

Porous multishell
hollow Cu_2O
microspheres
experiment



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Preparation of Porous Multishell Hollow Cu₂O Microspheres and their catalytic activity in photodegradation of Rhodamine-B

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Abstract

In this study, Porous Multishell Hollow Cu₂O Microspheres were fabricated by One-Pot solvothermal method of copper(II) with glutamic acid under 160 °C. The as-prepared monodisperse Cu₂O hollow microspheres were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscope (TEM), Fourier transform infrared spectroscopy (FTIR), photoluminescence (PL), and thermogravimetry-differential thermal analysis (TG-DTA). The formation of hydroxyl radicals ($\cdot\text{OH}$) on the surface of UV-illuminated Cu₂O is probed by photoluminescence using terephthalic acid as a probe molecule. The photocatalytic activity of monodisperse Cu₂O hollow microspheres have been tested by degradation of Rhodamine B (RhB) and PL spectral changes of terephthalic acid under UV light. The results showed that the optimum amount of glutamic acid is 0.05 g and reaction time was 24 h, respectively.

1. Introduction

Transition metal oxides with different nanostructures have drawn much attention in recent years because of their fascinating applications in optoelectronics and outstanding structural flexibility combined with unique properties with potential applications.[10–17] So the transition metal oxides are an important class of semiconductors. Among these

transition metal oxides, Cuprous oxide (Cu₂O) is a p-type semiconductor material with a narrow band gap (2 eV) and a large excitation binding energy of 140 meV, it is non-toxic, inexpensive and abundant that widely used in photocatalysis, gas sensors, lithium-ion batteries, electronics, solar energy conversion, magnetic storage, and so on. To date, different Cu₂O nanostructures use capping agent or surface active agent have been synthesis, such as cetyltrimethylammonium bromide (CTAB), polyvinylpyrrolidone (PVP) and sodium dodecyl sulfate (SDS) were widely used to synthesize Cu₂O nanowires, Cu₂O nanotubes, Cu₂O nanothreads, Cu₂O nanocubes, flower-like Cu₂O, urchin-like Cu₂O, hollow Cu₂O spheres. Hollow spheres have attracted great interest because of their special properties including low density, high surface area, good surface permeability and distinct optical properties. [15] Wang's group add of cetyltrimethylammonium bromide developed a facile room temperature solution route for synthesis of double-wall Cu₂O hollow spheres. Zeng et al. [9] reported the preparation of hollow Cu₂O nanospheres from a reductive conversion of aggregated CuO nanocrystallites and the formation of CuO microspheres by a two-tiered organizing scheme. However, the poor conductivity limits Cu₂O further application.

In the present work, Porous Multishell Hollow Cu₂O Microspheres have been synthesized using one-pot solvothermal method of copper nitrate with glutamic acid under 160 °C after different hydrothermal time. Morphological, structural and optical properties and thermal behavior of the products have been identified using scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), Fourier transformer

infrared (FTIR) spectroscopy, UV-visible and NIR spectroscopy and thermogravimetry and differential thermal analysis (TG and DTA) and photoluminescence (PL). The other aim of present work is the investigation of the photocatalytic degradation of RhB under UV light radiation at ambient temperature and using of Cu₂O nanopowders synthesized with different hydrothermal time. The porous Multishell Hollow Cu₂O Microspheres exhibit a high photocatalytic activity due to the fact that Cu₂O Microspheres have a high specific surface area and a larger band gap.

2. Experimental

2.1 Synthesis of Hollow Cu₂O Microspheres

Analytical grade copper nitrate (Cu(NO₃)₂ · 3H₂O, purity: 99.5%), L-glutamic acid, and Rhodamine B (C₂₈H₃₁ClN₂O₃, purity: 99.5%) were purchased from SigmaAldrich and were used without further purification. Deionized water was used for all synthesis and posttreatment processes. In a typical synthesis, 0.645 g Cu(NO₃)₂ · 3H₂O and 0.05g glutamic acid were dissolved in 75 ml absolute ethanol stirred until Cu(NO₃)₂ · 3H₂O was completely dissolved to form a navy blue solution. After filtered with the filter paper, the filtrate was then transferred into a stainless steel autoclave with a Teflon liner of 100 ml capacity and heated at 160 °C for different time. After cooling at room temperature, the product was centrifuged, washed with deionized water and absolute ethanol several times and dried in an oven at 60 °C for 12 h.

2.2 Characterization

X-ray diffraction (XRD) was used to identify product phases and corresponding crystallite size. XRD patterns were obtained using a D8 X-ray diffractometer (Bruker AXS, German) with CuK α 1 radiation ($\lambda = 1.5406 \text{ \AA}$). The accelerating voltage, emission current, and scanning speed were 40 kV, 49 mA and 0.02 $^{\circ}/s$, respectively. Scanning electron microscopy (SEM) was performed with a S3400 SEM (Rili, Japan) at an accelerating voltage of 15 kV. Transmission electron microscopy (TEM) analysis was conducted using a Tecnai G20 microscope at an accelerating voltage of 200 kV. The Fourier transform infrared spectra (FTIR) of the samples were recorded on a Nicolet Forier 5700 spectrometer in the range of 400-4000 cm^{-1} using conventional KBr pellets. Photoluminescence (PL) spectra of the samples were measured at room temperature with a Hiachi FL4500 fluorescence spectrophotometer, with an excitation wavelength of 315 nm, the scanning speed is 1200 nm/min, and a PMT voltage of 700 V. The width of the excitation slit and emission slit was 5 nm. For thermal analysis, 10 mg of the dried Cu₂O powders was used in TG/DTA thermal analyzer (Pyris Diamond TG/DTA) at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ from 20 to 800 $^{\circ}\text{C}$ in an inert gas atmosphere.

2.3 Photocatalytic performance

Photocatalytic activity of the Hollow Cu₂O Microspheres was evaluated by the degradation RhB aqueous solution under a 15 W ultraviolet lamp at room temperature (ca. 20 $^{\circ}\text{C}$). In each experiment, 0.04 mg of the prepared powders were dispersed in 30 ml of RhB aqueous solution with a concentration of $1.0 \times 10^{-5} \text{ M}$ in a rectangle cell (52 W \times 155 L \times 30 H mm),

and the solution was placed in the dark for 30 min before illumination to ensure the establishment of an adsorption-desorption equilibrium between the photocatalyst powders and RhB. Then the solution was irradiated with a 30 mW/cm² UV light ($\lambda = 365$ nm), and during irradiation about 3 ml of the suspension was taken from the mixture at regular intervals (20 min) and centrifuged to separate the photocatalyst particles. To determine the degree of degradation the supernatant was analyzed by a UV-vis spectrophotometer (UV3010) to measure the concentration of RhB which exhibits characteristic absorption at 554 nm [11]

2.4 Analysis of hydroxyl radical ($\cdot\text{OH}$)

The formation rates of hydroxyl radicals ($\cdot\text{OH}$) on the surface of the UV-illuminated Cu₂O were performed by a photoluminescence (PL) method using terephthalic acid as a probe molecule method as follows. 0.04 g of Cu₂O powder sample was dispersed in a 30 ml of 5×10^{-4} M terephthalic acid aqueous solution with a concentration of 2×10^{-3} M NaOH in a dish with a diameter of about 9.0 cm. The experiment was carried out under UV irradiation using a 15 W ultraviolet lamp (25 cm above the dishes). The average light intensity striking on the surface of the reaction solution was about 30 mW cm⁻², as measured by a UV radiometer with the peak intensity of 365 nm. PL spectra of generated luminescent 2-hydroxyterephthalic acid (TAOH) were measured on a Hitachi FL4500 fluorescence spectrophotometer. After UV irradiation for every 15 min, the reaction solution was irradiated to measure the increase of the PL intensity at 390 nm of TAOH excited by 315 nm light.

3. Results and Discussion

3.1 XRD analysis

The crystalline structures of the as-prepared samples were examined by X-ray diffraction. Fig. 1 shows the XRD patterns of the as-prepared samples synthesized with different amounts of glutamic acid. The results illustrate that with increase glutamic acid from 0.02, 0.03, 0.04, 0.05 to 0.06 g all the samples appear the sphere Cu₂O [JCPDS No, 01-1142]. For the samples prepared with the amount of glutamic acid below 0.05 g, the intermediate product copper hydroxynitrate is dominant, but there is a amount of sphere Cu₂O found in it. The peak at $2\theta = 12.8^\circ$ corresponds to the (011) plane diffraction of the copper hydroxynitrate [JCPDS No, 03-0061], with the amount of glutamic acid increase the diffraction peak of copper hydroxynitrate become weaker to disappears and the sphere Cu₂O peaks intensities steadily become stronger, implying that glutamic acid acted as a reducing agent in the reaction process.

To investigate the growth process of porous multishell hollow Cu₂O microspheres, time-dependent experiments were studied by hydrothermal reaction. Fig. 2 shows that the products obtained at 160 °C with 0.05 g glutamic acid for 2 h are 5 µm hollow microspheres were well-crystallized but still the intermediate product copper hydroxynitrate. With increase reaction time to 24 h, the intermediate product copper hydroxynitrate complete transformed into cubic symmetry Cu₂O, no obvious diffraction peaks of impurities were observed, indicating the high purity of the synthesized products. Also the intense and sharp diffraction peaks indicate

that well crystallized Cu₂O nanocrystals can be obtained under reaction time is 24 h. But further prolongation of reaction time to 48 h resulted in the intensities of the diffraction peaks of Cu₂O are not increase significantly. It can be founded that with increase in reaction time the intensity of diffraction peaks increased, indicating the improvement in the crystallinity. [8] The diffraction peaks becomes narrower as the reaction time increased, indicating the increase in the crystallite size.

3. 2 FTIR Studies.

Fig. 4 showed the FTIR spectra of the Cu₂O samples synthesized with addition of different amount of glutamic acid in the region of 400–4000 cm⁻¹, which are relate to IR-active fundamental vibrations of Cu₂O itself and vibrations associated with surface adsorbates. The intense vibrational bands at 3000-3600 cm⁻¹ were attributed to O–H stretching vibrations and at ~1635 cm⁻¹ corresponded to H–O–H bending vibration all of surface adsorbed H₂O.[30] The bands at 3000-3600 cm⁻¹ was split into two components centered at ~3184 and ~3403 cm⁻¹, corresponding to chemically adsorbed water complexes and physically adsorbed H₂O, respectively. Besides, the IR band ~1346 cm⁻¹ and ~1652 cm⁻¹ are assigned to the surface monodentate carbonate-like (CO₃) and bicarbonate species (HCO₃) vibrational modes that because of adsorbed CO₂ from the atmosphere.

A metal oxide generally gives absorption bands below ~1000 cm⁻¹ that arises from stretching vibration mode of M–O bond. So the IR-active

fundamental vibrations of Cu₂O nanocrystals appear in 400–1000 cm⁻¹, the band at 456 cm⁻¹ and 633 cm⁻¹ are attributed to the stretching vibrations of Cu¹⁺–O bond confirm the formation of Cu₂O phase.

3. SEM and TEM images.

3.4 Mechanism for the formation of porous multishell hollow Cu₂O microspheres

The formation of porous multishell hollow Cu₂O microspheres can be explained by a self-transformation process of the metastable aggregated particles accompanied by the Ostwald ripening [11–31]. Similar mechanisms have been involved in the preparation of Cu₂O, TiO₂ and CdMoO₄ hollow spheres [31]. The formation mechanism of porous multishell hollow Cu₂O microspheres in this work is proposed as illustrated in Fig. During the Ostwald ripening process in order to reduce the higher surface energy, the crystallites at the center relocate themselves to the shell that formed the hollow structures. [14] Initially in the synthesis process, under the 160 °C hydrothermal conditions the uniform distribution of Cu²⁺ ions combine with glutamic acid to form Cu₂(OH)₃NO₃ as intermediate hollow microsphere template. The aggregated spherical particles have many voids in the surface, the reducing agent quickly through the channels in the intermediate hollow microsphere template precipitate product in the internal surface of the shell form double shells. Also the internal microsphere surface is loosely with many voids that not used up intermediate would grow third shells on the inner double shells and so on. At

last form porous multishell hollow Cu₂O microspheres. With the solvothermal time increase, glutamic acid contributed to the morphological evolution on the microstructure transformation and acted as a reducing agent the copper (Cu²⁺) reduced to copper (Cu⁺), last cuprous oxide precipitated out because it have a low solubility in ethanol.

3. 5 Photocatalytic Activity.

The photocatalytic activities of the as-prepared porous multishell hollow Cu₂O microspheres were evaluated by photocatalytic degradation of RhB dye in aqueous solution under UV light irradiation at room temperature. The RhB characteristic absorption at 554 nm was chosen to monitor the amount of RhB left during photocatalytic degradation process. Fig. 6 shows the UV-vis absorption spectrum of the RhB aqueous solution in the presence of (0.04 g) porous multishell hollow Cu₂O microspheres under UV light irradiation. For comparison, the photocatalytic activities of the Cu₂O nanoparticles synthesized were all evaluated under the same conditions. It is observed that with time extended the absorption peaks of RhB diminish gradually, indicating the photocatalytic degradation of RhB. During the whole process there is no new absorption peak appear indicates the complete photodegradation of RhB. It can be seen that the samples of use 0.05g glutamic acid at solvothermally treated time increased from 2h to 48h, the degradation rate increase from 8.43% to 35.78%. Among them solvothermally treated 24h show the best performance, which show a 55.3% decrease of RhB after 40 min UV irradiation. Based on the above experimental results, this is not surprising because of the Cu₂O band gap is

2. 17 eV and it can be excited by photons with wavelengths below 349 nm (our light source is 365 nm UV light). [P2499] Also the unique porous multishell hollow structure which can be considered as an ideal transport way for reactant and product molecules moving in or out of the photocatalyst, making the chemical reactions occurring more quickly and easily. According to the present study nanoparticles size and crystalline nature play an important role in influence the photocatalytic activity.