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## Hybrid $\text{Cu}_x\text{O}-\text{TiO}_2$ porous hollow nanospheres: preparation, characterization and photocatalytic properties†

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A series of  $\text{Cu}_x\text{O}-\text{TiO}_2$  hollow nanospherical composites with different mass percents of copper were prepared by an impregnation method, and the  $\text{TiO}_2$  hollow nanospheres were prepared by hydrolysis of tetraethoxy titanium on the surface of spherical  $\text{SiO}_2$  nanoparticles and corrosion of  $\text{SiO}_2$  in NaOH solution.  $\text{Cu}_x\text{O}-\text{TiO}_2$  hollow nanospheres displayed higher photocatalytic activities towards acetaldehyde degradation to  $\text{CO}_2$  than  $\text{TiO}_2@\text{SiO}_2$  nanospheres and  $\text{TiO}_2$  hollow nanospheres under UV and visible-light irradiation due to the narrowed band gap of  $\text{TiO}_2$  and enhanced charge separation after copper was introduced. In particular, the  $\text{Cu}_x\text{O}-\text{TiO}_2$  hollow nanospheres show high catalytic activities in degradation under visible-light irradiation.

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### 1. Introduction

In the past decades, titanium dioxide ( $\text{TiO}_2$ ) has attracted increasing attention due to its extensive application such as in sensor technology,<sup>1,2</sup> pigments,<sup>3</sup> solar cells,<sup>4</sup> self-cleaning coatings<sup>5</sup> and photocatalysis.<sup>6,7</sup> Particularly, study on the photocatalytic properties of  $\text{TiO}_2$  is the most common because of its several advantages including low cost, innocuity, chemical stability and high refractive index.<sup>8–11</sup> However, there are some disadvantages in using  $\text{TiO}_2$ , such as small surface area, phase transition, crystal growth and low quantum efficiency, which limit the photocatalytic efficiency of the catalysts.<sup>12–14</sup>

In order to overcome these problems, many investigations have been reported.<sup>15–17</sup> Morphology control and preparation of titania-based materials are two very effectual strategies.<sup>18</sup> One of the most efficient ways is to coat  $\text{TiO}_2$  in form of a layer on surface of core materials with high surface area, such as  $\text{ZrO}_2$ ,  $\text{MoO}_3$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{SiO}_2$ .<sup>19,20</sup> Silica is one of the best core materials for its well-known surface chemistry, absorption capacity, controllable preparation and it can be easily eliminated.<sup>21</sup> Another is to synthesize  $\text{TiO}_2$  with different morphologies and microstructures to enhance the surface area of the semiconductor. Many new morphologies of  $\text{TiO}_2$  were synthesized in the past years, such as nanotubes, nanorods, and hollow spheres, *etc.*<sup>22</sup> The synthesis of

$\text{TiO}_2$  hollow nanosphere is especially concerned for its large surface area, low density, and high light-harvesting efficiency.<sup>23,24</sup>

Volatile organic compound is the sources of indoor air pollution, and it is always the central issues in the environmental protection field. Among various photocatalytic oxidations over semiconductors,  $\text{TiO}_2$  photocatalyst possesses the function of air purification. Despite of good photocatalytic activities,  $\text{TiO}_2$  is only effective to degrade some photosensitive organic compounds under ultraviolet (UV) irradiation with strong intensity. However, the intensity of UV-light from common filament lamp is below several  $\mu\text{W cm}^{-3}$ , which is one thousand times low to the sunlight.<sup>25</sup> So the catalyst cannot reach the desired effect to get rid of the indoor contaminated gases. Therefore, development of visible-light-sensitive photocatalysts based on  $\text{TiO}_2$  is necessary.

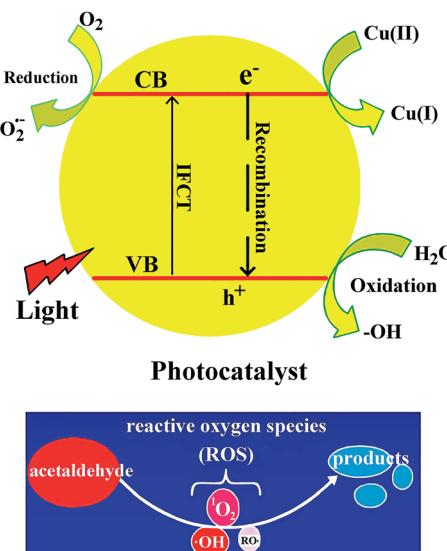
Another, due to high prices and scarce of the noble metal, attention has been given to search an alternative catalytic component to replace the noble metal. Such as, copper or copper oxide is better substitute component because of their low cost and wide use. In 2009,  $\text{TiO}_2$  powder grafted by  $\text{Cu}^+$  ions was found to be sensitive to visible light by Irie and his co-workers,<sup>26</sup> which lighted up the hope to  $\text{TiO}_2$  on its applications in daily life. They studied the photocatalytic activity of  $\text{Cu}/\text{TiO}_2$  under visible light irradiation. Huang *et al.* prepared the  $\text{CuO}/\text{TiO}_2$  by the deposition–precipitation (DP) and investigated its catalytic behavior.<sup>27</sup> Also, Gnanasekaran *et al.* did many research to expand the absorption of  $\text{TiO}_2$  to the visible light range for improving the photocatalytic efficiency.<sup>28,29</sup> Although photocatalytic efficiency of  $\text{TiO}_2$  is improved markedly, catalytic efficiency of the catalyst is still unsatisfying. Based on these works, we determine to use high specific surface area porous  $\text{TiO}_2$  hollow spheres as the carrier of loading copper, and study their catalytic activities by degradation of acetaldehyde gas.

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Scheme 1 Possible mechanism on degradation of acetaldehyde under the existence of  $\text{Cu}_x\text{O}@\text{TiO}_2$  catalysts.

In this paper,  $\text{TiO}_2@\text{SiO}_2$  core-shell nanosphere was prepared by using silica gel nanosphere as hard template, and  $\text{TiO}_2$  hollow nanosphere was obtained after  $\text{SiO}_2$  was etched by  $\text{NaOH}$  solution with a certain concentration.  $\text{Cu}^{2+}$  ions were adsorbed and  $\text{Cu}_x\text{O}$  was formed on the surface of the  $\text{TiO}_2$  hollow nanosphere to enhance separation of the photo-generated charge carriers. Four kinds of photocatalysts,  $\text{TiO}_2@\text{SiO}_2$  nanosphere,  $\text{TiO}_2$  hollow nanosphere,  $\text{Cu}_x\text{O}-\text{TiO}_2@\text{SiO}_2$  nanosphere and  $\text{Cu}_x\text{O}-\text{TiO}_2$  hollow nanosphere, were synthesized. The catalytic activities of these catalysts were studied by degradation of acetaldehyde under UV and visible-light irradiations. The results indicate that all catalysts have good catalytic activities in degradation of acetaldehyde under UV-light irradiation, and the  $\text{Cu}_x\text{O}-\text{TiO}_2$  hollow nanosphere shows high catalytic activities in the degradation under visible-light irradiation. As shown in Scheme 1, the visible-light is considered to initiate interfacial charge transfer. If the photon energy of light is greater than the semiconductor band gap, the electron ( $e^-$ ) on the valence band will be excited to the conduction band and the hole ( $h^+$ ) will be generated at the valence band. When  $\text{Cu}_x\text{O}-\text{TiO}_2$  is used as photocatalyst, electrons in the valence band (VB) of  $\text{TiO}_2$  are stimulated and directly transferred to  $\text{Cu}(\text{II})$  to form  $\text{Cu}(\text{I})$ , as well as holes ( $h^+$ ) in the VB of  $\text{TiO}_2$ . Also the adsorbed  $\text{O}_2$  on the surface can capture the electrons in VB of  $\text{TiO}_2$ , but it is harder than that of  $\text{Cu}(\text{II})$ . Thus, the energy to separate electrons and holes becomes low, which narrows the band gap of  $\text{TiO}_2$  and prolongs the absorption edge from UV-light to visible-light region. The holes produced in VB of  $\text{TiO}_2$  decompose organic substances.

## 2. Experimental

### 2.1. Chemicals and instruments

All chemicals used are of analytical reagent grade available from a commercial supplier without further purification.

Tetraethoxysilane (TEOS,  $\geq 99\%$ ) and copper chloride dihydrate ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , AR) were purchased from Sinopharm Chemical Reagent Company (in Shanghai, PR China). Tetraethoxy titanium ( $\text{C}_8\text{H}_{20}\text{O}_4\text{Ti}$ ,  $\geq 98\%$ ) was purchased from Aladdin Industrial Corporation (in Shanghai, PR China). L-Lysine (BR) was purchased from Beijing Biological Technology Company (in Beijing, PR China). Hydrochloric acid (38 wt%), acetic acid (38 wt%), sodium hydroxide (AR) and ethanol (AR, 99%) were all purchased from Beijing Chemical Reagent Company (in Beijing, PR China).

Fourier transform infrared (FT-IR) spectra of the samples were recorded in range of  $4000\text{--}400\text{ cm}^{-1}$  with  $2\text{ cm}^{-1}$  resolution on a Bruker Vector-22 Fourier transform spectrometer (made in Germany). Electronic micrographs (including energy-dispersive X-ray spectroscopy, EDS) of the samples were observed using a S-4700 scanning electron microscope (SEM, made in Japan) operated at 15 kV, a J-2010 high resolution transmission electron microscope (HRTEM, made in Japan) and a Tecnai G<sup>2</sup> 20S-TWIN transmission electron microscope (TEM, made in USA) operated at 200 kV, respectively. Crystal structures of samples were determined by powder X-ray diffraction (PXRD), using a Rigaku D/MAX diffractometer (made in Japan) with  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.15406\text{ nm}$ , scanning speed =  $10^\circ \text{ min}^{-1}$ ).  $\text{N}_2$  sorption isotherms of the samples were recorded on a Quantachrome NOVA 2000e sorption analyzer (made in USA) at the temperature of liquid nitrogen (77 K). Samples were degassed at  $200^\circ\text{C}$  overnight prior to the measurement. Surface areas and pore size distributions of the samples were obtained by Brunauer–Emmett–Teller (BET) method and calculated using Barrett–Joyner–Halenda (BJH) model, respectively. UV-Vis absorption of the samples were obtained by Perkin Elmer Lambda 900 UV-Vis spectrophotometer (made in Germany) in range of  $220\text{--}800\text{ cm}^{-1}$ . X-ray photoelectron spectroscopic (XPS) analysis was measured on Shimadzu ESCA-250 and ESCA-1000 spectrometers (made in Japan) with  $\text{Mg K}\alpha$  X-ray sources.

STEM analysis was conducted on a JEOL JEM 2200FS equipped with a CEOS aberration corrector (CEOS GmbH, Heidelberg, Ger). Images and EDS maps were acquired in analytical mode (AMAG), with a probe size of 0.8 nm and a nominal beam current of 450 pA. The EDS signal was collected with a Bruker X-Flash silicon-drift detector and was processed using the Bruker Esprit software. EDS maps were collected for  $>10$  min. The final resolution of the EDS maps was estimated to be  $\sim 0.8$  nm.

### 2.2. Synthesis of $\text{TiO}_2@\text{SiO}_2$ nanosphere

Silica nanosphere was used as template to synthesize  $\text{TiO}_2$  hollow nanosphere, and its synthesis was according to the method in ref. 30.

$\text{TiO}_2@\text{SiO}_2$  with core-shell structure was composed via sol-gel method. Primarily, the as-prepared  $\text{SiO}_2$  nanosphere with diameter about 25 nm was dispersed in an ethanol solution (ethanol in water) and oscillated in ultrasonic oscillator for several minutes. A solution of tetraethoxy titanium in ethanol was then added dropwise to 35 mL of the above dispersion system with continuous stirring. And a mixture solution of 35



mL of absolute ethanol, 2.0 mL acetic acid and two drops of hydrochloric acid was added to the mixture rapidly. After stirred for 30 min, the mixture was heated at 40 °C and stirred vigorously for 1.0 h. The final product  $\text{TiO}_2@\text{SiO}_2$  nanosphere was obtained after the mixture was filtered, washed with water and ethanol for several times, dried at 70 °C for about 4.0 h and calcined at 550 °C for 4.0 h.

### 2.3. Synthesis of $\text{TiO}_2$ hollow nanosphere

The silica template was removed by immersing  $\text{TiO}_2@\text{SiO}_2$  nanosphere in a NaOH solution (3.0 M) at 60 °C for 8.0 h under continuous stirring, and the hollow nanosphere was obtained after the mixture was centrifuged, washed with ethanol and water for several times and dried at 60 °C for 4.0 h.

### 2.4. Synthesis of $\text{Cu}_x\text{O}-\text{TiO}_2$ hollow nanosphere and $\text{Cu}_x\text{O}-\text{Ti}-\text{TiO}_2@\text{SiO}_2$ nanosphere

The  $\text{Cu}_x\text{O}-\text{TiO}_2$  hollow nanosphere and  $\text{Cu}_x\text{O}-\text{TiO}_2@\text{SiO}_2$  nanosphere were prepared by an impregnation method using  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  as source of  $\text{Cu}^{2+}$  ions. 1.0 g of  $\text{TiO}_2$  hollow nanosphere (or  $\text{TiO}_2@\text{SiO}_2$  nanosphere) was added into 10 mL distilled water in a vial reactor. Different amounts of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (mass percents of  $\text{Cu}^{2+}$  relative to  $\text{TiO}_2$  are 0.25%, 0.50% and 1.0%, respectively) were added to the above reactor, and the system was heated at 90 °C for 1.0 h under continuous stirring. The products were obtained by centrifuged, washed with water for several times and dried at 110 °C overnight. The products are named as 0.25%- $\text{Cu}_x\text{O}-\text{TiO}_2$  hollow nanosphere, 0.5%- $\text{Cu}_x\text{O}-\text{TiO}_2$  hollow nanosphere and 1.0%- $\text{Cu}_x\text{O}-\text{TiO}_2$  hollow nanosphere, respectively; or 0.25%- $\text{Cu}_x\text{O}-\text{TiO}_2@\text{SiO}_2$  nanosphere, 0.5%- $\text{Cu}_x\text{O}-\text{TiO}_2@\text{SiO}_2$  nanosphere and 1.0%- $\text{Cu}_x\text{O}-\text{TiO}_2@\text{SiO}_2$  nanosphere, respectively.

### 2.5. Measurement of photocatalytic activities

Photocatalytic activities of the synthesized materials were evaluated by degradation of acetaldehyde in gas phase under ultraviolet and visible-light irradiations. 0.05 g microsphere powder was uniformly spread in a sample holder, which was placed on the bottom of a 500 mL cylinder-type Pyrex glass vessel. The glass vessel was flushed with  $\text{O}_2$  (20%)/ $\text{N}_2$  gas to remove carbon dioxide from the system, and the relative humidity of atmosphere inside the vessel was controlled to 45% by passing the  $\text{O}_2/\text{N}_2$  gas through chilled water formerly. 5.2 mL acetaldehyde was introduced into the reaction vessel using a Pressure-Lock syringe to reach a concentration of 200 ppmv. After kept for 15 min in dark environment, the glass vessel was irradiated from top by a 150 W xenon lamp (Hayashi UV410) which emits light of wavelength range of 350–400 nm at an intensity of 3.0 mW cm<sup>-2</sup>. The degradation of acetaldehyde and the generation of carbon dioxide were monitored using a gas chromatograph (SP-2100A, BFRL Co.), equipped with a 2 m Porapak-Q column and a flame ionization detector.

The same method was used in visible-light irradiation (420 nm in wavelength and 119 mW cm<sup>-2</sup> in intensity) to the degradation of acetaldehyde to check the photocatalytic activities of the samples.

## 3. Results and discussion

### 3.1. Characterizations of the catalysts synthesized

SEM images of silica nanosphere (used as template) and  $\text{TiO}_2@\text{SiO}_2$  nanosphere, TEM image of  $\text{TiO}_2$  hollow nanosphere and HRTEM image of  $\text{Cu}_x\text{O}-\text{TiO}_2$  hollow nanosphere are shown in Fig. 1. It is found that the silica has regular ball-shape morphology with an average diameter about 25 nm (Fig. 1A). The average diameter of the microsphere increases to about 35 nm after  $\text{TiO}_2$  framework formed on the surface (Fig. 1B). After immersed in NaOH solution (3.0 M) at 60 °C for 8.0 h, Si–O structure in  $\text{TiO}_2@\text{SiO}_2$  nanosphere was damaged and the shell of  $\text{TiO}_2$  remained. TEM image (Fig. 1C) indicates that final product has regular microspherical morphology with hollow structure, and its average diameter is about 35 nm. The shell thickness of these hollow microspheres is about several nanometers. HRTEM image (Fig. 1D) shows that there are  $\text{Cu}_x\text{O}$  clusters attached on the highly crystallized  $\text{TiO}_2$  surfaces and formed clear lattice fringes. Particle size distributions of unmodified  $\text{SiO}_2$  nanosphere,  $\text{TiO}_2@\text{SiO}_2$  nanosphere and  $\text{TiO}_2$  hollow nanosphere are also shown in Fig. 1.

The FT-IR spectra of  $\text{SiO}_2$  nanosphere,  $\text{TiO}_2@\text{SiO}_2$  nanosphere and  $\text{TiO}_2$  hollow nanosphere are shown in Fig. 2. All the samples have stretching and bending vibrations absorptions of hydroxyl groups from surface of the samples and the adsorbed water, which are at 3400 and 1600 cm<sup>-1</sup> respectively.<sup>31</sup> The antisymmetric stretching vibration absorption of Si–O–Si in  $\text{SiO}_2$  (Fig. 2a) and  $\text{TiO}_2@\text{SiO}_2$  nanospheres (Fig. 2b) are found at 1100 cm<sup>-1</sup>, but it cannot be observed in Fig. 2c. Disappearance of Si–O–Si absorption in Fig. 2c indicates that there isn't any  $\text{SiO}_2$  in the  $\text{TiO}_2$  hollow nanosphere. Vibration absorption of Ti–O–Si in  $\text{TiO}_2@\text{SiO}_2$  (Fig. 2b) is found at 960 cm<sup>-1</sup>,<sup>32</sup> indicating that the framework of (Ti–O)<sub>n</sub> was connected on the surface of silica gel after tetraethoxy titanium was adsorbed and hydrolyzed. At the same time, the absorptions of Ti–O in  $\text{TiO}_2@\text{SiO}_2$  and  $\text{TiO}_2$  hollow nanospheres are found at about 520 cm<sup>-1</sup>.

EDS spectrum of  $\text{TiO}_2@\text{SiO}_2$  nanosphere (Fig. 3A) shows that the nanosphere is consisted by Si (20.49%), Ti (7.86%) and O (71.65%) elements, proving the existence of both  $\text{SiO}_2$  and  $\text{TiO}_2$  frameworks in the sample. Calculation indicates that the proportion of  $\text{TiO}_2$  and  $\text{SiO}_2$  in  $\text{TiO}_2@\text{SiO}_2$  nanosphere is about 1 : 3. However, only Ti and O elements are found in Fig. 3B, and the proportion of Ti and O is about 1 : 2, which confirms the removal of template and generation of  $\text{TiO}_2$  hollow nanosphere.

The crystal phases of  $\text{TiO}_2$  largely determines their suitabilities for photocatalytic activities.<sup>33,34</sup> The powder X-ray diffraction (PXRD) patterns of  $\text{TiO}_2@\text{SiO}_2$  nanosphere and  $\text{TiO}_2$  hollow nanospheres deposited by different concentrations of  $\text{Cu}^{2+}$  ions are shown in Fig. 4. Six characteristic peaks of anatase  $\text{TiO}_2$  are observed at 25.2° (101), 37.8° (004), 48.1° (200), 53.9° (105), 56.1° (211) and 62.7° (204) in  $\text{Cu}_x\text{O}-\text{TiO}_2@\text{SiO}_2$  nanospheres (Fig. 4A), which are indexed to diffractions of  $\text{TiO}_2$  (ref. 35) except for the diffractions of  $\text{SiO}_2$  at 21.79°. However, when the Cu content in the nanocomposite, diffraction peaks of two weak diffractions of  $\text{Cu}_x\text{O}$  ( $\text{CuO}$  and  $\text{Cu}_2\text{O}$ ) were observed in 27.5° and 42.3°.<sup>36</sup> As to  $\text{Cu}_x\text{O}-\text{TiO}_2$  hollow nanosphere (Fig. 4B), seven characteristic



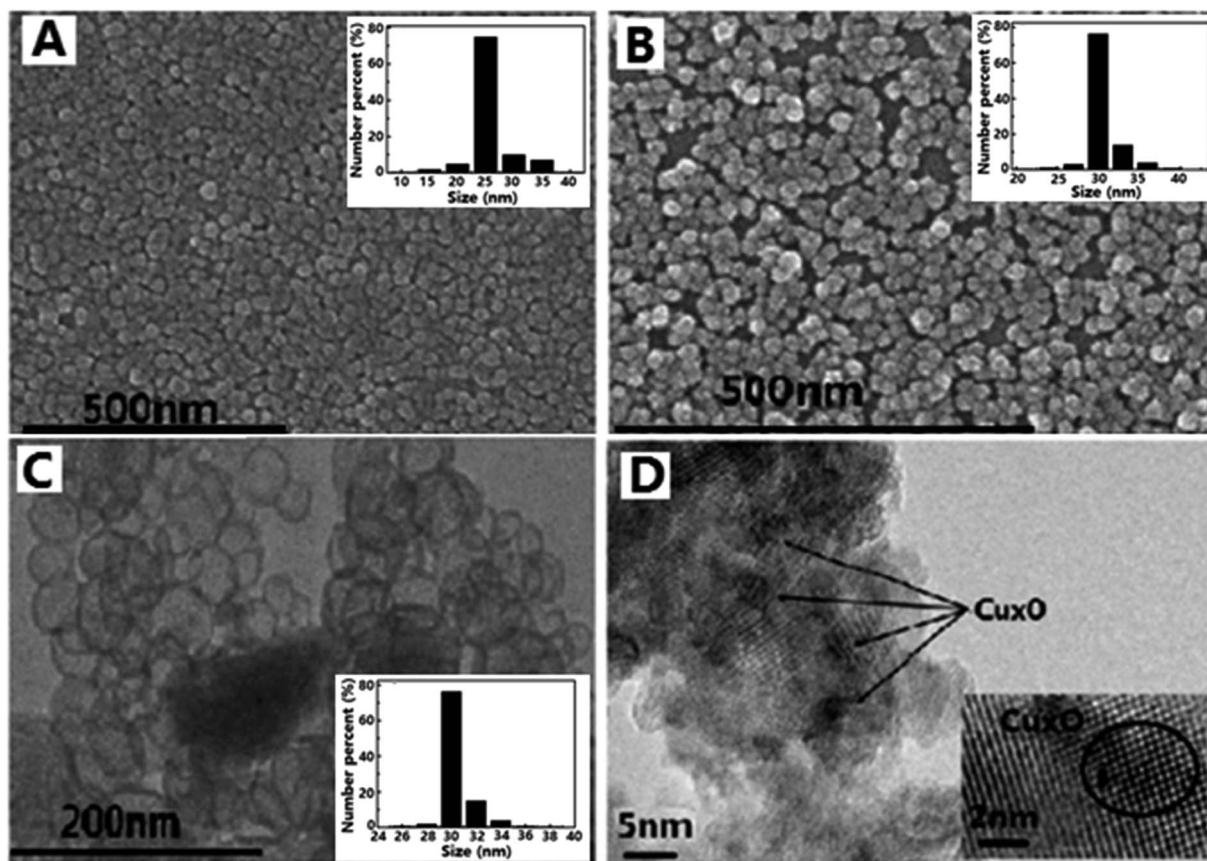


Fig. 1 SEM images and particle size distributions of unmodified  $\text{SiO}_2$  (A) nanosphere and  $\text{TiO}_2@\text{SiO}_2$  nanosphere (B); TEM image and particle size distribution of  $\text{TiO}_2$  hollow nanosphere (C) and HRTEM image of  $\text{Cu}_x\text{O}-\text{TiO}_2$  hollow nanosphere (D).

diffractions from anatase  $\text{TiO}_2$  are observed, and all the diffractions are stronger than the corresponding diffractions in  $\text{Cu}_x\text{O}-\text{TiO}_2@\text{SiO}_2$  nanosphere. Also the diffractions associated with  $\text{Cu}_2\text{O}$  at  $27.5^\circ$  and  $42.3^\circ$  on the surface of  $\text{TiO}_2$  hollow nanosphere are found (Fig. 4B). All the results indicate that  $\text{Cu}_x\text{O}$  was attached to the surface of  $\text{TiO}_2$ , and the diffraction intensity from  $\text{Cu}_2\text{O}$  increases with its content. Elemental mapping analysis of the sample  $\text{Cu}_x\text{O}-\text{TiO}_2$  hollow nanosphere (shown in Fig. S1 in the ESI<sup>†</sup>) indicates that the Cu element

distributed uniformly though its content on  $\text{TiO}_2$  surface was little.

Nitrogen adsorption-desorption isotherms of  $\text{TiO}_2@\text{SiO}_2$  and  $\text{TiO}_2$  hollow nanospheres are shown in Fig. 5. Isotherms exhibiting behavior between those of types I and IV are characteristic of mesopores, according to IUPAC classifications. In addition, the prepared  $\text{TiO}_2@\text{SiO}_2$  nanosphere and  $\text{TiO}_2$  hollow nanosphere own surface areas of  $251 \text{ m}^2 \text{ g}^{-1}$  and  $402 \text{ m}^2 \text{ g}^{-1}$ , pore volumes of  $0.613 \text{ cm}^3 \text{ g}^{-1}$  and  $0.983 \text{ cm}^3 \text{ g}^{-1}$ , respectively. These parameters are far more than those of P25 ( $49 \text{ m}^2 \text{ g}^{-1}$  of surface area and  $0.090 \text{ cm}^3 \text{ g}^{-1}$  of pore volume), a kind of commercial  $\text{TiO}_2$  microsphere.

In order to explore the chemical states of some relative elements in the nanocomposite samples, X-ray photoelectron spectroscopy (XPS) was carried out. In Fig. 6A, two peaks at 463.9 eV and 458.2 eV were observed from the Ti 2p spectrum, which are assigned to Ti 2p<sub>1/2</sub> and Ti 2p<sub>3/2</sub>. No obvious differences were observed between the two spectra of  $\text{TiO}_2$  and 0.5%- $\text{Cu}_x\text{O}-\text{TiO}_2$  hollow nanospheres, which indicate that  $\text{Cu}_x\text{O}$  was deposited on the surface of  $\text{TiO}_2$  hollow nanospheres rather than the lattice. As shown in Fig. 6B, the appearance of CuO can be confirmed by the binding energies of 934.6 and 954.5 eV, respectively. There are another two characteristic peaks located at binding energies of 932.5 and 952.5 eV, which can be assigned to Cu(i) in  $\text{Cu}_2\text{O}$ .<sup>37</sup> Mole ratio of  $\text{Cu}^+$  to  $\text{Cu}^{2+}$  is about

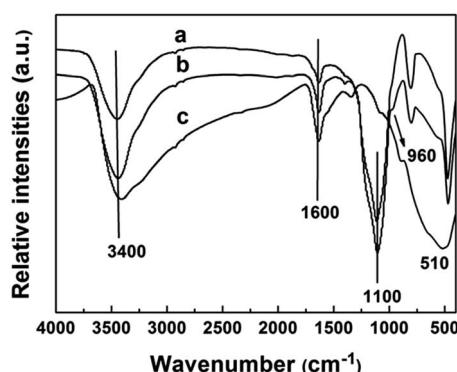


Fig. 2 FT-IR spectra of  $\text{SiO}_2$  nanosphere (a),  $\text{TiO}_2@\text{SiO}_2$  nanosphere (b) and  $\text{TiO}_2$  hollow nanosphere (c).

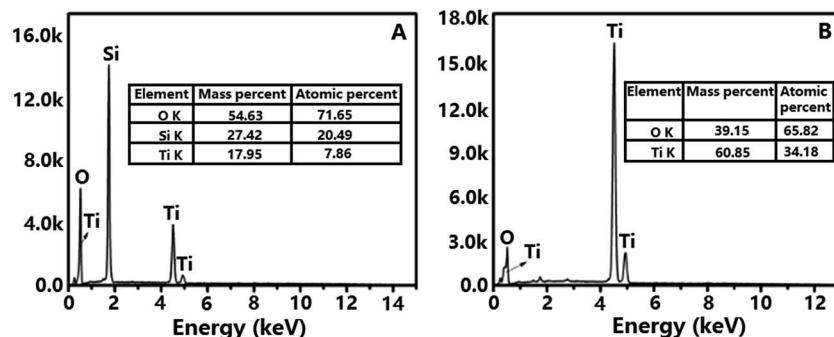


Fig. 3 EDS spectra of  $\text{TiO}_2@\text{SiO}_2$  nanosphere (A) and  $\text{TiO}_2$  hollow nanosphere (B).

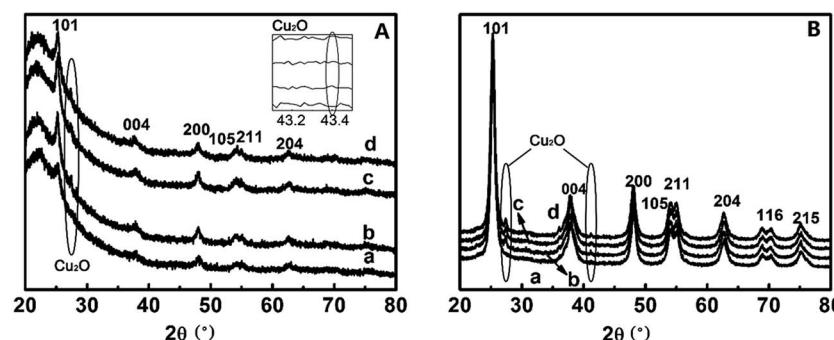


Fig. 4 (A) XRD patterns of  $\text{TiO}_2@\text{SiO}_2$  nanospheres ((a)  $\text{TiO}_2@\text{SiO}_2$ ; (b) 0.25%– $\text{Cu}_x\text{O}-\text{TiO}_2@\text{SiO}_2$ ; (c) 0.5%– $\text{Cu}_x\text{O}-\text{TiO}_2@\text{SiO}_2$ ; (d) 1.0%– $\text{Cu}_x\text{O}-\text{TiO}_2@\text{SiO}_2$ ); (B) XRD patterns of  $\text{TiO}_2$  hollow nanospheres ((a)  $\text{TiO}_2$  hollow sphere; (b) 0.25%– $\text{Cu}_x\text{O}-\text{TiO}_2$  hollow sphere; (c) 0.5%– $\text{Cu}_x\text{O}-\text{TiO}_2$  hollow sphere; (d) 1.0%– $\text{Cu}_x\text{O}-\text{TiO}_2$  hollow sphere).

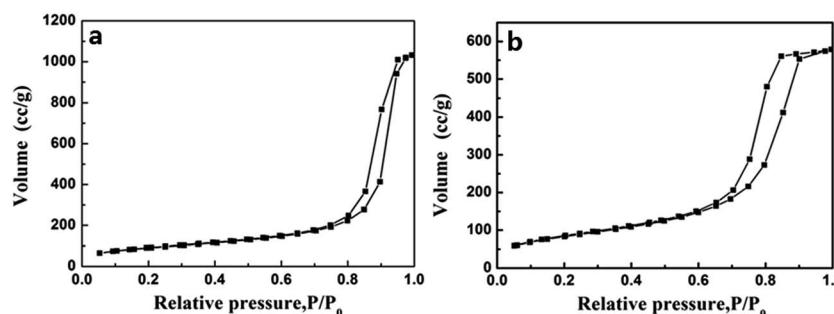


Fig. 5 The N<sub>2</sub> adsorption–desorption isotherms of  $\text{TiO}_2@\text{SiO}_2$  nanosphere (a) and  $\text{TiO}_2$  hollow nanosphere (b).

1.6 : 1, which calculated from the peak area in Fig. 6B. In process of the reaction, the hydrated  $\text{Cu}^{2+}$  ions were firstly adsorbed on the surface of  $\text{TiO}_2$  hollow nanospheres. Some of  $\text{Cu}^{2+}$  ions were hydrolyzed to  $\text{Cu}(\text{OH})_2$  in this system, and later they were changed into  $\text{CuO}$  under a certain temperature (110 °C). Due to the semiconductive property, the electron–holes in  $\text{TiO}_2$  would be separated under illumination of UV-light in the sunshine, and the electrons separated would be transferred to  $\text{Cu}^{(\text{II})}$  to form  $\text{Cu}_2\text{O}$ .

UV-Vis absorption spectra (shown in Fig. 7) indicate that all the samples, including  $\text{TiO}_2@\text{SiO}_2$  nanosphere,  $\text{TiO}_2$  hollow nanosphere,  $\text{Cu}_x\text{O}-\text{TiO}_2@\text{SiO}_2$  nanosphere and  $\text{Cu}_x\text{O}-\text{TiO}_2$  hollow nanosphere, have the intrinsic interband absorptions of

$\text{TiO}_2$  at about 400 nm. The weak absorptions in range of 400–500 nm are assigned to the interfacial charge transfer in  $\text{Cu}_x\text{O}-\text{TiO}_2@\text{SiO}_2$  nanosphere and  $\text{Cu}_x\text{O}-\text{TiO}_2$  hollow nanosphere. In addition, the absorptions from 600 to 800 nm in the spectra of  $\text{Cu}_x\text{O}-\text{TiO}_2@\text{SiO}_2$  nanosphere and  $\text{Cu}_x\text{O}-\text{TiO}_2$  hollow nanosphere are assigned to the intrinsic excitation band of  $\text{Cu}_x\text{O}$  and the d–d transition of  $\text{Cu}(\text{II})$ .<sup>33</sup> Sequence of absorption intensities in range of 500–800 nm of the relative materials is  $\text{TiO}_2@\text{SiO}_2$  nanosphere ≡  $\text{TiO}_2$  hollow nanosphere <  $\text{Cu}_x\text{O}-\text{TiO}_2@\text{SiO}_2$  nanosphere <  $\text{Cu}_x\text{O}-\text{TiO}_2$  hollow nanosphere, indicating that the  $\text{Cu}^{2+}$  ions on the surface of  $\text{TiO}_2$  strengthen the absorption of the host in visible-light region, and the intensified degree on the absorptions increases with the increasing contents of Cu

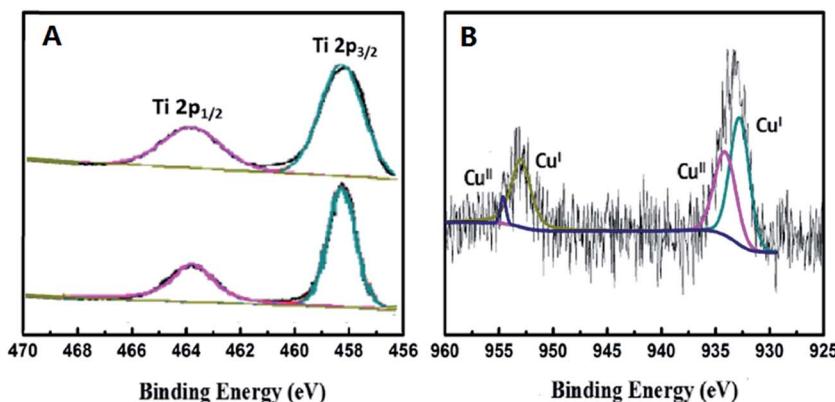


Fig. 6 XPS analysis of Ti 2p in  $\text{TiO}_2$  hollow nanosphere (A) and Cu 2p in 0.5%- $\text{Cu}_x\text{O}-\text{TiO}_2$  hollow nanosphere (B).

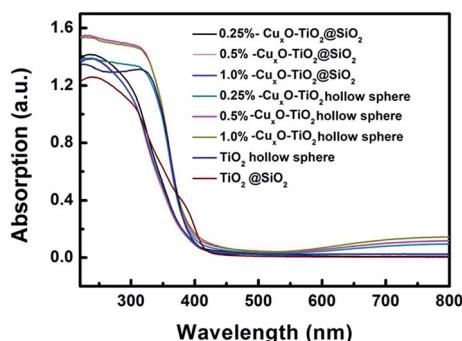


Fig. 7 UV-Vis absorption spectra of  $\text{TiO}_2@\text{SiO}_2$ ,  $\text{TiO}_2$  hollow nanosphere and  $\text{Cu}_x\text{O}-\text{TiO}_2@\text{SiO}_2$  and  $\text{Cu}_x\text{O}-\text{TiO}_2$  hollow nanospheres.

element in the composite materials, especially to  $\text{TiO}_2$  hollow nanosphere.

### 3.2. Studies on catalytic activities of the catalysts

Photocatalytic activities of the catalysts were evaluated by monitoring degradation of acetaldehyde under UV-light and visible-light irradiations, and the initial concentration of acetaldehyde gas in all the experiments is about 200 ppmv. The first is to check the activities of the catalysts in a dark environment

without any light irradiation. It was found that the concentration of acetaldehyde was almost not changed except for a little amount of acetaldehyde adsorbed (less than 20% of acetaldehyde adsorbed and less than 5% of  $\text{CO}_2$  produced, which could be found from Fig. 8), which means that the acetaldehyde was not decomposed in dark under existence of the catalysts. However, the degradation of acetaldehyde happened when the reactor was irradiated by UV-light or visible-light, and large amount of  $\text{CO}_2$  generated at the same time. Fig. 8 and 9 display the degradation of acetaldehyde and the generation of  $\text{CO}_2$  in the systems under UV-light and visible-light irradiations, respectively. As shown in Fig. 8, the catalytic performance of  $\text{TiO}_2$  hollow nanosphere was superior to  $\text{TiO}_2@\text{SiO}_2$  nanosphere. Also it was found that the content of copper on the surface of  $\text{TiO}_2$  affected the activities of catalysts deeply. The catalytic efficiency of 0.5%- $\text{Cu}_x\text{O}-\text{TiO}_2$  hollow nanosphere is higher than that of 0.25%- $\text{Cu}_x\text{O}-\text{TiO}_2$  hollow nanosphere. When the copper content is up to 0.5%, increase on catalytic efficiency of the hollow nanosphere is not evident. The above-mentioned regularity can be also found in the  $\text{Cu}_x\text{O}-\text{TiO}_2@\text{SiO}_2$  nanospherical system. The decomposed rate of acetaldehyde by different catalysts under UV-light irradiation can be calculated by amount of the residual acetaldehyde and the generated  $\text{CO}_2$ . In the system of 0.5%- $\text{Cu}_x\text{O}-\text{TiO}_2$  hollow nanosphere, about 99.72–99.74% acetaldehyde was degraded

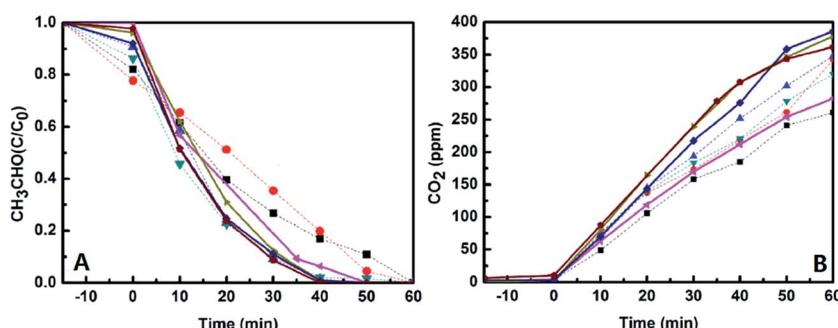
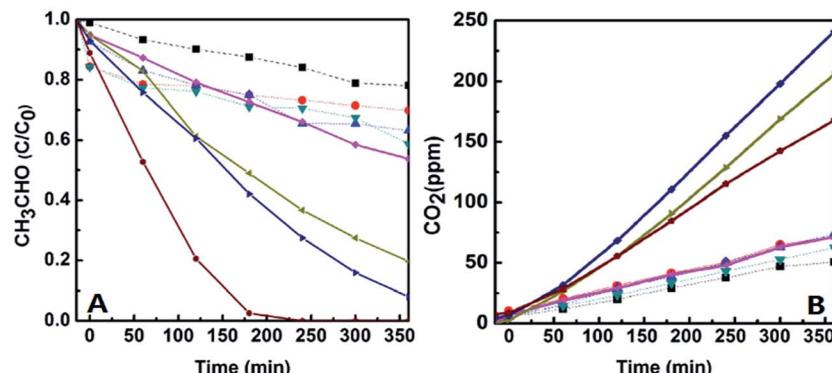


Fig. 8 Degradation of acetaldehyde with the variation of times (A) and amount of  $\text{CO}_2$  generated (B) under UV light irradiation and existence of the catalysts (■:  $\text{TiO}_2@\text{SiO}_2$ ; ●: 0.25%- $\text{Cu}_x\text{O}-\text{TiO}_2@\text{SiO}_2$ ; ▲: 0.5%- $\text{Cu}_x\text{O}-\text{TiO}_2@\text{SiO}_2$ ; ▼: 1.0%- $\text{Cu}_x\text{O}-\text{TiO}_2@\text{SiO}_2$ ; ▲:  $\text{TiO}_2$  hollow sphere; ▶: 0.25%- $\text{Cu}_x\text{O}-\text{TiO}_2$  hollow sphere; ◆: 0.5%- $\text{Cu}_x\text{O}-\text{TiO}_2$  hollow sphere; ◉: 1.0%- $\text{Cu}_x\text{O}-\text{TiO}_2$  hollow sphere).



**Fig. 9** Degradation of acetaldehyde with the variation of times (A) and amount of  $\text{CO}_2$  generated (B) under visible light irradiation and existence of the catalysts (■:  $\text{TiO}_2@\text{SiO}_2$ ; ●: 0.25%- $\text{Cu}_x\text{O}-\text{TiO}_2@\text{SiO}_2$ ; ▲: 0.5%- $\text{Cu}_x\text{O}-\text{TiO}_2@\text{SiO}_2$ ; ▼: 1.0%- $\text{Cu}_x\text{O}-\text{TiO}_2@\text{SiO}_2$ ; ▲:  $\text{TiO}_2$  hollow sphere; ▲: 0.25%- $\text{Cu}_x\text{O}-\text{TiO}_2$  hollow sphere; ▲: 0.5%- $\text{Cu}_x\text{O}-\text{TiO}_2$  hollow sphere; ●: 1.0%- $\text{Cu}_x\text{O}-\text{TiO}_2$  hollow sphere).

after 60 minutes. Some data relating to degradation efficiency of acetaldehyde under UV-light and visible-light irradiations catalyzed by the relative catalysts are listed in Tables 1 and 2. The clearance ratio is specific value of practical production and theoretical yield of  $\text{CO}_2$ .

Meanwhile, degradations of acetaldehyde irradiated under visible-light under the catalysts were studied, which are shown in Fig. 9. Little  $\text{CO}_2$  generated from degradation of acetaldehyde under the existence of  $\text{TiO}_2@\text{SiO}_2$  nanosphere and  $\text{TiO}_2$  hollow nanosphere for the wide band gap of  $\text{TiO}_2$ . However in  $\text{Cu}_x\text{O}-\text{TiO}_2$  hollow nanospherical systems, acetaldehyde could be degraded to  $\text{CO}_2$  commendably despite of the efficiencies lower than in UV-light. There is about 62.77–62.79% acetaldehyde was degraded in 0.5%- $\text{Cu}_x\text{O}-\text{TiO}_2$  hollow nanosphere catalytic system, and the catalyst exhibits the best catalytic performance among all the catalysts. Only 20.52–20.54% of acetaldehyde was degraded in 0.5%- $\text{Cu}_x\text{O}-\text{TiO}_2@\text{SiO}_2$  nanosphere catalytic system. Concentration of  $\text{CO}_2$  generated in 0.5%- $\text{Cu}_x\text{O}-\text{TiO}_2$

hollow nanosphere system reached 241 ppm after 6 h, which is more than three times to the  $\text{CO}_2$  generated in  $\text{Cu}_x\text{O}-\text{TiO}_2@\text{SiO}_2$  nanosphere system (74 ppm) in the same time. Such high degradation efficiency of acetaldehyde under visible-light irradiation was seldom reported.

Photocatalytic reaction under existence of the semiconductor is a complicated phenomenon. It includes light absorption, stimulation and transference of the carrier and redox reaction on the catalyst surface. Position of energy band determined by the electronic structure in the semiconductor is one of the main controlling factors on photocatalytic activity, which affects range of the light wavelength on catalyst responsibility directly. The visible-light is considered to initiate interfacial charge transfer. Electrons in the valence band (VB) of  $\text{TiO}_2$  are directly transferred to  $\text{Cu}(\text{II})$  to form  $\text{Cu}(\text{I})$ , as well as holes ( $\text{h}^+$ ) in the VB of  $\text{TiO}_2$ . Thus, the energy to separate electrons and holes becomes low, which narrows the band gap of  $\text{TiO}_2$  and prolongs the absorption edge from UV-light to visible-light

**Table 1** Initial concentration of acetaldehyde, the amount of  $\text{CO}_2$  generated and decomposed rate of acetaldehyde after 60 minutes under UV light irradiation (THN:  $\text{TiO}_2$  hollow nanosphere, TS:  $\text{TiO}_2@\text{SiO}_2$ )

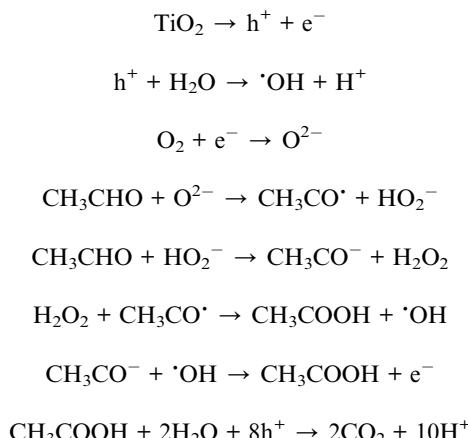
Sample	TS	0.25% $\text{Cu}_x\text{O}-\text{TS}$	0.5% $\text{Cu}_x\text{O}-\text{TS}$	1.0% $\text{Cu}_x\text{O}-\text{ST}$	THN	0.25% $\text{Cu}_x\text{O}-\text{THN}$	0.50% $\text{Cu}_x\text{O}-\text{THN}$	1.0% $\text{Cu}_x\text{O}-\text{THN}$
$C_{\text{CH}_3\text{CHO}}$ (ppmv)	193.611	194.139	181.5	193.842	180.361	199.796	193.545	186.103
$C_{\text{CO}_2}$ (ppmv)	260.989	342.129	347.763	319.558	282.625	378.431	386.044	361.759
Decomposed rate (%)	67.39–67.41	88.10–88.12	95.78–95.80	82.42–82.44	78.17–78.19	94.69–94.71	99.72–99.74	97.19–97.21

**Table 2** Initial concentration of acetaldehyde, the amount of  $\text{CO}_2$  generated and decomposed rate of acetaldehyde after 6 hours under visible light irradiation (THN:  $\text{TiO}_2$  hollow nanosphere, TS:  $\text{TiO}_2@\text{SiO}_2$ )

Sample	TS	0.25%- $\text{Cu}_x\text{O}-\text{TS}$	0.5%- $\text{Cu}_x\text{O}-\text{TS}$	1.0%- $\text{Cu}_x\text{O}-\text{TS}$	THN	0.25%- $\text{Cu}_x\text{O}-\text{THN}$	0.5%- $\text{Cu}_x\text{O}-\text{THN}$	1.0%- $\text{Cu}_x\text{O}-\text{THN}$
$C_{\text{CH}_3\text{CHO}}$ (ppmv)	197.620	179.355	180.328	183.991	174.042	178.035	192.159	200.409
$C_{\text{CO}_2}$ (ppmv)	50.635	71.583	74.029	62.534	71.488	205.675	241.276	168.007
Decomposed rate (%)	12.80–12.82	19.95–19.97	20.52–20.54	17.69–17.71	20.53–20.55	54.99–55.01	62.77–62.79	41.91–41.93



region. The holes produced in VB of  $\text{TiO}_2$  decompose organic substances. The catalytic degradation mechanism of acetaldehyde is shown in the following equations:<sup>38</sup>



Due to the larger surface area and more exposed active sites, the catalytic activity of  $\text{Cu}_x\text{O}-\text{TiO}_2$  hollow nanosphere is higher than that of the catalyst  $\text{Cu}_x\text{O}-\text{TiO}_2@\text{SiO}_2$  nanosphere. Moreover, the separation of electrons and holes became easier with  $\text{Cu}^{2+}$  increased on the surface of  $\text{TiO}_2$ , and superior catalytic activity of the catalyst was exhibited.

## 4. Conclusions

In summary, four kinds of photocatalysts,  $\text{TiO}_2@\text{SiO}_2$  nanosphere,  $\text{TiO}_2$  hollow nanosphere,  $\text{Cu}_x\text{O}-\text{TiO}_2@\text{SiO}_2$  nanosphere and  $\text{Cu}_x\text{O}-\text{TiO}_2$  hollow nanosphere, were synthesized. All the materials were found to have good photocatalytic activities in degradation of acetaldehyde under UV-light irradiations. Compared with  $\text{TiO}_2@\text{SiO}_2$  nanosphere,  $\text{TiO}_2$  hollow nanosphere and  $\text{Cu}_x\text{O}-\text{TiO}_2@\text{SiO}_2$  nanosphere,  $\text{Cu}_x\text{O}-\text{TiO}_2$  hollow nanosphere was superior for being used as catalyst in degradation of acetaldehyde under visible-light irradiation. The impregnated  $\text{Cu}^{2+}$  ions on the surface of  $\text{TiO}_2$  hollow nanosphere were possibly to enhance the separation of photo-generated charge carriers.

## Conflict of interest

The authors declare no competing financial interest.

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