Cu-doped TiO₂ brookite photocatalyst with enhanced visible light photocatalytic activity

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Cu-doped TiO₂ having a brookite phase and showing enhanced visible light photocatalytic activity was synthesized using a mild solvothermal method. The as-prepared samples were characterized by various techniques, such as X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy, transmission electron microscopy, X-ray photoelectron spectroscopy, UV-Vis diffuse reflectance spectroscopy. Photocatalytic activity of Cu-doped brookite TiO₂ nanoparticles was evaluated by photodegradation of methylene blue under visible light irradiation. The X-ray diffraction analysis showed that the crystallite size of Cu-doped brookite TiO₂ samples decreased with the increase of Cu concentration in the samples. The UV-Vis diffuse reflectance spectroscopy analysis of the Cu-doped TiO₂ samples showed a shift to lower energy levels in the band gap compared with that of bare phase brookite TiO₂. Cu doped brookite TiO₂ can obviously improve its visible light photocatalytic activity because of Cu ions acting as electron acceptors and inhibiting electron-hole recombination. The brookite TiO₂ sample with 7.0 wt.% Cu showed the highest photocatalytic activity and the corresponding degradation rate of MB (10 mg/L) reached to 87 % after visible light illumination for 120 min, much higher than that of bare brookite TiO₂ prepared under the same conditions (78 %).

Keywords: TiO₂; brookite; copper; solvothermal method; photocatalytic activity

1. Introduction

Titanium dioxide (TiO₂), a kind of semiconductor material with excellent photoelectric properties, has been widely used in various areas, such as solar energy conversion [1], lithium ion batteries [2], photocatalysis [3], sensors [4], and so on. However, the photocatalytic application of TiO₂ has been significantly limited due to its wide band gap and high electron-hole recombination rate. In order to enhance the photocatalytic activity of TiO₂, several methods have been developed such as coupling of TiO₂ particles with other semiconductor particles, and doping of metals and non-metals [5, 6]. Choi et al. [7] reported that a dopant ion acted as an electron trap or hole trap, which would prolong the life-time of the generated charge carriers, resulting in an enhancement in photocatalytic activity. Transition metals exhibit two or more oxidation

states that enable the enhancement of the photocatalytic activity of TiO₂ when doped with transition metals [8, 9]. Doping with transition metal ions have been reported to change physical properties of TiO₂ crystals, such as lifetime of electron-hole pairs and adsorption characteristics [10], which can also tune the optical band gap, thus shifting the light absorption region from UV to visible light [6, 11]. Wilke and Breuer [10] studied the complex interactions between variation in lifetime of charge carriers, adsorption properties and photocatalytic behavior by doping titania with Cr³⁺ and Mo⁵⁺ ions, and they found that new trapping sites were introduced by incorporation of transition metal ions which affected the lifetime of the charge carriers. Many other transition metals, such as copper (Cu) [11, 12], cobalt (Co) [13], vanadium (V) [14], tungsten (W) [15], and iron (Fe) [16], have been also used as doping agents to improve the photocatalytic performance of TiO₂ catalysts.

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TiO₂ exists in three main crystalline polymorphs: rutile (tetragonal, space group P4₂/mm), anatase (tetragonal, space group I4₁/amd) and brookite (orthorhombic, space group Pbca) [17–19]. Among the above TiO₂ polymorphs, brookite TiO₂ was reported to be a good ingredient for photovoltaic devices and it has the highest photocatalytic activity per surface area among TiO₂ polymorphs. Though it is more difficult to prepare bare brookite TiO₂ than other polymorphs, several methods have been developed to prepare bare brookite TiO₂ during the past ten years, and much more understanding related to the preparation and properties of brookite TiO₂ has been achieved [20–25]. Further research works show that brookite TiO₂ catalysts with enhanced photocatalytic activity can also be obtained by improving specific surface area [26] or doping with transition metals ions [27, 28], noble metals [29, 30] and lanthanides [31, 32].

In the present study, brookite TiO₂ nanoparticles doped with copper ions were synthesized by solvothermal method using tetrabutyl titanate (Ti(OC₄H₉)₄, TBOT), oxalic acid, NaOH and copper nitrate (Cu(NO₃)₂·3H₂O) as starting materials. XRD, FT-IR, SEM, TEM, XPS and UV-Vis (DRS) were employed to characterize the structure and morphology of the samples. Photocatalytic activities of Cu-doped brookite TiO₂ were evaluated by photodegradation of liquid methylene blue (MB) under visible light irradiation.

2. Experimental

2.1. Materials

Tetrabutyl titanate (Ti(OC₄H₉)₄, TBOT) of analytical grade, oxalic acid (H₂C₂O₄·2H₂O), and copper nitrate (Cu(NO₃)₂·3H₂O) were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. Analytical grade sodium hydroxide (NaOH), N,N-dimethylformamide (DMF), and absolute ethanol were purchased from Kewei Company of the Tianjin University. All chemicals were directly used without further purification.

2.2. Synthesis of Cu-doped brookite TiO₂ nanoparticles

The preparation method of Cu-doped brookite TiO₂ is similar to that of bare brookite TiO₂, which has been reported in our previous work [33]. To prepare Cu-doped brookite TiO₂, 1.0 mL of TBOT was first added drop by drop under vigorous stirring into 50 mL of DMF solution containing a certain amount of copper nitrate. Then 1.50 g oxalic acid was slowly added into the above mixture and a yellow transparent solution was obtained. The pH value of the resulted solution was adjusted to 9–10 using 2.0 mol·L^{−1} NaOH during this process. After stirring for another 1 h, the resulting suspension was transferred to a 100 mL Teflon-lined stainless steel autoclave and heated at 180 °C for 8 h in an electric oven. After slowly being cooled down to room temperature, the white precipitate was collected by centrifugation and washed with distilled water and absolute ethanol for several times, and then dried at 80 °C overnight. Finally, the obtained samples were calcined at 500 °C for 2 h.

To investigate the effect of Cu doping concentration on the structure and photocatalytic activity of brookite TiO₂, a series of brookite TiO₂ containing different percentage by weight of Cu (1.0 wt.%, 3.0 wt.%, 5.0 wt.%, 7.0 wt.%, 10.0 wt.%) were prepared.

2.3. Characterization

The structure and crystallinity of the Cu-doped brookite TiO₂ were analyzed by powder X-ray diffraction (XRD) on a DX-2700BH X-ray diffractometer using CuKα radiation as the X-ray source. The accelerating voltage and the applied current were 35 kV and 25 mA, respectively. The crystallite sizes of the samples were estimated by the Scherrer equation:

$$D = K\lambda / \beta \cos \theta \quad (1)$$

where D is the crystallite size, K = 0.89 is a coefficient, β is the half-height width of the diffraction peak, θ is the diffraction angle, and λ is the wavelength of X-ray in nanometers corresponding to the CuKα irradiation. The morphology and microstructure of the prepared samples

were examined by field emission scanning electron microscope (Hitachi, S-4800) and transmission electron microscope (JEM, 2100F). The FT-IR spectra of the Cu-doped brookite TiO_2 were obtained by AVATAR330 Fourier transform infrared spectroscopy (Thermo Nicolet, US) using KBr pressed discs method. X-ray photoelectron spectroscopy (XPS) was recorded on a Thermo SCIENTIFIC ESCALAB 250XI X-ray photoelectron spectrometer with an $\text{AlK}\alpha$ source (1486.8 eV). The shift of binding energy due to relative surface charging was corrected using the C 1s level at 284.8 eV as an internal standard. The UV-Vis diffuse reflectance spectra were recorded using a UV-Vis spectrophotometer (UV-2600, Shimadzu, Japan) and then converted into absorption spectra via the Kubelka-Munk transformation.

photodegradation of liquid methylene blue (MB). A Xenon lamp (HXS-F/UV 300, Beijing NBet Technology Co., Ltd.) was used as a light source. To provide only visible light, a glass optical filter was used to cut off the UV light with wavelength below 420 nm. In a typical photoactivity measurement reaction, 15 mg of the catalyst was added to 75 mL of aqueous MB solution (10 mg/L). For establishment of the adsorption/desorption equilibrium between the catalyst and substrate (MB), the suspension was magnetically stirred for 30 min before the start of illumination. Samples were collected periodically and centrifuged, and the concentration of MB solution was analyzed by recording variations in the absorption in UV-Vis spectra of MB using an UV-Vis spectrophotometer (Shimadzu UV-1240). According to the standard curve of concentration and absorption, the value of C/C_0 was calculated to measure the degradation efficiency [34].

3. Results and discussion

3.1. XRD analysis

XRD pattern of Cu-doped brookite TiO_2 crystallites is shown in Fig. 1. Characteristic peaks at 25.3° , 30.7° , 40.1° , 48.0° , 55.2° , 64.5° , 70.5° representing the crystal planes for (1 2 0), (1 2 1), (0 2 2), (2 3 1), (2 4 1), (2 5 1) and (3 3 2) can be observed in Fig. 1a, which are identical to the standard card of brookite TiO_2 (JCPDS Card No. 12-1360). There have no peaks appeared showing the presence of CuO when the dosage of Cu is below 7.0 wt.%, suggesting that no new phase related to CuO has been formed or CuO has been formed and exists as amorphous phase. However, two weak peaks can be observed at 35.5° and 38.7° , which are identified as copper oxide (45-1548) when the dosage of Cu is 10.0 wt.%.

It can be concluded that CuO is formed on the surface of TiO_2 because the diffraction peak shape of brookite TiO_2 is almost unchanged. A detailed XRD pattern of the samples with the Cu dosage below 7.0 wt.% at $2\theta = 20^\circ$ to 35° has been shown in Fig. 1b. A small red shift of the diffraction peaks of Cu doped brookite TiO_2 compared to

Fig. 1. XRD patterns of brookite TiO_2 with different copper loadings.

2.4. Photocatalytic activity test

The photocatalytic activity of Cu-doped brookite TiO_2 nanoparticles was evaluated by

that of bare phase brookite TiO₂ can be observed in Fig. 1b, suggesting that Cu atoms incorporated into the TiO₂ lattice either moved to the substitutional sites in the TiO₂ lattice or to the octahedral interstitial sites [8]. The incorporation of Cu atoms into TiO₂ or the formation of solid solution can result in smaller lattice spacing of TiO₂, which is observed in the XRD pattern as a red shift.

3.2. Fourier transform infrared spectroscopy (FT-IR)

In order to further confirm the bonding in the composition, FT-IR spectra were taken for the doped TiO₂ nanoparticles with different copper loadings as shown in Fig. 2. In the spectra, the broad absorption band between 3600 cm⁻¹ and 3300 cm⁻¹ is ascribed to the stretching vibrations of water, and the absorption band between 1660 cm⁻¹ and 1630 cm⁻¹ is ascribed to the stretching vibrations of crystallization water [35, 36].

Fig. 2. FT-IR spectra of brookite TiO₂ with different copper loadings.

The broad absorption band between 3600 cm⁻¹ and 3300 cm⁻¹ for the brookite TiO₂ sample with 7.0 wt.% Cu was found to be higher than those for other samples, indicating that the former had more surface hydroxyl groups. It is well-known that the TiO₂ superficial hydroxyl group plays an important role in photocatalytic activity [37]. Moreover, the broad absorption band between 400 cm⁻¹ and 800 cm⁻¹ is attributed to the vibration

absorption of the Ti–O–Ti linkages in TiO₂ nanoparticles [38, 39].

3.3. SEM and TEM analysis

The morphologies of the bare brookite TiO₂ and doped brookite TiO₂ powders with different concentrations of copper were investigated by scanning electron microscopy (SEM) and transmission electronic microscopy (TEM) as shown in Fig. 3. It can be observed in Fig. 3a to Fig. 3f that all the samples exhibit quasi-spherical structures, which are composed of a large number of nanoparticles. No significant changes can be observed in the morphology of brookite TiO₂ doped with different concentrations of Cu.

The average crystallite size of the quasi-spherical structures decreases with the increase of Cu-doping concentration, which is consistent with the result of XRD analysis. Fig. 3g is the TEM image of brookite TiO₂ doped with 7.0 wt.% Cu, showing that the quasi-spherical structures are composed of many smaller particles.

3.4. XPS analysis

The incorporation of copper into the TiO₂ lattice and its valence states were measured by XPS technique. Fig. 4a shows an overview XPS spectra for the bare brookite TiO₂ and the brookite TiO₂ sample doped with 7.0 wt.% Cu. The peaks of Ti 2p, O 1s, and C 1s can be observed in both of the samples. The Cu 2p peaks can also be observed in the full-range XPS survey spectrum of the brookite TiO₂ sample doped with 7.0 wt.% Cu in addition to the Ti 2p, O 1s and C 1s peaks, which is agreement with the result reported by Li et al. [40]. The Ti 2p_{1/2} and Ti 2p_{3/2} spin-orbital splitting photoelectrons for both samples are located at binding energies of 458.3 eV and 464.1 eV, respectively, as seen in Fig. 4b, which are comparable with those of 458.5 eV and 464.3 eV reported previously in the literature [41]. Both Ti 2p signals are highly symmetric, and no shoulders are observed on the lower energy side of Ti 2p_{3/2} signal. The binding energy splitting of Ti 2p is 5.65 eV, which agrees well with the result for Ti⁴⁺ ions in TiO₂ [27]. The FWHM of the Ti 2p_{3/2} signal for the brookite TiO₂

Fig. 3. SEM and TEM images of brookite TiO_2 with different copper loadings: (a) bare brookite TiO_2 and brookite doped with Cu (b) 1.0 wt.%, (c) 3.0 wt.%, (d) 5.0 wt.%, (e) and (g) 7.0 wt.%, (f) 10.0 wt.%.

sample with 7.0 wt.% Cu is slightly larger than that for the bare one, which is due to the existence of multiple Ti species and strong electronic interaction between Cu and Ti in the nanocomposites [42]. Fig. 4c shows the high resolution XPS spectra of O 1s for the brookite TiO_2 sample with 7.0 wt.% Cu. The broad and asymmetric peak of O 1s was partitioned into two peaks, 529.4 eV and 530.3 eV (Fig. 4c). The binding energy peak at 530.3 eV can be attributed to the O–Ti bonding of TiO_2 according to the literature [40]. However, the binding energy peak at 530.3 eV can be attributed to both brookite TiO_2 [41] and CuO, because the binding energy peak of CuO is also at 529.6 eV according to the report by Moralesa et al. [43]. Fig. 4d shows the Cu 2p core-level XPS spectrum of the brookite TiO_2 sample with 7.0 wt.% Cu. The Cu 2p level was resolved into Cu $2p_{1/2}$ in the range of 952.1 to 954.3 eV (broad peak) and Cu $2p_{3/2}$ in the range of 932.3 eV to 934.3 eV, corresponding to the typical values of the Cu^0 , Cu^{1+} and Cu^{2+} copper species, respectively [12, 43]. Moreover, the presence of copper in the Cu^{2+} oxidation state can be

identified because of the presence of the characteristic shake-up satellite lines of CuO at about 942 eV and 962 eV, which are attributed to shake-up transitions by a ligand-metal 3d charge transfer [40, 43, 44]. Moreover, the Cu $2p_{1/2}$ and $2p_{3/2}$ peaks are relatively broad and seem to be influenced by the presence of TiO_2 .

3.5. UV-Vis diffuse reflectance spectroscopy (UV-Vis DRS)

The bandgap energy of the samples could be estimated using a UV-Vis diffuse reflectance spectrum (DRS). Fig. 5a shows the UV-Vis absorption spectra of the bare brookite TiO_2 and Cu-doped brookite TiO_2 samples. A red shift in the absorption edge of the Cu-doped brookite TiO_2 can be observed compared to the bare brookite TiO_2 . By plotting the square root of the absorption coefficient of the material versus energy, the band gap of the particles can be determined by extrapolating the linear region of the plot to zero, as shown in Fig. 5b to Fig. 5f. The band gap of the bare brookite TiO_2 and doped brookite TiO_2 samples with

Fig. 4. XPS spectra of the bare brookite TiO₂ and 7.0 wt.% Cu-doped brookite TiO₂: (a) survey spectra; (b) Ti 2p; (c) O 1s; (d) Cu 2p.

the increase of Cu doping concentration from 1.0 wt.% to 10.0 wt.% was calculated to be 3.330 eV, 3.313 eV, 3.203 eV, 3.216 eV, 3.186 eV and 3.292 eV, respectively. It can be observed that the band gap value of brookite TiO₂ decreases due to doping with Cu ions and the band gap of the brookite TiO₂ with 7.0 wt.% Cu is the narrowest. Choi et al. [45] studied the role of metal ion dopants in quantum sized TiO₂ and proposed that there was an optimal concentration of metal ions used as doping agents.

Here, 7.0 wt.% is supposed to be the optimal concentration of Cu to improve the band gap of brookite TiO₂. The band gap of brookite TiO₂ is narrowed by incorporation of Cu ions, which confirms that a portion of Cu ions doped into the TiO₂ lattice alters the energy gap and causes an extension of TiO₂ absorption into the visible region. These results are in agreement with the previous reports that a redshift of the absorption edge of TiO₂ can be obtained by doping with transition metal ions [6, 10]. However, an opposite result has also been reported by Rajamannan et al. [46]. They studied the liner and nonlinear optical properties of Cu-doped anatase TiO₂ and achieved a completely different conclusion that the indirect band gap of TiO₂ increased gradually with the increase of Cu doping concentration. Therefore, the effect of Cu ions on the band gap of TiO₂ needs further study in the following work.

3.6. Photocatalytic performance evaluation

The visible-light photocatalytic activity of Cu-doped brookite TiO₂ catalysts was evaluated by using methylene blue (MB, 10 mg/L) as a probe molecule under visible light irradiation, as shown in Fig. 6. The degradation efficiency of the catalyst (C/C_0) plotted against the irradiation time (t) is shown in the Fig. 6a for the bare TiO₂ and Cu-doped brookite TiO₂ samples. Low decolorization efficiency of MB (<10 %) is observed after 30 min dark adsorption. However, when the light is on, all the photocatalysts exhibit high photocatalytic activity in the degradation of MB under visible light irradiation. The brookite TiO₂ sample doped

Fig. 5. (a) UV-Vis absorption spectra of the bare brookite TiO_2 and Cu-doped brookite TiO_2 ; (b-f) Kubelka-Munk plots of band gap energy for Cu-doped TiO_2 nanoparticles.

with 7.0 wt.% Cu shows the highest decolorization efficiency of 87 % after 120 min of visible light irradiation, which is higher than that of bare brookite TiO_2 (78 %) and other brookite TiO_2 samples doped with 1.0 wt.% Cu (81 %), 3.0 wt.% Cu (80 %), 5.0 wt.% Cu (81 %), and 10.0 wt.% Cu (84 %). Fig. 6b shows the kinetic curves of photocatalytic reaction for the bare brookite TiO_2

and Cu-doped brookite TiO_2 samples, and the kinetic constant (k) is 0.00951 (bare brookite TiO_2), 0.01322 (1.0 wt.% Cu), 0.01223 (3.0 wt.% Cu), 0.01243 (5.0 wt.% Cu), 0.01608 (7.0 wt.%), and 0.0141 (10.0 wt.% Cu), respectively. As shown in Fig. 6b, the brookite TiO_2 sample doped with 7.0 wt.% Cu shows the biggest value of kinetic constant k , which indicates that this sample shows

the highest photocatalytic activity. According to the FT-IR results, the doped brookite TiO₂ sample with 7.0 wt.% Cu has more superficial hydroxyl group than other samples, which plays an important role in photocatalytic activity [37]. Furthermore, the incorporation of Cu ions into brookite TiO₂ crystal lattice improves the visible light response ability by narrowing the band gap of brookite TiO₂, which also changes the electron transfer pathway, inhibiting electron-hole recombination. That's to say that interfacial charge-transfer excitation of electrons in the valence band of TiO₂ to copper ions can proceed, which inhibits electron-hole recombination [47]. Eshaghi et al. [27] investigated the effect of Cu loading on the surface properties of brookite TiO₂ thin films and found that Cu ions behaved as electron acceptors under UV light irradiation, which improved the photoreactivity of titania by inhibiting electron-hole recombination. A similar result has also been obtained by López et al [12] who reported Cu ions as electron captor inducing a low electron-hole recombination.

Moreover, it can also be observed in Fig. 6a that the photocatalytic degradation rate of MB increased first and then decreased with the increase of Cu doping concentration, showing that copper ions can behave as electron captor when the Cu doping concentration is lower (below 7.0 wt.% under our experimental conditions). The copper ions can also move into electron-hole recombination sites with excessive Cu doping concentration, which inhibits the photocatalytic reaction and results in low photocatalytic degradation rate. Di Paola et al. [32] reported that there was an optimum degree of loading at which photoactivity was maximum. When the doping level is low, the surface barrier becomes higher and the space charge region becomes narrower as the concentration of loading ions increases, resulting in an increase of the efficiency of electron-hole separation and an enhancement of the photocatalytic properties [48]. However, when the doping level is beyond a certain value, the space charge layer becomes very narrow and the penetration depth of light exceeds the space charge layer, resulting in the recombination of the electron-hole pairs and a decrease in the photocatalytic properties.

Fig. 6. Photocatalytic conversion of MB under visible light irradiation ($\lambda = 420$ nm) and first-order kinetics for the MB photodegradation on the Cu-doped TiO₂.

4. Conclusions

In this study, Cu-doped brookite TiO₂ photocatalysts were prepared using a facile solvothermal method and evaluated in terms of performance by the degradation of MB aqueous solution under visible-light irradiation. Experimental results indicated that quasi-spherical brookite TiO₂ structures accompanied with a large number of nanoparticles, were obtained under solvothermal condition at 180 °C for 8 h. The doping of Cu has little effect on the structure of brookite TiO₂ samples, while the crystal size of the samples was decreased with the increase of the concentration of Cu in the samples. Photocatalytic test showed that 7.0 wt.% Cu-doped brookite TiO₂ revealed the highest photocatalytic activity under visible light irradiation, and the corresponding degradation rate

of methylene blue ($10 \text{ mg}\cdot\text{L}^{-1}$) reached to 87 % after visible light illumination for 120 min. Copper ions act as electron acceptors and induce a low electron-hole recombination. As a result, higher photocatalytic activity of Cu-doped brookite TiO_2 has been obtained than that of bare brookite TiO_2 under visible light irradiation.

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