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Transmission electron microscopy and Raman characterization of copper (I) oxide microspheres composed of nanoparticles

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ABSTRACT

The high-resolution transmission electron microscope and Raman spectroscopy were used to investigate the microstructures and Raman scattering property of copper (I) oxide microspheres composed of nanoparticles. High-resolution transmission electron microscope images indicate that the copper (I) oxide microspheres are composed of nanoparticles with random growth direction, indicating that there are many defects in microspheres. The Raman spectrum shows that infrared active mode, which must be odd parity and is Raman forbidden for bulk crystal due to its inversion symmetry, is activated and shows up in Raman scattering spectrum. On the basis of investigations of the microstructure features of copper (I) oxide microspheres, we attribute the appearance of IR active mode in Raman scattering spectrum to the breakdown of the symmetry of the lattice due to the presence of defects in the prepared copper (I) oxide microspheres as observed in HRTEM images.

1. Introduction

Copper (I) oxide (Cu_2O) is a p-type metal oxide semiconductor with a direct band gap of ~2.17 eV and therefore exhibits unique physical and chemical properties [1–3]. For instance, it was reported that excitons could coherently propagate through single crystalline Cu_2O. Thus, it might be possible to convert photons into excitons, which then could travel through small apertures or small dimension waveguides with little loss by scattering and diffraction, while at the end of the path the excitons could be converted back into photons [4]. Recently, it has been found that Cu_2O microspheres can be used as the negative electrode material for lithium ion batteries [3]. Cu_2O could also be used as a stable catalyst for water splitting under visible light irradiation although its exact role is unclear [5]. These novel physical properties make Cu_2O a promising material in the applications of solar energy conversion, catalysis, gas sensors, and negative-electrode materials for lithium ion batteries. Therefore, synthesis and studies of physical property of Cu_2O have received a considerable attention in recent years.

Until date, different methods have been employed to synthesize Cu_2O micro- and nano-structures with well-defined morphologies. For example, multishelled Cu_2O spheres were successfully synthesized by using cetyltrimethylammonium bromide (CTAB) multilamellar vesicles as templates at room temperature [6]. Submicrometer Cu_2O hollow spheres were prepared by using a multiple emulsion (O/W/O) as the template [7]. Cu_2O hollow nanospheres were synthesized via a solvothermal route by using N,N-dimethylformamide as a reducing agent under 150–180 °C for 20–40 h [8]. In this work, we employed a facile solution phase method for large scale synthesis of Cu_2O microspheres and investigated the microstructure features and Raman scattering property of the as-prepared Cu_2O microspheres. The Raman spectrum shows that infrared (IR) active mode, which must be odd parity and is Raman forbidden for bulk crystal due to its inversion symmetry, is activated and shows up clearly in Raman scattering spectrum. We attribute the appearance of IR active mode in Raman scattering spectrum to the breakdown of the symmetry of the lattice due to the presence of defects as observed in high-resolution transmission electron microscopy (HRTEM) images of Cu_2O microspheres.

2. Material and methods

The synthesis of Cu_2O spheres was carried out at room temperature. In a typical procedure, 0.75 g of copper (II) sulfate pentahydrate ($CuSO_4{\cdot}5H_2O$) was dissolved in 200 mL water, and then 3 mL of hydrazine monohydrate ($N_2H_4{\cdot}H_2O$) solution with concentration of 10 M was added into the above solution with constant stirring. The color of the solution was gradually turned into red. After stirring for 10 min, the red precipitate was centrifuged, washed with deionized water and ethanol for several times, and then dried in a vacuum oven at 50 °C for 5 h.

X-ray powder diffraction (XRD) pattern was obtained on a Rigaku (Japan) D_{max} γ_A rotation anode X-ray diffractometer equipped with the graphite monochromatized Cu K_α radiation

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(λ = 1.54178 Å), employing a scanning rate of 0.02° s^{-1} in the 2θ range from 10 to 90°. Scanning electron microscopy (SEM) images were taken with a HITACHS-4200 scanning electron microscope. Transmission electron microscopy (TEM) images were taken with a JEM-200 CX transmission electron microscope, using an accelerating voltage of 200 kV. HRTEM was carried out on a JEOL-2010 transmission electron microscope, using an accelerating voltage of 200 kV. Laser Raman spectroscopy was obtained by using a LABRAM-HR Confocal Laser MicroRaman spectrometer at room temperature. The 633 nm line of the laser was used as the excitation sources, with the capability of supplying 250 mW.

3. Results and discussion

The crystalline structure and chemical composition of the as-prepared Cu_2O microspheres were investigated by XRD. Fig. 1 shows a typical XRD diffraction pattern of the as-prepared Cu_2O microspheres. The XRD diffraction pattern contains five peaks that are clearly distinguishable and broadened. All of the diffraction peaks can be perfectly indexed to cubic phase Cu_2O with lattice constant of a = 4.269 Å (JCPDS No. 5-666, $Pn\bar{3}m$). The peaks at 2θ values of 29.56°, 36.48°, 42.39°, 61.59° and 73.76° correspond to (1 1 0), (1 1 1), (2 0 0), (2 2 0), and (3 1 1) lattice planes of standard crystalline Cu_2O, respectively. The Cu_2O lattice constant obtained by refinement of XRD data for the as-prepared sample is a = 4.326 Å, consistent with the stand value of bulk Cu_2O crystals (JCPDS No. 5-666, $Pn\bar{3}m$). Thus the XRD result indicates that the as-prepared product is composed of pure cubic phase Cu_2O.

The morphology and size of the as-prepared products were characterized by SEM. Fig. 2 shows the SEM images of the as-synthesized Cu_2O microspheres. Low- and medium-magnification SEM images (Fig. 2a–c) clearly indicate that a large quantity of spherical particles with a narrow size distribution was achieved. An average diameter of the spheres is about 1100 nm. The high-magnification image (Fig. 2d) demonstrates that the as-prepared Cu_2O spheres are composed of small nanoparticles.

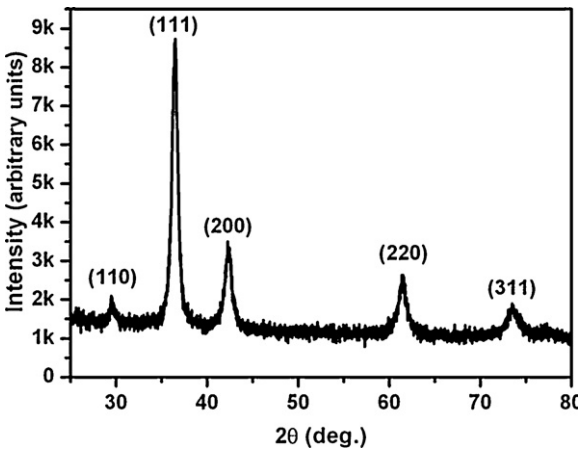

Fig. 1. XRD pattern of the as-prepared Cu_2O microspheres.

The morphology and size of the as-prepared Cu_2O microspheres were further investigated by TEM. Fig. 3a and b shows TEM images of the as-prepared Cu_2O microspheres with different magnifications. Low-magnification TEM image as indicated in Fig. 3a shows that the as-prepared product is composed of microspheres with uniform diameter of about 1100 nm, which is consistent with the observed result in SEM images. Fig. 3b is high-magnification TEM image of a single microsphere, clearly showing that the prepared

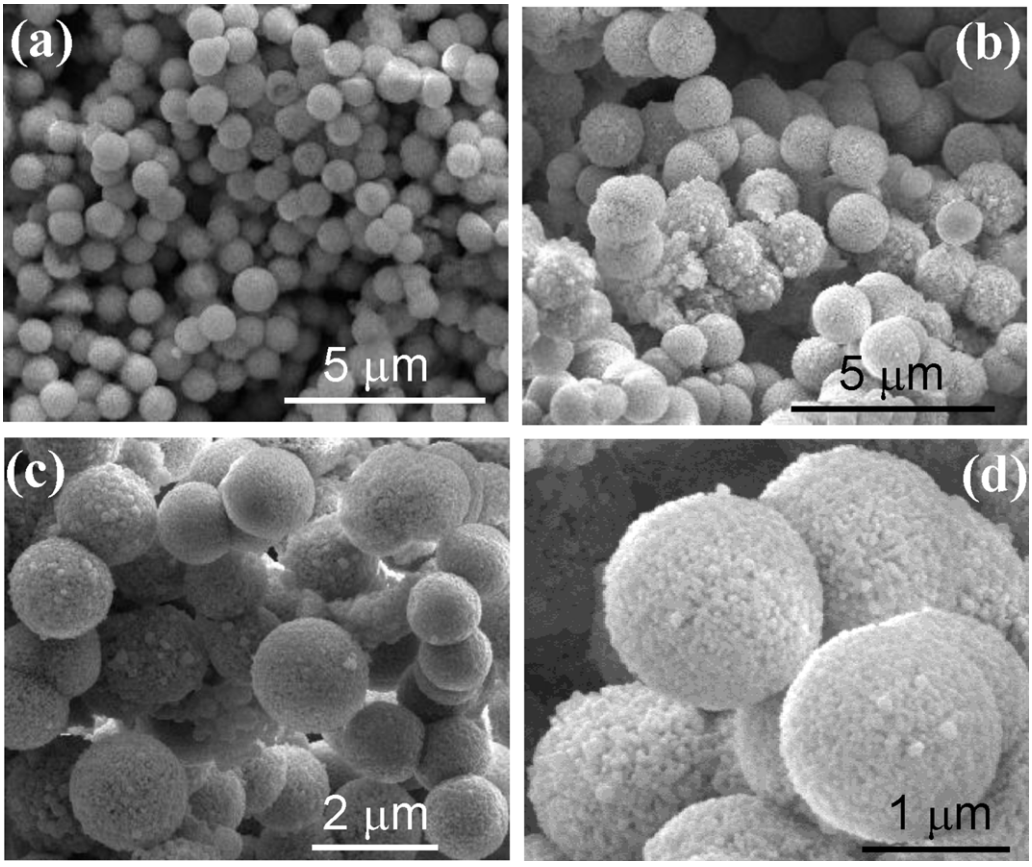

Fig. 2. SEM images of the as-prepared Cu_2O microspheres at different magnifications.