Solid-State Thermal Decomposition Method for the Preparation of CuO Nanoparticles

A. Dehno Khalaji\textsuperscript{a,}\textsuperscript{*}, K. Jafari\textsuperscript{b}, S. Maghsodlou Rad\textsuperscript{a}

\textsuperscript{a} Department of Chemistry, Faculty of Science, Golestan University, Gorgan, Iran
\textsuperscript{b} College of Chemistry, Shahrood University of Technology, Shahrood, Iran

Abstract

In this paper, CuO nanoparticles have been synthesized via solid-state thermal decomposition using copper(II) Schiff base complexes as new precursors at 600°C under air atmosphere for 3 h. Surface morphology of the products were characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and scanning electron microscopy (SEM).

1. Introduction

Recently, the preparation of transition metal oxides nanoparticles with specific size and morphology have been an increasing interest due to their properties and applications [1-7]. CuO is a well known p-type semiconductor with a narrow band gap of 1.2 eV. It has a wide range of applications as catalysis, batteries, gas sensors and transistors [8-13]. Until now, various different methods have been developed to preparation of CuO nanoparticles including hydrothermal reaction, electrochemical, thermal evaporation and decomposition [8-17]. Currently, the solid-state thermal decomposition of Schiff base complexes as new precursors is being used more and more [119-21], and as compared to conventional methods, it is much faster, economical and cleaner. Different shapes of CuO nanosized such as nanorods, nanosphere and nanowire have been synthesized by various methods [8-17].

In this study, we decided to used simple, low-cost, green and reproducible process for the
preparation of CuO nanoparticles from unsymmetric copper(II) Schiff base complexes as new precursors (Scheme 1).

\[ \begin{align*}
R1 &= H & R2 &= H & (1) \\
R1 &= CH_3O^- & R2 &= H & (2) \\
R1 &= H & R2 &= Br & (3)
\end{align*} \]

Scheme 1. Chemical structure of Cu(II) Schiff base complexes

2. Experimental

2.1. Materials and characterization

All reagents and solvents for synthesis and analysis were commercially available and used as received without further purifications. Fourier Transform Infrared spectra were recorded as a KBr disk on a FT-IR Perkin–Elmer spectrophotometer. X-ray powder diffraction (XRD) pattern of the complex was recorded on a Bruker AXS diffractometer D8 ADVANCE with Cu-Kα radiation with nickel beta filter in the range 2θ = 10°–80°. Scanning electron microscopy (SEM) images were obtained on Philips XL-30ESEM. All complexes were synthesized from Cu(NO_3)_2·3H_2O following a published procedure [22,23].

2. 2. Synthesis of [Cu(salph)(Py)]NO_3 (1)

An aqueous solution of Cu(NO_3)_2·3H_2O (2.63 gr, 0.01 mol in 2 mL) was added to stirred solution of salicylaldehyde (1.22 gr, 0.01 mol) in methanol (30 mL) followed by pyridine (0.02 mol). The mixture was stirred at 50°C for 1 h, and then 1.08 g (0.01 mol in 15 mL methanol) of 1,2-phenylenediamine was dropwise added. The mixture was stirred for 12 h in air at room temperature. The dark-red solid was obtained after the solvent was evaporated slowly for several days at room temperature, then the products were collected by filtration, and dried in vacuum. FT-IR (KBr pellet, cm⁻¹): 3320, 3275 (NH_2), 1611 (C=N).

2. 3. Synthesis of [Cu(MeO-salph)(Py)]NO_3 (2)

This dark-red solid was prepared by the some procedure using 3-methoxysalicylaldehyde (1.05 g, 0.01 mol). FT-IR (KBr pellet, cm⁻¹): 3323, 3274 (NH_2), 1615 (C=N).

2. 4. Synthesis of [Cu(Br-salph)(Py)]NO_3 (3)

This dark-red solid was prepared by the some procedure using 5-bromosalicylaldehyde (2.01 g, 0.01 mol). FT-IR (KBr pellet, cm⁻¹): 3321, 3276 (NH_2), 1613 (C=N).

2. 5. Preparation of CuO nanoparticles

The complexes were loaded in to a crucible and then were placed in oven and heated at a rate of 10°C/min in air. Nanoparticles of CuO were synthesized at 500°C after 3 h, washed with ethanol and dried at room temperature. The synthesized CuO nanoparticles were characterized by FT-IR, XRD and SEM.

3. Results and discussion

Fig.1 shows FT-IR spectra of CuO nanoparticle were formed via solid-state thermal decomposition of 1 at 500°C. The peak at 531 cm⁻¹ assigned to
Cu-O stretching [12]. Existence of free precursor is ruled out due to the absence of stretching vibrations of CH, C=N and other groups of the ligand.

Fig. 1. XRD pattern of as-synthesized sample.

Figs. 2-4 show the XRD pattern (10<2θ<80) of the CuO nanoparticles obtained from copper(II) complexes 1-3, respectively. All the diffraction peaks can be indexed to pure CuO monoclinic phase [12,18]. No other impurities were detected by XRD analysis, indicating the phase purity of CuO nanoparticles.

Fig. 2. XRD pattern of CuO prepared from 1.

Fig. 3. XRD pattern of CuO prepared from 2.

Fig. 4. XRD pattern of CuO prepared from 3.

The SEM images of the CuO nanoparticles were taken (Figs. 5-7, respectively) and confirm the spherical morphology of CuO nanoparticles.

Fig. 5. SEM image of CuO prepared from 1.

Fig. 6. SEM image of CuO prepared from 2.

Fig. 7. SEM image of CuO prepared from 3.
4. Conclusion
In summary, we have successfully prepared spherical CuO nanoparticles by solid-state thermal decomposition. This method is facile, inexpensive, nontoxic and can be extended for preparation of other transition metal oxide nanoparticles.

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References