1. Introduction

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

In order to overcome these problems, many investigations have been reported.$^{15}$–$^{17}$ Morphology control and preparation of titania-based materials are two very effectual strategies.$^{18}$ One of the most efficient ways is to coat TiO$_2$ in form of a layer on surface of core materials with high surface area, such as ZrO$_2$, MoO$_3$, Fe$_2$O$_3$ and SiO$_2$.$^{19,20}$ Silica is one of the best core materials for its well-known surface chemistry, absorption capacity, controllable preparation and it can be easily eliminated.$^{21}$ Another is to synthesize TiO$_2$ with different morphologies and microstructures to enhance the surface area of the semiconductor. Many new morphologies of TiO$_2$ were synthesized in the past years, such as nanotubes, nanorods, and hollow spheres, etc.$^{22}$ The synthesis of TiO$_2$ hollow nanosphere is especially concerned for its large surface area, low density, and high light-harvesting efficiency.$^{23}$–$^{25}$

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, TiO$_2$ photocatalyst possesses the function of air purification. Despite of good photocatalytic activities, 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 $\mu$W cm$^{-2}$, which is one thousand times low to the sunlight.$^{26}$ 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 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, TiO$_2$ powder grafted by Cu$^{2+}$ ions was found to be sensitive to visible light by Irie and his co-workers,$^{27}$ which lighted up the hope to TiO$_2$ on its applications in daily life. They studied the photocatalytic activity of Cu/TiO$_2$ under visible light irradiation. Huang $et$ $al.$ prepared the CuO/ TiO$_2$ by the deposition–precipitation (DP) and investigated its catalytic behavior.$^{28}$ Also, Gnanasekaran $et$ $al.$ did many research to expand the absorption of TiO$_2$ to the visible light range for improving the photocatalytic efficiency.$^{29,30}$ Although photocatalytic efficiency of 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 TiO$_2$ hollow spheres as the carrier of loading copper, and study their catalytic activities by degradation of acetaldehyde gas.
In this paper, TiO$_2$@SiO$_2$ core–shell nanosphere was prepared by using silica gel nanosphere as hard template, and TiO$_2$ hollow nanosphere was obtained after SiO$_2$ was etched by NaOH solution with a certain concentration. Cu$^{2+}$ ions were adsorbed and Cu$_x$O was formed on the surface of the TiO$_2$ hollow nanosphere to enhance separation of the photo-generated charge carriers. Four kinds of photocatalysts, TiO$_2$@SiO$_2$ nanosphere, TiO$_2$ hollow nanosphere, Cu$_x$O–TiO$_2$@SiO$_2$ nanosphere and Cu$_x$O–TiO$_2$ hollow nanosphere, were synthesized. The catalytic activities of these catalysts were studied by degradation of acetaldehyde under UV and visible-light irradiation. The results indicate that all catalysts have good catalytic activities in degradation under visible-light irradiation, and the Cu$_x$O–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 Cu$_x$O–TiO$_2$ is used as photocatalyst, electrons in the valence band (VB) of TiO$_2$ are stimulated and directly transferred to Cu(n) to form Cu(n$^-$), as well as holes (h$^+$) in the VB of TiO$_2$. Also the adsorbed O$_2$ on the surface can capture the electrons in VB of TiO$_2$, but it is harder than that of Cu(n). Thus, the energy to separate electrons and holes becomes low, which narrows the band gap of TiO$_2$ and enlarges the absorption edge from UV-light to visible-light region. The holes produced in VB of TiO$_2$ decompose organic substances.

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

Tetraethoxysilane (TEOS, ≥99%) and copper chloride dihydrate (CuCl$_2$·2H$_2$O, AR) were purchased from Sinopharm Chemical Reagent Company (in Shanghai, PR China). Tetraethoxy titanium (C$_6$H$_{18}$O$_{4}$Ti, ≥98%) was purchased from Aladdin Industrial Corporation (in Shanghai, PR China). 1-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 4000–400 cm$^{-1}$ with 2 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) at 15 kV, a J-2010 high resolution transmission electron microscope (HRTEM, made in Japan) and a Tecnai G$^2$ 20S-TWIN transmission electron microscope (TEM, made in USA) 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 Cu K$\alpha$ radiation ($\lambda = 0.15406$ nm, scanning speed = 10° min$^{-1}$). 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 °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 was obtained by Perkin Elmer Lambda 900 UV-Vis spectrophotometer (made in Germany) in range of 220–800 cm$^{-1}$. X-ray photoelectron spectroscopic (XPS) analysis was measured on Shimadzu ESCA-250 and ESCA-1000 spectrometers (made in Japan) with 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 ~0.8 nm.

2.2. Synthesis of TiO$_2$@SiO$_2$ nanosphere

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

TiO$_2$@SiO$_2$ with core–shell structure was compositored via sol-gel method. Primarily, the as-prepared 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 TiO2@SiO2 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 TiO2 hollow nanosphere
The silica template was removed by immersing TiO2@SiO2 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.

The Cu2O–TiO2 hollow nanosphere and Cu2O–TiO2@SiO2 nanosphere were prepared by an impregnation method using CuCl2·2H2O as source of Cu2+ ions. 1.0 g of TiO2 hollow nanosphere (or TiO2@SiO2 nanosphere) was added into 10 mL distilled water in a vial reactor. Different amounts of CuCl2·2H2O (mass percents of Cu2+ relative to TiO2 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%-Cu2O–TiO2 hollow nanosphere, 0.5%-Cu2O–TiO2 hollow nanosphere and 1.0%-Cu2O–TiO2 hollow nanosphere, respectively; or 0.25%-Cu2O–TiO2@SiO2 nanosphere, 0.5%-Cu2O–TiO2@SiO2 nanosphere and 1.0%-Cu2O–TiO2@SiO2 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 O2 (20%)/N2 gas to remove carbon dioxide from the system, and the relative humidity of atmosphere inside the vessel was controlled to 45% by passing the O2/N2 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. The crystal phases of TiO2 largely determines their suitability for photocatalytic activities.
diffractions from anatase TiO$_2$ are observed, and all the diffractions are stronger than the corresponding diffractions in Cu$_x$O–TiO$_2$@SiO$_2$ nanosphere. Also the diffractions associated with Cu$_2$O at 27.5° and 42.3° on the surface of TiO$_2$ hollow nanosphere are found (Fig. 4B). All the results indicate that Cu$_x$O was attached to the surface of TiO$_2$, and the diffraction intensity from Cu$_2$O increases with its content. Elemental mapping analysis of the sample Cu$_x$O–TiO$_2$ hollow nanosphere (shown in Fig. S1 in the ESI†) indicates that the Cu element distributed uniformly though its content on TiO$_2$ surface was little.

Nitrogen adsorption–desorption isotherms of TiO$_2$@SiO$_2$ and 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 TiO$_2$@SiO$_2$ nanosphere and TiO$_2$ hollow nanosphere own surface areas of 251 m$^2$ g$^{-1}$ and 402 m$^2$ g$^{-1}$, pore volumes of 0.613 cm$^3$ g$^{-1}$ and 0.983 cm$^3$ g$^{-1}$, respectively. These parameters are far more than those of P25 (49 m$^2$ g$^{-1}$ of surface area and 0.090 cm$^3$ g$^{-1}$ of pore volume), a kind of commercial 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$_{1/2}$ and Ti 2p$_{3/2}$. No obvious differences were observed between the two spectra of TiO$_2$ and 0.5%-Cu$_x$O–TiO$_2$ hollow nanospheres, which indicate that Cu$_x$O was deposited on the surface of 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 Cu$_2$O.$^{27}$ Mole ratio of Cu$^+$ to Cu$^{2+}$ is about...
1.6 : 1, which calculated from the peak area in Fig. 6B. In process of the reaction, the hydrated Cu$^{2+}$ ions were firstly adsorbed on the surface of TiO$_2$ hollow nanospheres. Some of Cu$^{2+}$ ions were hydrolyzed to Cu(OH)$_2$ in this system, and later they were changed into CuO under a certain temperature ($110 \degree \mathrm{C}$). Due to the semiconductive property, the electron–holes in TiO$_2$ would be separated under illumination of UV-light in the sunshine, and the electrons separated would be transferred to Cu(II) to form Cu$_2$O.

UV-Vis absorption spectra (shown in Fig. 7) indicate that all the samples, including TiO$_2$@SiO$_2$ nanosphere, TiO$_2$ hollow nanosphere, Cu$_x$O–TiO$_2$@SiO$_2$ nanosphere and Cu$_x$O–TiO$_2$ hollow nanosphere, have the intrinsic interband absorptions of TiO$_2$ at about 400 nm. The weak absorptions in range of 400–500 nm are assigned to the interfacial charge transfer in Cu$_x$O–TiO$_2$@SiO$_2$ nanosphere and Cu$_x$O–TiO$_2$ hollow nanosphere. In addition, the absorptions from 600 to 800 nm in the spectra of Cu$_x$O–TiO$_2$@SiO$_2$ nanosphere and Cu$_x$O–TiO$_2$ hollow nanosphere are assigned to the intrinsic excitation band of Cu$_x$O and the d–d transition of Cu(II).[^33]

[^33]: Sequence of absorption intensities in range of 500–800 nm of the relative materials is TiO$_2$@SiO$_2$ nanosphere < TiO$_2$ hollow nanosphere < Cu$_x$O–TiO$_2$@SiO$_2$ nanosphere < Cu$_x$O–TiO$_2$ hollow nanosphere, indicating that the Cu$^{2+}$ ions on the surface of 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.
element in the composite materials, especially to TiO₂ 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 CO₂ 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 CO₂ generated at the same time. Fig. 8 and 9 display the degradation of acetaldehyde and the generation of CO₂ in the systems under UV-light and visible-light irradiations, respectively. As shown in Fig. 8, the catalytic performance of TiO₂ hollow nanosphere was superior to TiO₂@SiO₂ nanosphere. Also it was found that the content of copper on the surface of TiO₂ affected the activities of catalysts deeply. The catalytic efficiency of 0.5%-CuO–TiO₂ hollow nanosphere is higher than that of 0.25%-CuO–TiO₂ 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 CuₓO–TiO₂@-SiO₂ 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 CO₂. In the system of 0.5%-CuₓO–TiO₂ hollow nanosphere, about 99.72–99.74% acetaldehyde was degraded without any light irradiation.
after 60 minutes. Some data relating to degradation efficiency of acetaldehyde under UV-light and visible-light irradiations catalyzed by the relative catalysts are list in Tables 1 and 2. The clearance ratio is specific value of practical production and theoretical yield of CO₂.

Meanwhile, degradations of acetaldehyde irradiated under visible-light under the catalysts were studied, which are shown in Fig. 9. Little CO₂ generated from degradation of acetaldehyde under the existence of TiO₂@SiO₂ nanosphere and TiO₂ hollow nanosphere for the wide band gap of TiO₂. However in CuO–TiO₂ hollow nanospherical systems, acetaldehyde could be degraded to CO₂ commendably despite of the efficiencies lower than in UV-light. There is about 62.77–62.79% acetaldehyde was degraded in 0.5% CuO–TiO₂ 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% CuO–TiO₂@SiO₂ nanosphere catalytic system. Concentration of CO₂ generated in 0.5% CuO–TiO₂ hollow nanosphere system reached 241 ppm after 6 h, which is more than three times to the CO₂ generated in CuO–TiO₂@SiO₂ 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 TiO₂ are directly transferred to Cu(II) to form Cu(I), as well as holes (h⁺) in the VB of TiO₂. Thus, the energy to separate electrons and holes becomes low, which narrows the band gap of TiO₂ and prolongs the absorption edge from UV-light to visible-light.

Table 1 Initial concentration of acetaldehyde, the amount of CO₂ generated and decomposed rate of acetaldehyde after 60 minutes under UV light irradiation (THN: TiO₂ hollow nanosphere, TS: TiO₂@SiO₂)

<table>
<thead>
<tr>
<th>Sample</th>
<th>TS</th>
<th>0.25% CuO-TS</th>
<th>0.5% CuO-TS</th>
<th>1.0% CuO-ST</th>
<th>THN</th>
<th>0.25% CuO-THN</th>
<th>0.50% CuO-THN</th>
<th>1.0% CuO-THN</th>
</tr>
</thead>
<tbody>
<tr>
<td>C&lt;sub&gt;CH₃CHO&lt;/sub&gt; (ppmv)</td>
<td>193.611</td>
<td>194.139</td>
<td>181.5</td>
<td>193.842</td>
<td>180.361</td>
<td>199.796</td>
<td>193.545</td>
<td>186.103</td>
</tr>
<tr>
<td>C&lt;sub&gt;CO₂&lt;/sub&gt; (ppmv)</td>
<td>260.989</td>
<td>342.129</td>
<td>347.763</td>
<td>319.558</td>
<td>282.625</td>
<td>378.431</td>
<td>386.044</td>
<td>361.759</td>
</tr>
<tr>
<td>Decomposed rate (%)</td>
<td>67.39–67.41</td>
<td>88.10–88.12</td>
<td>95.78–95.80</td>
<td>82.42–82.44</td>
<td>78.17–78.19</td>
<td>94.69–94.71</td>
<td>99.72–99.74</td>
<td>97.19–97.21</td>
</tr>
</tbody>
</table>

Table 2 Initial concentration of acetaldehyde, the amount of CO₂ generated and decomposed rate of acetaldehyde after 6 hours under visible light irradiation (THN: TiO₂ hollow nanosphere, TS: TiO₂@SiO₂)

<table>
<thead>
<tr>
<th>Sample</th>
<th>TS</th>
<th>0.25% CuO-TS</th>
<th>0.5% CuO-TS</th>
<th>1.0% CuO-ST</th>
<th>THN</th>
<th>0.25% CuO-THN</th>
<th>0.50% CuO-THN</th>
<th>1.0% CuO-THN</th>
</tr>
</thead>
<tbody>
<tr>
<td>C&lt;sub&gt;CH₃CHO&lt;/sub&gt; (ppmv)</td>
<td>197.620</td>
<td>179.355</td>
<td>180.328</td>
<td>183.991</td>
<td>174.042</td>
<td>178.035</td>
<td>192.159</td>
<td>200.409</td>
</tr>
<tr>
<td>C&lt;sub&gt;CO₂&lt;/sub&gt; (ppmv)</td>
<td>50.635</td>
<td>71.583</td>
<td>74.029</td>
<td>62.534</td>
<td>71.488</td>
<td>205.675</td>
<td>241.276</td>
<td>168.007</td>
</tr>
</tbody>
</table>
region. The holes produced in VB of TiO₂ decompose organic substances. The catalytic degradation mechanism of acetaldehyde is shown in the following equations:

\[
\begin{align*}
\text{TiO}_2 & \rightarrow h^+ + e^- \\
h^+ + H_2O & \rightarrow 'OH + H^+ \\
O_2 + e^- & \rightarrow O^{2-} \\
CH_3CHO + O^{2-} & \rightarrow CH_3CO' + HO_2^- \\
CH_3CHO + HO_2^- & \rightarrow CH_3CO^- + H_2O_2 \\
H_2O_2 + CH_3CO' & \rightarrow CH_3COOH + 'OH \\
CH_3CO^- + 'OH & \rightarrow CH_3COOH + e^- \\
CH_3COOH + 2H_2O + 8h^+ & \rightarrow 2CO_2 + 10H^+
\end{align*}
\]

Due to the larger surface area and more exposed active sites, the catalytic activity of Cu₃O⁻-TiO₂ hollow nanosphere is higher than that of the catalyst Cu₃O⁻-TiO₂@SiO₂ nanosphere. Moreover, the separation of electrons and holes became easier with Cu²⁺ increased on the surface of TiO₂, and superior catalytic activity of the catalyst was exhibited.

4. Conclusions

In summary, four kinds of photocatalysts, TiO₂@SiO₂ nanosphere, TiO₂ hollow nanosphere, Cu₃O⁻-TiO₂@SiO₂ nanosphere and Cu₃O⁻-TiO₂ hollow nanosphere, were synthesized. All the materials were found to have good photocatalytic activities in degradation of acetaldehyde under UV-light irradiations. Compared with TiO₂@SiO₂ nanosphere, TiO₂ hollow nanosphere and Cu₃O⁻-TiO₂@SiO₂ nanosphere, Cu₃O⁻-TiO₂ hollow nanosphere was superior for being used as catalyst in degradation of acetaldehyde under visible-light irradiation. The impregnated Cu²⁺ ions on the surface of TiO₂ hollow nanosphere were possibly to enhance the separation of photo-generated charge carriers.

Conflict of interest

The authors declare no competing financial interest.

Acknowledgements

We thank the projects of National Natural Science Foundation of China (No. U1362113 and No. 21521005) and the PetroChina Co. Ltd. For financial support.

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