Defect-mediated of Cu@TiO₂ core–shell nanoparticles with oxygen vacancies for photocatalytic degradation 2,4-DCP under visible light irradiation

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A B S T R A C T
Cu@TiO₂ core–shell nanoparticles with different mass ratios of Cu to TiO₂ were facilely synthesized via wet chemical approaches, and were characterized by transmission electron microscopy, scanning electron microscopy, UV–vis diffuse reflection absorption spectroscopy, X-ray photoelectron spectroscopy and electron paramagnetic resonance. The photocatalytic efficiency of Cu@TiO₂ nanoparticles was evaluated by degradation of 2,4-dichlorophenol, a typical persistent organic pollutant, under visible light irradiation. The results show that the oxygen vacancy creation obviously enhances the visible-light absorption of TiO₂. Meanwhile, the Cu nanoparticle incorporation into the TiO₂ can effectively improve charge-separation efficiency of Cu@TiO₂ under visible-light irradiation, thereby enhancing the photocactivity.

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1. Introduction

As one of the most promising photocatalysts, TiO₂ has attracted significant attention due to its high photocatalytic activity, non-toxicity, physical and chemical stability. However, the high rate of photogenerated charge carriers recombination and the large band gap of TiO₂ result in the low quantum efficiency of photocatalytic reactions and the ineffective utilization of visible light or sunlight for TiO₂ which limit its usage in the visible light region [1–5]. It is known that couple noble metal with TiO₂ can greatly enhance the overall photocatalytic activity. Especially, heterostructures with metal core and TiO₂ shell not only have controllable chemical and colloidal stability within the shell but also charge effectively transfer between noble metal cores and TiO₂ [6,7]. Among all metals, copper as an important class of metal nanostructures has been increasingly studied due to its unusual properties and potential applications in thermal conducting, nanofluids and catalysts [8]. Compared to silver and gold, Cu behaves low price and stability at high frequencies, high-purity, uniformly shape and

nanostructured, thus, Cu is highly desirable for use in microelectronics and catalysis [9–13].

Herein, we report for the first time on a new photocatalyst composed of Cu@TiO₂ core–shell nanoparticles, i.e., TiO₂ particles wrapped on copper nanoparticles. To assess the activity of the core–shell nanostructured photocatalyst, comparative studies on photodegradation of 2,4-dichlorophenol (DCP), a typical persistent organic pollutant, at core–shell nanostructured Cu@TiO₂ and its counter parts were conducted. Changing the concentration of CuCl₂ solution in the process of preparing Cu nanoparticles can tune the visible light responsibility of Cu@TiO₂. Moreover, the uniqueness of Cu@TiO₂ lies in the controllable chemical stability and effective charge transfer between Cu core and TiO₂ shell. In addition, the shell of TiO₂ can protect Cu against oxidation.

2. Experimental

2.1. Preparation of nanosized copper particles

Cu@TiO₂ samples were synthesized by a wet chemical approach. Cu nanoparticles were prepared by following a protocol developed by Xiong et al. [14]. 50 mL L-ascorbic acid aqueous solution (0.6 M) was added dropped into the CuCl₂·2H₂O solution (4.75 mM, 50 mL)
in an oil bath at 80 °C under magnetic stirring. Cu precipitates were obtained after 16 h reaction, then, separated by centrifugation, washed with absolute ethyl alcohol for three times.

2.2. Synthesis of Cu-core/TiO₂-shell nanoparticles

The wet Cu was dispersed into 50 mL of ethanol by ultrasonic treatment, and followed by dropwise addition of 118 mL of 0.03 M Ti(OBu)₄ ethanol solution under stirring. After 2 h, 116.5 mL mixed solution of water and absolute ethyl alcohol (volume ratio of water/absolute ethyl alcohol was 0.11) was dropped into the mixture, and the reaction was kept stirring at 300 rpm for another 2 h. The resulted composites were centrifuged, washed thoroughly with absolute ethanol and deionized water in sequence then dried at room temperature. As characterized below, the composite material thus prepared consists of mostly core–shell nanoparticles. Using the same protocol, a series of samples were prepared by changing the concentration of added CuCl₂ solution. The actual mass ratio of TiO₂ to Cu in Cu@TiO₂ composites under different concentrations of CuCl₂ was determined by atomic absorption spectroscopy. In the present work, Samples with mass ratios of 1.53%, 1.27%, 1.07%, 0.86% and 0.49% were prepared, and they are denoted as Cu@TiO₂-A, Cu@TiO₂-B, Cu@TiO₂-C, Cu@TiO₂-D and Cu@TiO₂-E, respectively.

2.3. Characterization

The morphology of the Cu and Cu@TiO₂ nanostructures were observed using ZEISS SUPRA55VP scanning electron microscope (SEM). The microstructure of the Cu and Cu@TiO₂ nanostructures were studied with a HITACHI H-600 transmission electron microscope (TEM). UV–vis diffuse reflectance (DRS) of the samples was recorded by a Thermo Scientific Evolution 220 spectrometer. Electron paramagnetic resonance (EPR) spectra were recorded on a Bruker Elexsys E500 spectrometer. Surface composition analysis of Cu@TiO₂ was recorded using an ESCALAB Mark II X-ray photoelectron spectroscopy (XPS). The reactor was illuminated by a 350 W Xe lamp equipped with an ultraviolet cut-off filter (>400 nm). The intensity of the light on sample system was measured to be 0.068 W/cm² by using a spectroradiometer. 2,4-dichlorophenol was sampled and the absorbance change at 282 nm was monitored using UV–vis spectroscopy (Shimadzu UV-1800).

3. Results and discussion

3.1. Characterization of the copper particles

Fig. 1 shows the time evolution of the UV–vis absorption spectra during the time course of preparation. Initially, no characteristic absorption peak is observed. After 2 h, the absorption peak around 320 nm emerges which was induced by the oxidation product of l-ascorbic. With the reaction progressing, the absorption peak gets intense, and a second peak with comparable intensity shows up. The second peak is significantly red-shifted due to the growth of copper nanoparticles [15,16]. The whole synthesis process (including reduction reaction and Cu nanoparticles growth) was completed within 14 h as indicated by the fact that the UV–vis absorption spectra recorded after 14 h and 16 h are overlapped.

As shown in Fig. 2, the EDS spectrum only exhibits the characteristic peaks of Cu which means that the obtained product is composed of pure Cu.

3.2. Characterization of the Cu@TiO₂ nanoparticles

XRD patterns of the prepared Cu nanoparticles and Cu@TiO₂ products were shown in Fig. 3. High crystallinity is confirmed by the strong diffraction peaks. The diffraction peaks at 43.0, 50.1 and 74.4 are indexed to (1 1 1), (2 0 0) and (2 2 0) planes, respectively, which match well with the standard pattern of copper (JCPDS No. 03-1015). It is obvious that the Cu@TiO₂ nanocomposites with different Cu loadings exhibit similar XRD patterns. The peaks at 2θ values of 25.3, 37.8, 48.0, 53.9, 55.1, 62.7, 68.8, 70.3, and 75.0 can be indexed to (1 0 1), (0 0 4), (2 0 0), (1 0 5), (2 1 1), (2 0 4), (1 1 6), (2 2 0), and (2 1 5) crystal planes of anatase TiO₂ (JCPDS file: 010562), respectively. No typical diffraction peaks belonging to the Cu are observed in the Cu@TiO₂ core–shell nanocomposites. The reason
can be ascribed to the even distribution and low weight loading of metal nanoparticles in the TiO$_2$.

Fig. 4a and b shows the SEM and TEM images of the Cu and Cu@TiO$_2$ samples as synthesized above. Both particles are in well-defined spherical shape. The average diameter of the Cu@TiO$_2$ composite particles is about 458 nm, while Cu core is about 375 nm and the TiO$_2$ shell is about 83 nm. Pure Cu nanoparticles before coupling with TiO$_2$ are basically solid sphere as shown in Fig. 4c.

Fig. 4. SEM (a) and TEM (c) images of Cu nanoparticles; (b) and (d) are SEM and TEM images of the prepared Cu@TiO$_2$ nanoparticles with mass ratio of 1.07% (TiO$_2$ : Cu).

Fig. 5. XPS spectra of Ti 2p (a) and O 1s (b) in TiO$_2$ nanoparticles, and Ti 2p (c), O 1s (d), Cu 2p (e) in the Cu@TiO$_2$ nanoparticles.
The contrast between dark center and gray edge with the thickness is observed in Fig. 4d. This indicates that the Cu nanoparticles were successfully coated with the TiO₂ and further confirmed the formation of core–shell structure.

To investigate the chemical states of the elements in TiO₂ and Cu@TiO₂ samples, Ti 2p, O 1s and Cu 2p core levels were measured by XPS, and the results are presented in Fig. 5. As shown in Fig. 5a and b, for bare TiO₂, the XPS peaks of Ti 2p, Ti 2p1/2 (464.5 eV) and Ti 2p3/2 (458.3 eV) peaks are shown in Fig. 5a. The peak separation between the 2p1/2 and 2p3/2 lines is 6.2 eV, which are assigned to the Ti^{4+} oxidation state [17]. The XPS peak of O 1s in Fig. 5b is observed at 530.8 eV which is the characteristic of metallic oxides. For the Cu@TiO₂ nanoparticles, the XPS of the samples are mainly composed of Ti, O and Cu. With respect to the XPS peaks of Ti 2p in Fig. 5c, although there are slight differences in the locations of binding energies of Ti 2p1/2 and Ti 2p3/2 compared with the bare TiO₂, they are all still in good agreement with the values of Ti^{4+} [17]. The O 1s binding energies in Fig. 5d reveal lattice oxygen (530.0 eV) existing at the composite surface. These results further confirm the presence of TiO₂ at the composite surface [18]. The peaks observed at 952.55 eV and 932.6 eV (Fig. 5b) can be ascribed to Cu 2p1/2 and Cu 2p3/2 of the metallic copper [19] indicating that a certain quantity of encapsulated Cu nanoparticles must be naked after Ar⁺ sputtered for 600s. The peak can be fitted with the nonlinear least-squares fitting program using Gaussian–Lorentzian peak shapes [20].

Our results point out that Cu...
nanoparticles were covered by TiO$_2$ and protected from oxidation as detected.

### 3.3. Optical and photocatalytic properties

UV–vis diffuse reflection spectra of Cu@TiO$_2$ with different mass ratios of Cu to TiO$_2$ compared with TiO$_2$ are displayed in Fig. 6. Compared with TiO$_2$, there is a critical point for mass ratio of TiO$_2$ to Cu when at around 1.53% where an enhancement of the visible-light absorption between 400 and 600 nm is generated [21].

The absorption intensity gradually strengthens with decrease in the mass ratio of TiO$_2$ to Cu.

Fig. 7 illustrates the photocatalytic activity of Cu@TiO$_2$ with different mass ratios for the degradation of 2,4-DCP under visible light irradiation. Without incorporation of Cu, the pure TiO$_2$ shows 10.49% degradation in visible light, while the photocatalytic performance of TiO$_2$ can be flexibly tuned by incorporation of different weights of Cu particles as shown in Fig. 7a and b, in which optimum performance is reached when the concentration of CuCl$_2$ solution is 4.75 mM. The degradation of 2,4-DCP can be fitted to a pseudo-first-order reaction with a simplified Langmuir–Hinshelwood model [22]. The variation of kinetic rate constant with the concentration of CuCl$_2$ solution follows the order C > D > B > E > A, and the corresponding value is 0.257 h$^{-1}$, 0.234 h$^{-1}$, 0.219 h$^{-1}$, 0.178 h$^{-1}$ and 0.147 h$^{-1}$, respectively. Therefore, the incorporation of Cu plays an important role in the photocatalytic degradation process.

The tested sample retains photocatalytic activity after three successive cycles of complete degradation 2,4-DCP under visible light irradiation (Fig. 8). From Fig. 8a, it is clear that the degradation efficiency of Cu@TiO$_2$ core–shell nanoparticles almost maintains the same level as the original one and shows a minor reduction by about 3.2% after three cycles of 2,4-DCP degradation. Furthermore, from the XRD patterns, there is no obvious difference observed for the samples before and after the degradation reaction (Fig. 8b), further indicating the stability of the sample.

### 3.4. Mechanism for enhanced activity of Cu@TiO$_2$ core–shell nanoparticles

To explore the mechanism involved in Cu@TiO$_2$ photocatalysis, reactive species involved in the photocatalytic reaction was explored using t-BuOH, KI and benzoquinone (BQ) as scavenger of HO$^\cdot$, VB hole and O$_2$$^{-}\cdot$, respectively [23]. As can be seen from Fig. 9, excess KI shows a negligible effect on the photocatalytic oxidation of 2,4-DCP. Also, the degradation rate of 2,4-DCP is not affected by the addition of t-BuOH. However, the addition of excess BQ significantly inhibits the decomposition of 2,4-DCP compared with no scavenger at the same conditions, indicating that the 2,4-DCP photodegradation is proceeded by O$_2$$^{-}\cdot$ to a large degree [24].

The superoxide radicals O$_2$$^{-}\cdot$ discussed so far were further investigated by the electron paramagnetic resonance (EPR) (Fig. 10) spectrum recorded at room temperature confirming the significant presence of oxygen vacancies in the Cu@TiO$_2$, with a strong signal at g = 2.004 induced by electrons trapped on oxygen vacancies [25]. Without incorporated with the Cu, TiO$_2$ sample does not
contain any paramagnetic sites, as evidenced by a flat line shown in Fig. 10, whereas Cu@TiO$_2$ sample shows an intense signal at $g=2.004$ shows up, which can be assigned to the single electron trapped on the oxygen vacancy states [26]. It should be noted that the oxygen vacancy formation does not accompany with the formation of Ti$^{4+}$ defects, as can be seen from the X-ray photoelectron spectra (Fig. 5a), suggesting that almost no Ti$^{3+}$ defects are formed during the oxygen vacancies formation [27]. The contribution of the signal at $g=2.004$ steadily increases, since the O$^{2-}$ species are affected by the content of the Cu. The relative intensities of the O$^{2-}$ species follows the approximate trend of $E>D>C+B>A$, apart from the expected line broadening effects due to residual oxygen [28]. Based on the above observations, the mechanism of degradation of 2,4-DCP under visible light irradiation over Cu@TiO$_2$ is proposed as shown in Scheme 1. It is believed that the core–shell structure of Cu@TiO$_2$ could favor charge transfer and inhibit recombination of photogenerated hole–electron pairs. Under the visible light excitation, the oxygen vacancy states can promote the visible-light absorption and the generation of the photoexcited electron–hole pairs over the surface of TiO$_2$ [29]. These photoexcited electrons and holes would suffer from both charge recombination and interfacial charge-transfer processes. Since Cu nanoparticles in the cores of Cu@TiO$_2$ nanospheres are good electron acceptors, they could promote the photoelectron transportation from TiO$_2$ shells and retard the recombination of photoexcited electron–holes on TiO$_2$ shells. Therefore, the efficiency toward photocatalytic redox process is improved. The adsorbed 2,4-DCP in solution interacts with photogenerated holes. In addition, the photogenerated electrons trapped by Cu particles can also be captured by oxygen, which produces superoxide radicals, as evidenced by the ESR analysis. These oxygen-containing species (O$_2$ or O$_2^{-}$) then are able to oxidize the 2,4-DCP.

4. Conclusions

The present study demonstrates that Cu@TiO$_2$ core–shell nanoparticles have been successfully fabricated via a facile in situ hydrolysis method. The incorporation of Cu core into the shell of TiO$_2$ contributes to the enhancement of visible light photocatalytic activity of TiO$_2$. The oxygen vacancy states can promote the visible-light absorption and the generation of the photoexcited electron–hole pairs over the surface of TiO$_2$. The enhanced photocactivity lies crucially on the contribution role of Cu nanoparticles acting as electron reservoir in prolonging the lifetime of photogenerated charge carriers. The reaction mechanism of the photocatalytic reaction over Cu@TiO$_2$ is also proposed by using different radical scavengers and EPR analysis. It is hoped that the present work could render guided information for steering toward the design and application of Cu@TiO$_2$ core–shell nanoparticles with visible light driven photocatalytic activity.

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