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Synthesis and characterization of monodispersed copper oxide and their precursor powder

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ABSTRACT

Monodispersed powders of copper oxide precursor were produced in spherical and bipyramidal particle morphologies by the urea-based homogenous precipitation method. Composition of the starting reactant mixtures and synthesis conditions had significant effect on the morphology of the precipitated particles. Extensive optimization of these parameters was thus performed, in order to explore the key factors responsible for the production of monodispersed systems of the precipitated powders. It was observed that the particles obtained from the copper nitrate–urea system were spherical and amorphous copper (II) basic carbonate, while those produced in copper–chloride–urea solution were bi-pyramidal and crystalline copper (II) basic chloride. On controlled calcination at the elevated temperatures both of these compounds transformed into crystalline copper oxide powders with identical crystal structures, though with different crystallite sizes. In both cases, the particles retained their original shape integrity to a maximum extent and showed no sign of sintering.

1. Introduction

Copper oxide is a well-known *p*-type semiconductor and has got immense attention of the researchers in recent years due to its importance in various applications such as gas and glucose sensors, heterogeneous catalysts, anode in lithium–ion batteries [1], high temperature superconductors, and optical switching devices [2,3]. Copper oxide possesses a unique crystalline structure among the 3d transition metal monoxides, due to which it exhibits super-magnetic properties [4]. Similarly, Kiyuel and Chongyoup [5] employed copper oxide particles for the enhancement of heat transfer in nanofluids. During their study, they observed that besides other factors, thermal conductivity of the nanofluids was dependent upon the shape and size of the dispersed copper oxide particles in the liquid medium. Zhang, et al. [6] also reported that particle size affected the electrochemical properties of copper oxide. Jianpeng, et al. [7] successfully employed copper oxide particles for the photodegradation of various dyes of environmental concern. These researchers reported that morphology of the copper oxide particles significantly affected their photocatalytic activities. The same oxide was also used as a reductant in the cerium zirconium systems [8] as well as in the textiles industries for achieving biocidal activity [9]. In addition, Jinhual et al. [10] modified the surface of SnO_2 with copper oxide, which led to the improvement in its sensitivity towards the detection of H_2S gas.

It was generally observed in the above mentioned applications that particle morphology of the copper oxide powder had obvious effect on their physical properties. As such, there exists a need for developing methods for the production of copper oxide powder comprising particles of different morphologies. In this regard, a number of techniques, such as chemical vapor deposition, hydrothermal, sol–gel homogeneous precipitation, etc. have been developed by the researchers for the production of copper oxide particles in various shapes and sizes [11–14]. All those techniques have their merits and demerits in term of economy, ease, etc. Among these methods, urea-based homogeneous precipitation method has widely been used for the production of powders of inorganic compounds, composed of uniform fine particles in different shapes and sizes [15–21]. In this method, aqueous solutions composed of metal salt and urea are heated above 80 °C which decompose urea and generate CO_3^- and OH^- in the solution. The latter ions precipitates out the dissolved metal ions in the form of compounds composed of metal and OH^- ions in combination with either CO_3^- or anion of the metal salt, depending upon their solubility in the host solution. To our experience, this method has a great versatility as compared to other methods in terms of tailoring the particles morphology to the desired extent. In the present work, the urea-based homogeneous precipitation method is used in which copper nitrate–urea and copper chloride–urea systems were employed as the starting materials. On heating at 85 °C, these

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solutions led to the precipitation of copper basic carbonate and copper basic chloride, composed of uniform particles in spherical and bi-pyramidal shapes, respectively. Both the precipitated compounds are classified as mineral pigments [22]. On controlled heat treatment, these compounds converted into copper oxide powder and the particles kept their original shape integrity to a reasonable extent.

2. Experimental

2.1. Materials

A reagent grade urea (Scharlau), $Cu(NO_3)_2{\cdot}3H_2O$ (Scharlau), $CuCl_2{\cdot}2H_2O$ (Scharlau), and ethanol (Scharlau) were used without further purification. All the stock and working solutions were prepared in deionized distilled water. Pyrex glass vessels were used for the preparation of solutions and for carrying out the reactions. All the solutions were filtered through membrane filters to remove any possible impurities from the solutions.

2.2. Preparations of CuO precursors

Copper oxide precursor powders were produced by the homogeneous precipitation method. In this method, 100 mL of a reactant mixture, composed of 0.4 mol/L urea and 0.005–0.03 mol/L either of copper nitrate or copper chloride was heated at 85 °C for various periods of time (10–60 min) in tightly stoppered Pyrex glass vessels. Precipitated solids appeared in the homogeneous reactant mixtures, which were isolated from the mother liquors by filtration through membrane filters, washed with water and ethanol and then dried in open air.

2.3. Heat treatment

Selected batches of the as precipitated solids were heated in a programmable tube furnace (Nebertherm, M7/11) for up to 700 °C at the heating rate of 10 °C/min. The sample was kept in the furnace for 1 h and the furnace was turned off. After cooling to room temperature, the samples were removed from the furnace and stored in a desiccator.

2.4. Characterization

2.4.1. Scanning electron microscopy (SEM)

Particle morphology of the desired powder samples was analyzed with scanning electron microscopy (SEM: JSM-6490, JEOL). In each analysis, the sample was mounted on a sample stub with the help of carbon conducting tape and sputtered with gold in Auto Fine Coater (JFC-1600, JEOL) for 30 s. The stubs containing the samples were then placed in the sample chamber of the SEM. After evacuating the machine according to the standard procedures, the samples were investigated for their particles morphology. The distance of the sample from the tip of electron gun and the accelerating voltage were adjusted to 10 mm and 15 kV, respectively.

2.4.2. Fourier transform infrared spectrometry (FTIR)

Selected samples of the as-precipitated and calcined powders were analyzed with fourier transform infrared spectrometry (Schimadzue, IRprestige-21, FTIR-8400). For this purpose, appropriate amount of the powder was ground and mixed with IR grade potassium bromide using pistol and mortar. A small amount of this sample was transferred to sample cup of the Diffuse Reflectance Accessory (DRS-8000A) and then scanned in the region of 4000–400 cm^{-1}.

2.4.3. X-ray diffractometry (XRD)

Crystallinity of the desired powder samples was evaluated with X-ray diffractometry (XRD, JEOL JDX-3532) using CuK_α radiations. The scanning range for the sample was 2θ of 10–80°. The step angle was 0.05° and scan speed was 0.1°/s. The software, JDX-3500 was used to find out the crystalline phases in the sample.

2.4.4. Thermogravimetric/differential thermal analysis (TG/DTA)

Thermal analyses of the selected samples of the copper oxide precursor powders were performed by using thermogravimetric differential thermal analyzer (Diamond TG/DTA, PerkinElmer). The samples were heated from 30 to 800 °C at the rate of 10 °C/min using ceramic crucible and air atmosphere.

3. Results and discussions

3.1. Precipitation

Copper oxide precursor powders were synthesized by homogeneous precipitation method. In this method, aqueous solutions, composed of appropriate amounts of dissolved urea and copper nitrate or chloride transformed into dispersions of the precipitated greenish particles, when heated at 85 °C for various periods of time. In fact, the heating process decomposed the dissolved urea and generated hydroxide and carbonate ions in the same medium [23] according to the following reactions:

$$CO(NH_2)_2 \rightarrow NH_4^+ + NCO^- \tag{1}$$

$$NCO^- + 2H_2O \rightarrow CO_3^{2-} + NH_4{}^+ \tag{2}$$

$$CO_3^{2-} + H_2O \rightarrow HCO_3^- + OH^- \tag{3}$$

$$HCO_3^- + H_2O \rightarrow H_2CO_3 + OH^- \tag{4}$$

$$H_2CO_3 \rightarrow H_2O + CO_{2(g)} \tag{5}$$

The dissolved copper ions then reacted with the anionic species present in the ambient environment and produced precipitated particles. SEM analyses of the precipitated powder indicated that their particle morphology was dependent upon composition of the starting reactant solution and heating time. In most of the experiments, the precipitated products were either gelatinous or composed of irregular shaped particles. As such, extensive optimizations of the essential experimental parameters were carried out in order to explore the key factors, responsible for the production of monodispersed systems of the precipitated powders. It was further noted that particles of uniform size and shape were obtained under narrow set of the applied precipitation conditions.

3.1.1. Copper nitrate–urea system

Fig. 1A shows typical micrograph of the particles obtained by heating aqueous solutions, containing urea and copper nitrate in appropriate amounts. The precipitation reaction was initiated by the reaction of Cu^{2+} ions with the anionic species (OH^-, CO_3^{2-}) generated by the decomposition of urea, according to Eqs. 2 and 3. Despite of the presence of NO_3^- ions in the same medium, copper ions preferred to precipitate out in the form of copper basic carbonate due to its least solubility [24] under the ambient ionic population in the reactant mixture. The precipitation reaction thus took place according to the following equation:

$$2CU^{2+} + CO_3^{2-} + 2OH^- \rightarrow CUCO_3{\cdot}Cu(OH)_2 \tag{6}$$

The spherical shape of copper basic carbonate particles was ascribed to the possibility that in the initial stages of the precipitation process, oxygen of CO_3^{2-} ions competed with OH^- ion for closest coordination position around Cu^{2+} ions which resulted in three dimensional networks of strong bonds around Cu^{2+} and produced spherical clusters (nuclei) in the reaction