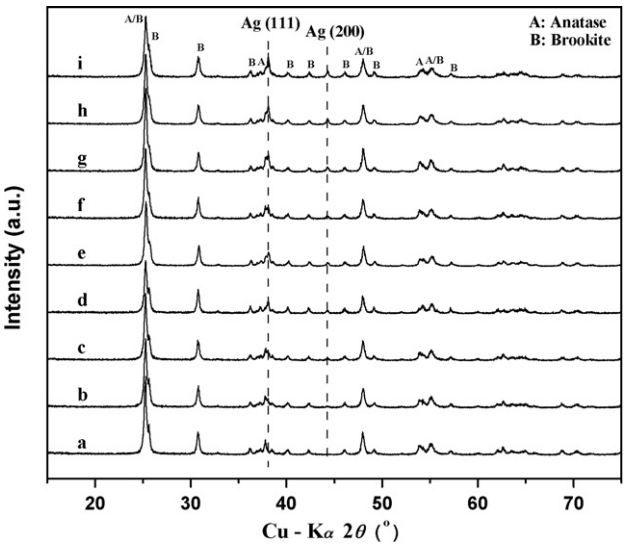

Fig. 1. XRD patterns of the Ag^0–TiO_2 composites with Ag^0 mol% of 0.0% (a), 0.5% (b), 1.0% (c), 1.5% (d), 2.0% (e), 2.5% (f), 3.0% (g), 4.0% (h) and 5.0% (i).

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 $Na_{2-x}(NH_4)_xTi_2O_5{\cdot}H_2O$ 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 (1 0 1) and A_B refers to the integrity intensity of brookite (1 2 1), K_A and K_B are constants of 0.886 and 2.721, respectively. The average grain size