Synthesis and characterization of nano-CuO and CuO/TiO₂ photocatalysts

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Abstract

CuO nanocrystals were prepared by thermal decomposition of Cu-oxalate at 400 °C; then CuO/TiO₂ core/shell nanocrystals were formed via the hydrolysis of titanium isopropoxide (TIP) on the surface of CuO nanocrystals. The characteristics of the synthesized nanocrystals were systematically studied using appropriate techniques, namely the morphology by using scanning electron microscopy (SEM), and the crystalline structure by x-ray powder diffraction (XRD) and Raman spectroscopy. The structure, shape and size of the CuO and CuO/TiO₂ nanocrystals could be tuned by changing various technological parameters: (i) the reaction/growth time (from several minutes to several hours), (ii) reaction temperature (from room temperature to 90 °C) and (iii) the molar ratios of the precursors. The results showed that the reaction temperature and the molar ratio of the precursors play important roles in controlling the morphology and size of both CuO and CuO/TiO₂ nanocrystals. With increasing reaction temperature, nano-CuO evolved from spherical shaped nanoparticles to microspheres. By shelling the large-bandgap TiO₂ layers on CuO nanocrystals, the core/shell structure is formed and the narrow-bandgap nano-CuO core is expected to be resistant to photocorrosion.

Keywords: CuO/TiO₂ core/shell nanocrystal, hydrolysis method, photocatalysts

Classification numbers: 2.03, 4.03, 5.07

1. Introduction

The oxides of transition metals are an important class of semiconductors and have been intensively studied because of their special properties for potential applications, such as for solar cells, electronics and photocatalysis [1–4]. Among various oxides of transition metals, copper oxides have attracted considerable attention due to their interesting photochemical and photomagnetic properties. Copper oxides (CuₓO) can exist in different stoichiometries and phases such as Cu₂O and CuO, which has a narrow bandgap energy in the range from 1.2 to 2 eV. CuO has been widely exploited for various applications such as photocatalysts, sensors, lithium ion electrode materials, optical switches and field-emission emitters. On the other hand, due to their shape- and size-dependent properties, one needs to consider the precise controllability of copper oxide chemical composition, size, shape and surface chemistry to obtain its chemical and physical properties as desired. Many recent efforts have been devoted to the synthesis of copper oxide nanostructures with various morphologies, such as particles [5–8], hollow spheres [1, 9], rods [10, 11], tubes [12], wires [13, 14] and flowers [15]. Different methods have been used to synthesize copper oxides, such as using templates, microwave-assistance, thermal decomposition and sonochemical and hydrothermal reactions. Moreover, these copper oxides are all visible-light-active and with the TiO₂ shelling they are expected to be resistant to the photocorrosion of the narrow-bandgap copper oxide core nanocrystals and to dramatically improve the charge separation efficiency and photoactivity by forming a heterojunction structure between TiO₂ and CuO, making them more useful in the fields of photosynthesis and pollutant treatment. Most studies have focused on CdS(Se, Te)/TiO₂ [16–18] or
ZnO(Cu₃O)/TiO₂ [19, 20] and have significantly improved the photocatalytic activity in the visible region. However, the synthesis techniques are usually complicated which makes the cost of the products higher. Therefore, it is necessary to develop CuO/TiO₂ heterojunctions at a large scale by cost-effective routes and enhance the charge separation efficiency and visible light photocatalytic activity for pollutant treatment and H₂ production applications.

In this report we present the results of the synthesis of CuO nanocrystals using the 400 °C thermal decomposition of stock Cu–oxalate prepared from Cu(NO₃)₂ and oxalic acid (OA), and the CuO/TiO₂ core/shell structure using the hydrolysis of titanium isopropoxide (TIP) on the surface of CuO nanocrystals. By controlling the technological parameters, such as the Cu : OA molar ratio and the reaction time/temperature of the Cu–oxalate formation process, we were able to obtain CuO nanocrystals with different shapes and sizes. Among the technological parameters, the reaction temperature and Cu:OA molar ratio are determined to be the key factors in controlling morphology and size.

2. Experimental

2.1. Materials

Copper nitrate tri-hydrate (Cu(NO₃)₂·3H₂O, 99%), OA (H₂C₂O₄, 98%), TIP (97%) and acetylacetone (98%) of analytical reagent quality were purchased from Sigma-Aldrich; absolute technical grade ethanol (Merck) and distilled water were used in preparing and cleaning the samples. All chemicals and solvents were used as received without further purification.

2.2. Synthesis of CuO nanocrystals

The synthesis of the CuO nanocrystals was formed by thermal decomposition of Cu–oxalate, which was prepared by precipitation of Cu(NO₃)₂ with OA in aqueous solution. The CuO powders of different sizes and shapes were synthesized by controlling technological parameters (such as the reaction temperature/time, Cu:OA molar ratio and initial concentration of the copper precursor) for fabricating Cu–oxalate. In a typical synthesis, 1.4493 g (6 mmol) Cu(NO₃)₂·3H₂O was dissolved in 40 ml of distilled water to form a blue solution in a three-neck flask. Subsequently, 0.3782 g (3 mmol) of OA was dissolved in 40 ml distilled water and formed a colorless solution which was injected into the flask containing Cu²⁺ precursor at room temperature and stirred vigorously. The mixture gradually changed into a cyan suspension over a few minutes. Then this reaction solution was stirred at room temperature for 10 minutes. The cyan precipitate was collected by centrifugation and washed several times with distilled water and ethanol. Next, the product was dried at 60 °C in air for 8 h. Finally, the obtained copper oxalate was calcined at 400 °C for 3 h to eliminate the residual particles and cooled down to room temperature naturally.

2.3. Synthesis of CuO/TiO₂ core/shell nanocrystals

To obtain CuO/TiO₂ core/shell nanocrystals, the precipitated CuO core nanoparticles (0.6 mmol) were dispersed in absolute ethanol (60 ml) at room temperature. After dispersion, the mixture solution of 1 ml TIP and 3 ml acetyl-acetone was quickly injected into the reaction flask containing the core nanocrystals at pH 5, which was controlled by dilute nitric acid. Subsequently, ethanol–water (50 ml, volume ratio = 6 : 1) solution was added dropwise to the above CuO–TIP with a dropping rate of 2 ml min⁻¹. After being stirred at room temperature for 5 h, the green black CuO/TiO₂ core/shell precipitate was collected by centrifugation and carefully washed several times with distilled water and absolute ethanol and dried at 60 °C in air for 8 h. Finally, the CuO/TiO₂ core/shell products were calcined at 400 °C for 3 h to eliminate the residual particles and cooled down to room temperature naturally.

2.4. Synthesis of CuO/TiO₂ nanocomposites

The synthesis of CuO/TiO₂ nanocomposites is briefly summarized as follows. First, 0.5 mmol of Degussa P25 TiO₂ powder (Aldrich analytical grade) was dispersed in 20 ml of absolute ethanol at room temperature. Next, 20 ml of Cu(NO₃)₂ 0.0125 M was added into the above TiO₂ suspension and stirred vigorously for 1 h at room temperature. Then 0.25 M NaOH was added dropwise into the reaction solution until the pH of the mixture reached 10. After being stirred at room temperature for 1 h, the black CuO/TiO₂ composite precipitate was extracted by centrifuging and rinsed several times with distilled water and absolute ethanol and dried at 60 °C in air for 8 h. The as-prepared composites were calcined at 400 °C for 3 h.

2.5. Morphological and structural characterization

Powder x-ray diffraction (XRD) patterns taken from a x-ray diffractometer (Siemens D5000) using Cu-Kα (1.5406 Å) radiation at a scan rate of 0.04° 2θ s⁻¹ were used to identify structural phases as well as to determine the particle size by using the Scherrer equation in which the full-width-at-half-maximum (FWHM) values of the diffraction peaks were corrected with the instrumental response. The micro-Raman measurements were performed at room temperature using the 632.8 nm line of a He–Ne laser as the excitation source. The spectra were recorded using a LABRAM-1B Horiba triple monochromator coupled to a CCD detector. The morphology of the synthesized CuO and CuO/TiO₂ nanocrystals was studied with a S4800 field emission SEM (FE-SEM, Hitachi, Japan) at an accelerating voltage of 5 kV. The nanocrystal size and shape were determined directly from the SEM images and compared to the values obtained from calculations made using the Scherrer equation.

3. Results and discussion

Various technological parameters (such as the Cu : OA molar ratio, the reaction time/temperature and the initial concentration of the copper precursor) were systematically
investigated with the aim of changing the morphological (shape and size) and photocatalytical properties of the obtained CuO nanocrystals. Figure 1 shows the XRD pattern of the obtained samples from the Cu-oxalate precursors prepared with a Cu:OA molar ratio of 2 : 1 at the different temperatures for 10 min. The strong and sharp diffraction peaks indicate the high crystalline quality of the samples. It can be seen that all the indexed diffraction peaks in the XRD pattern show the presence of monoclinic CuO (space group: C2/c) with lattice constants $a = 4.69$ Å, $b = 3.42$ Å.
and \( c = 5.13 \, \text{Å} \), which is in good agreement with the literature values for the bulk CuO (JCPDS 41–0254). No crystalline impurity peaks were observed, indicating the high purity of the product, which was obtained at room temperature (curve (a) in figure 1). The average crystalline size is calculated to be 21 and 14 nm using the Scherrer formula for the (002) and (111) planes, respectively, consistent with the corresponding SEM image of the CuO nanocrystals (see figure 2(b)). However, curve (b) in figure 1 displays the XRD pattern of the sample obtained at 75 °C, indicating both the monoclinic CuO and cubic Cu$_2$O phases (JCPDF 5-0667) exist. The average crystalline sizes of CuO and Cu$_2$O in the composite product are estimated for the main diffraction peaks of CuO (111) and Cu$_2$O (111) planes and the corresponding results are \( \sim 25 \) and 29 nm, in good accordance with the SEM image (figure 2(d)). When increasing the reaction temperature to 90 °C, the obvious decrease of the FWHM of the diffraction peaks indicates an increase in the size of CuO nanocrystals. In addition, the intensity ratio of the diffraction peaks of the Cu$_2$O (111) and CuO (111) planes increased significantly with reaction temperature, implying that the predominant formation of Cu$_2$O from the Cu–oxalate precursor occurs at higher temperature. This can be explained as OA has a double role in the nucleation and growth process of the Cu–oxalate compound: (i) as the precursors undergo the exchange ion reaction resulting in the formation of Cu–oxalate; (ii) as a reducing agent (Cu$^{2+}$ to Cu$^+$). Therefore, at higher temperatures the role of OA as the reducing agent was markedly increased, leading to the formation of Cu$_2$O with a large scale (inset figure 1).

![Figure 3](image-url)
The morphology of the products was investigated by SEM. Figure 2 displays the SEM images of the obtained CuO sample from thermal decomposition of the Cu–oxalate precursor with the Cu : OA molar ratio of 2 : 1 at different reaction temperature for 10 min. From the SEM images, we see that at room temperature and 75 °C, the synthesized copper oxides are nearly spherical nanoparticles with average diameters around 20 and 25 nm, respectively (figures 2(b) and (d)). These CuO nanoparticles are aggregated to produce the microsphere particles with a diameter in the range of 1.5–3 µm (figures 2(a) and (c)). Higher temperature promotes the reaction to happen quickly, leading to an increase of both CuO nanoparticle and microsphere size.

The change of reaction time, the Cu : OA molar ratio and the initial copper concentration for fabricating Cu–oxalate precursors did not affect the structural characteristics but could significantly affect the size and the shape of the obtained products. With a prolonged reaction time not only larger quantities of product are formed but also their mean size increases. In our experiments, the Cu : OA molar ratio and reaction temperature were kept to be constant at 2 : 1 and room temperature, respectively, while the reaction times were changed in the range of 5–60 min. For the Cu–oxalate precursor with the 5 min reaction, the CuO nanocrystal size was in the range of 15–20 nm. The CuO nanocrystals exhibited the tendency to combine together forming CuO microspheres with a diameter of around 2 µm. Evolution with the reaction time of the Cu–oxalate forming at room temperature indicates that with increasing reaction time, larger quantities of product aggregated to microspheres due to localized Ostwald ripening [21].

Figure 3 displays the SEM images of the samples obtained after calcinations of Cu–oxalate, which was prepared at room reaction temperature for 10 min with varied Cu : OA molar ratios. From the SEM images, we see that the CuO crystals do not seem to change in size with changing Cu : OA molar ratio (inset figures 3(a) and 3(f)), however, the size and shape of aggregated CuO crystals changes remarkably (figure 3). With a lower Cu : OA molar ratio (such as 0.5 : 1, 1 : 1 and 2 : 1), the products were formed mainly in the aggregated CuO microsphere shape, accompanied by an increase of mean size in the range of 2–3 µm; while with the higher Cu : OA molar ratio (Cu-rich, such as 3 : 1, 5 : 1 and 10 : 1) the products were not only transformed gradually from microsphere to cubic but the size also decreased (figure 3).

Figure 4 displays the XRD patterns of the CuO/TiO2 core/shell nanocrystals and CuO/TiO2 nanocomposites. As shown by curve (b) in figure 4, all the diffraction peaks could be indexed to the monoclinic CuO phase and the peaks corresponding to the anatase and rutile TiO2 phases, implying that CuO/TiO2 nanocomposites were produced [22]. After growing the TiO2 shell on the CuO surface, the XRD pattern was obtained mainly in a tetragonal anatase TiO2 structure (curve (a) in figure 4). However, we did not clearly observe the XRD peaks corresponding to the CuO monoclinic phase. This is understandable because (i) the lattice constants of tetragonal anatase TiO2 are similar to those of CuO and (ii) the peaks are too broad due to the small crystal size. Further structural analysis of CuO/TiO2 core/shell structure and CuO/TiO2 nanocomposites was carried out by Raman spectroscopy. Figure 5 illustrates the Raman spectra of CuO/TiO2 core/shell structures and nanocomposites. It is clearly seen that both the spectra show four peaks at 151, 399, 519 and 636 cm$^{-1}$ (corresponding to the E_g (144 cm$^{-1}$), B_1g (399 cm$^{-1}$), B_1g (519 cm$^{-1}$) and E_g (639 cm$^{-1}$) modes of anatase TiO2 crystals, respectively [23]) and peaks at 291 and 636 cm$^{-1}$ (belonging to the A_g (296 cm$^{-1}$) and B_2g (636 cm$^{-1}$) modes of CuO crystals, respectively [24]). The results have confirmed the formation of anatase-TiO2 from the titanium isopropoxide precursor. We expect the formation of the CuO/TiO2 core/shell structure because the epitaxial process generally gives rise to the formation of TiO2 on the surface of available CuO nanocrystals.

4. Conclusion
CuO nanocrystals were prepared at a large scale with different shapes and sizes by using the 400 °C thermal decomposition of stock Cu–oxalate and controlling the Cu : OA molar ratio. The reaction of Cu(NO3)2 and OA to form Cu–oxalate depends strongly on the reaction temperature and the Cu : OA molar ratio, which influence the shape and size of the CuO nanocrystals. With increasing reaction temperature from 30 to 90 °C, the size of the CuO/Cu2O composite microspheres increases from 1.5 to 3 µm and the content of Cu2O increases. When increasing the Cu : OA molar ratio in the range of 0.5–10, the aggregated CuO microspheres were transformed gradually into cubes which are formed.
from many nanoparticles. CuO/TiO$_2$ core/shell nanocrystals were fabricated by hydrolyzing titanium isopropoxide on the surface of CuO nanocrystals and confirmed by the XRD pattern.

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