



Research Article

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Synthesis and characterization of Cu_2BaO_4 nanoparticles from thermolysis of $[\text{Cu}(\text{Opd})_3]_2[\text{Ba}(\text{SCN})_6(\text{H}_2\text{O})_2]$ complex

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ABSTRACT

In this investigation, we report synthesis of new Copper - Barium complex. This compound has been characterized using FT-IR and UV-Vis spectroscopy. The electrochemical properties of compound have also been investigated by cyclic voltammetry and the complex shows irreversible redox behavior. Also in this study we report facile synthesis of Copper-Barium nanocomposites oxide under thermal decomposition, using $[\text{Cu}(\text{Opd})_3]_2[\text{Ba}(\text{SCN})_6(\text{H}_2\text{O})_2]$ precursor complex. Characterization of Copper-Barium Oxide nanocomposites was carried out by scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX), X-ray powder diffraction (XRD) and Fourier transform infrared (FT-IR) spectroscopy. The X-ray diffraction pattern at room temperature revealed that, highly pure and crystallized Cu_2BaO_4 with tetragonal structure.

Keywords: electrochemical properties, nanocomposite, thermal decomposition, scanning electron microscopy

INTRODUCTION

The unique properties of nano-sized metal oxides accelerate wide activities of research and open a series of technical applications, for instance in electronics, optics and catalysis¹. Current research interest in inorganic nanomaterials synthesis has focused more on controlling and tailor- making materials into nanoparticles, nanorods, nanotubes, nanoplates, etc. with the aim of streamlining their applications and efficiency^{2,3}. Among them, nanoparticles have been prepared by various physical and chemical techniques such as combustion method, microwave irradiation, hydrothermal, solvothermal method, sol-gel process, chemical spray pyrolysis, sonochemical method, polyol method, and so on⁴⁻¹⁸. Most of these methods need some special instruments, harsh conditions, and relatively high processing temperature higher than 350°C. In addition, these methods are either time-consuming or require expensive instruments. Among various soft chemical methods for preparing nanoscale materials, the thermal decomposition method is widely used due to the process simplicity¹⁹⁻²¹. This technique offers several unique advantages over other methods including easy work-up, low temperature processing, short reaction time, and production of inorganic nanomaterials with narrow size distribution.

In this work, we wish to describe the thermal decomposition of the $[\text{Cu}(\text{Opd})_3]_2[\text{Ba}(\text{SCN})_6(\text{H}_2\text{O})_2]$ complex, which resulted in the synthesis of Cu_2BaO_4 nanoparticles at 800°C temperature. The product was identified by various instrumental techniques such as X-ray diffraction (XRD), Fourier transform infrared (FT-IR), energy-dispersive X-ray spectroscopy (EDS) and Scanning electron microscope (SEM). This approach provides a one-step, simple, general, and inexpensive method for the preparation of the Cu_2BaO_4 nanoparticles.

EXPERIMENTAL SECTION

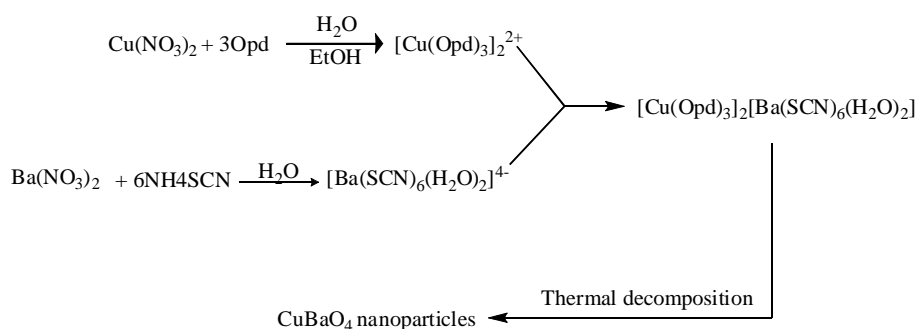
Materials and physical measurements

The raw materials used in this work were of purities above 99%, therefore no further purification was required. All solutions were prepared with double distilled deionized water. Elemental analyses (C,H,N) were determined on an Heraeus rapid analyzer. Fourier transform infrared (FT-IR) spectra were recorded using Bruker tensor 27 spectrophotometer in a KBr matrix. UV-Vis spectra were recorded on a JASCO V-570 spectrophotometer. The redox properties of the complexes were studied by cyclic voltammetry. Cyclic voltammogram was recorded by using a SAMA 500 Electro Analyzer. X-ray powder diffraction (XRD) measurements were performed using an X'pert diffractometer of Philips Company with graphite monochromatic Cu K α ($\lambda = 0.15418$ nm) radiation at room temperature in the 2θ range of 10-60°. The samples were characterized by using scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) techniques (Philips XL30) with gold coating. Conductivity measurements were performed using a WTW-F2000.

Preparation of [Cu(Opd) $_3$] $_2$ [Ba(SCN) $_6$ (H $_2$ O) $_2$] (1) complex

For the synthesis of this complex, the cations and anions were prepared separately and then added together and final product was obtained. The cationic section [Cu(Opd) $_3$] $_2^{2+}$: To a solution of Copper nitrate (0.555 g, 2 mmol) in double distilled deionized water (50 mL) was added a solution of O-phenylenediamine (0.746g, 6mmol) in Ethanol (10 mL) and the mixture was stirred at 60 °C for 12hour to give a dark-brown solution.

The anionic section [Ba(SCN) $_6$ (H $_2$ O) $_2$] $^{4-}$: To a solution of Barium nitrate (0.261 g, 1 mmol) in double distilled deionized water (50 mL) was added a solution of Ammonium thiocyanate (0.457g, 6 mmol) in H $_2$ O (10 mL) and the mixture was stirred at room temperature for 12 hour to give a clear solution. Then to a solution of [Cu(Opd) $_3$] $_2^{2+}$ was added a solution of [Ba(SCN) $_6$ (H $_2$ O) $_2$] $^{4-}$ and the mixture was stirred at room temperature for 24 hour to give a clear-brown solution. Brown crystals of (1) were obtained by slow evaporation of solvents and kept for further characterization, yield 79%. Anal. (Scheme 1)



Scheme 1 Materials produced and synthetic methods

Preparation of Copper-Barium oxide nanocomposite

The synthesis reported here, were carried out through solid-state thermolysis in the furnace under air atmosphere. In a typical synthesis, the precursor complex(1) was placed in a ceramic boat and calcined in the furnace at 800 °C for 4h under air atmosphere. After cooling at room temperature, black products were collected.

RESULTS AND DISCUSSION

Complex (1) was synthesized by the reaction of [Cu(Opd) $_3$] $_2^{2+}$ and [Ba(SCN) $_6$ (H $_2$ O) $_2$] $^{4-}$ in double distilled deionized water/ethanol in 1:1 molar ratio. Then the complex(1) was placed in a furnace and Cu $_2$ BaO $_4$ nanocomposites were formed by thermal decomposition. The electronic spectra of the complex (1) in water (Fig.1) exhibits absorption bands at 198nm and 249nm. These bands corresponding to n \rightarrow π^* and $\pi \rightarrow \pi^*$ transitions of NCS $^-$ group and phenylenediamin ligand respectively. A moderately intense peak observed at 419 nm may be assigned to the ligand to metal charge transfer (LMCT). The broad band at 705nm attributed to $^2\text{E}_g \rightarrow ^2\text{T}_2g$ of (d-d) transition metal 22 .

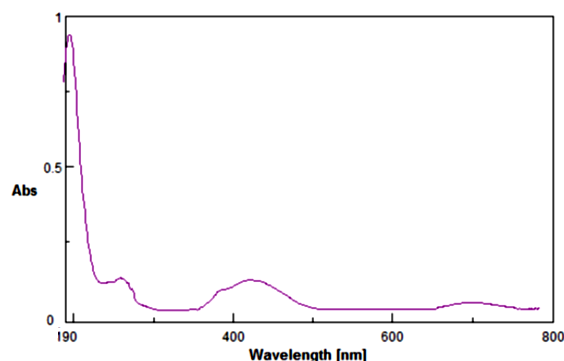


Fig. 1 UV-Vis spectra of $[\text{Cu}(\text{Opd})_3]_2[\text{Ba}(\text{SCN})_6(\text{H}_2\text{O})_2]$ complex

The cyclic voltammogram of the complex (**1**) were obtained at 25°C under an argon atmosphere in the DMF solution containing 0.1 M TBAH as supporting electrolyte and complex concentrations of 4×10^{-3} M at a glassy carbon working electrode. Ferrocene (Fc) was used as the internal standard and all redox potentials are referenced to the $\text{Fc}^{+/0}$ couple. Fig.2 shows the cyclic voltammogram of the $[\text{Cu}(\text{Opd})_3]_2[\text{Ba}(\text{SCN})_6(\text{H}_2\text{O})_2]$ complex. This compound display a irreversible oxidative response corresponding to a $\text{Cu}^{(\text{II})}/\text{Cu}^{(\text{I})}$ redox process at $E_{1/2} = 0.04$ V. Phenylenediamin ligand exhibits an irreversible wave at $E_{1/2} = -0.62$ V and a quasi-reversible wave at $E_{1/2} = -1.4$ V. The NCS^- ligand and Ba^{2+} ion are electro-inactive in the studied potential regions other was no peak for them²³.

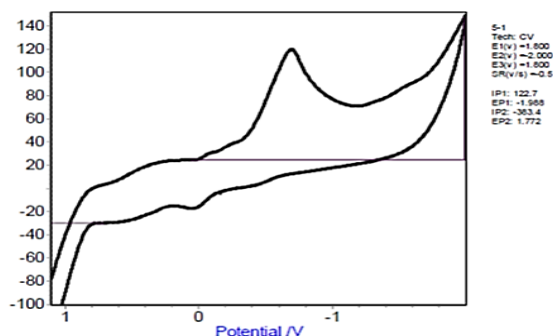


Fig. 2 Cyclic voltammogram of $[\text{Cu}(\text{Opd})_3]_2[\text{Ba}(\text{SCN})_6(\text{H}_2\text{O})_2]$ complex

The FT-IR spectrum of the $[\text{Cu}(\text{Opd})_3]_2[\text{Ba}(\text{SCN})_6(\text{H}_2\text{O})_2]$ complex and its decomposition products at different temperatures are shown in Fig.3. For the complex (Fig.3, curve a), the characteristic stretching bands of N-H, C=N and C=S groups are observed at approximately 3169 to 3341, 760, and 2067 cm^{-1} , respectively. As shown in Figure 3, curve b, the intensity of these bands decreases when the complex is heated at 800°C. At this temperature, there is absorption band at about 594 cm^{-1} , providing clear evidence for the presence of the crystalline Cu_2BaO_4 ²⁴.

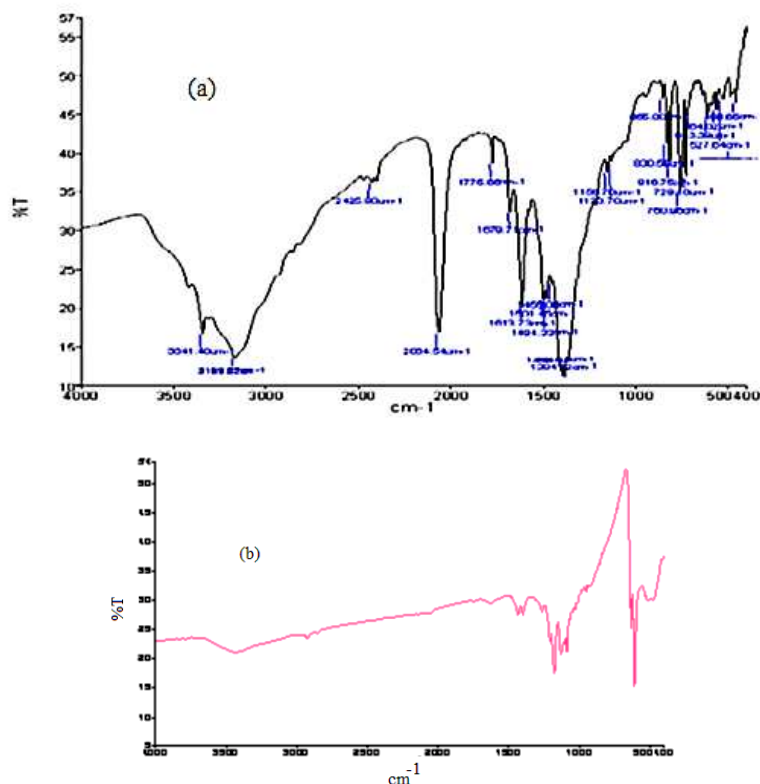


Fig. 3. FT-IR spectra of (a) $[\text{Cu}(\text{Opd})_3]_2[\text{Ba}(\text{SCN})_6(\text{H}_2\text{O})_2]$ and (b) CuBaO_4 nanocomposite

Fig. 4 shows XRD pattern for Cu_2BaO_4 nanoparticles calcinated at 800°C . It is obvious that all the diffraction peaks can be indexed to tetragonal phase Cu_2BaO_4 with $P6_3mc$ space group and lattice parameters of $a = 4.1409\text{\AA}$ and $c = 6.7198\text{\AA}$ (JCPDS file No. 42-0414). Compared with the standard diffraction pattern, no peaks of impurities were detected, indicating the high purity of the product. In addition, the intense and sharp diffraction peaks suggest the obtained product is well crystallized. The broadness of the peaks indicates the small dimensions of the produced Cu_2BaO_4 nanoparticles. Estimated from the Scherrer formula, $D = 0.89\lambda/\beta\cos\theta$, where D is the average grain size, λ is the X-ray wavelength (0.15418 nm) and θ and β are the diffraction angle and full-width at half maximum of an observed peak, respectively²⁵, upon the main peak, the average size of the particles of sample was calculated to be 52 nm which is in agreement with that observed from the SEM image.

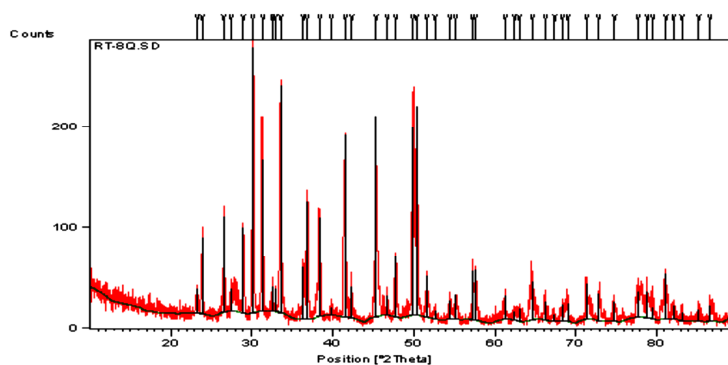


Fig. 4 XRD pattern of CuBaO_4 nanoparticles prepared by thermal decomposition of $[\text{Cu}(\text{Opd})_3]_2[\text{Ba}(\text{SCN})_6(\text{H}_2\text{O})_2]$ complex

The morphology of the Cu_2BaO_4 nanoparticles was characterized by scanning electron microscopy (SEM) and shows that it is composed of particles with sizes of about 59 nm. Fig.5, shows the SEM image of the Cu_2BaO_4 nanoparticles. As it can be seen, there is uniform nanometer scale particles with good size distribution have been observed for the nanoparticles.

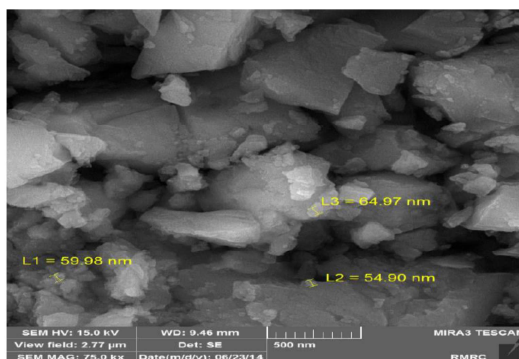


Fig. 5 SEM image of CuBaO_4 nanoparticles

To further confirm the chemical composition of the as-prepared Cu_2BaO_4 , EDAX spectrum was recorded. The very strong peaks related to Cu, Ba and O are found in the spectrum (Fig.6) and no impurity was detected.

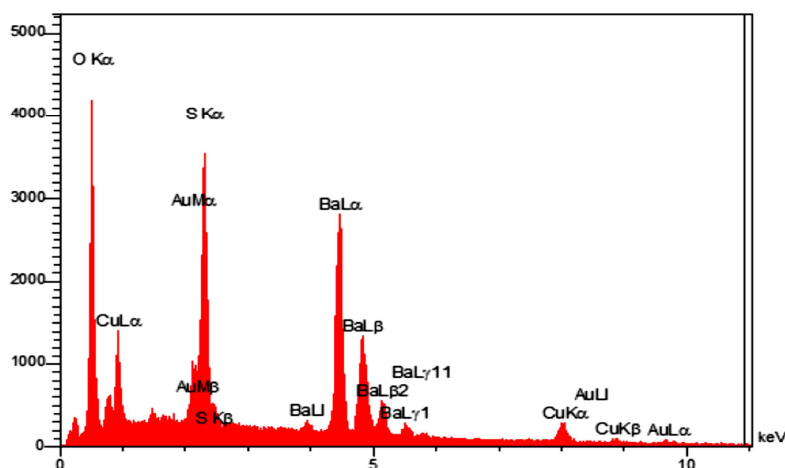


Fig. 6 EDX image of CuBaO_4 nanoparticles

CONCLUSION

In summary, we have successfully synthesized CuBaO_4 nanoparticles with the new Copper-Barium complex by thermal decomposition method. The size of the CuBaO_4 nanoparticles was measured both by XRD and SEM and the results were in very good agreement with each other. XRD reveals the phase pure formation of CuBaO_4 nanoparticles, which is further confirmed by FTIR. The Copper-Barium complex is a suitable precursor for preparation of Copper-barium Oxide nanoparticles with interesting morphologies. All results reveal that thermal decomposition method can be employed successfully as a simple, efficient, low cost, environmentally friendly and very promising method for the synthesis of nanoscale materials without a need for special conditions, such as long reaction times, and high pressure. This method may be extending to synthesize other metal nanoparticles oxide, nanowires, nanodisks and nanotubes.

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