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Synthesis of Copper Oxide Nanoparticles by Chemical Reduction of Copper Isophthalate Complex

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ABSTRACT

Here a simple method has been employed to synthesize copper oxide nanoparticles by chemical reduction of copper isophthalate complex in aqueous medium using ascorbic acid as a reducing agent. Experimental conditions are varied by changing the concentration of precursors and the presence of octanoic acid as a capping agent/ surfactant. The formation of nanoparticles was evidenced by the X-ray diffraction and transmission electron microscopy. The peaks in the XRDpattern correspond to the standard values of the copper (II) oxide.TEM analysis showed spherical nanoparticles with sizes in the range of 5 to 20 nm under different experimental conditions. Results show that the nanoparticles synthesized in the presence of octanoic acid are uniform and smaller in size as compared to nanoparticles synthesized in the absence of surfactant. Hence octanoic acid acts both as size controller and polymeric capping agent because it hinders the nanoparticles from aggregation through the polar groups, which strongly adsorb on the surface of nanoparticles.

Keywords: Nanoparticles, Chemical reduction, Surfactant, Transmission electron microscopy, Aggregation.

INTRODUCTION

Metal and metal oxides nanoparticles [1- 3] have attracted much attention of the researchers in nanoscience and nanotechnology over the past decade due to their unusual chemical and physical properties such as catalytic activity, optical and magnetic properties [4 -7]. Copper (II) oxide nanoparticles currently attract significant research attention owing to their widespread application in powder metallurgical materials and photoconductive devices. Copper oxide (CuO) is a semiconducting compound with narrow band gap and used for photoconductive and photothermal applications. The unique property of CuO is it acts as a semiconductor. Semiconductor materials have been particularly interesting because of their great practical importance in electronic and optoelectronic devices, such as electro chemical cell [8], gas sensors[9], magnetic storage devices [10], Nano fluid [11] and catalysts [12] etc. The favorable band gap of CuO (1.0 eV to 2.08 eV) makes it useful for solar energy conversion and it can be used for solar cell window preparations. There are many well-known methods [13] for the preparation of CuO nanoparticles including the hydrothermal reduction method [14], supercritical technique [15], micro emulsion technique [16], sono chemical reduction method [17], laser ablation technique [18], metal vapor synthesis method [19], electro reduction process[20] and aqueous solution reduction method [21].Among these methods, the aqueous solution reduction method is the most widely employed due to the advantages including high yield and quality of particles, simplicity of operation, limited equipment requirements, and ease of control. Selection of the type of the reducing agent strongly influences on the size of the resulting nanoparticles. Currently, the stabilization of nanoparticles by surfactants is perspective. They limit the process of the coagglomeration of nanoparticles and protect them from oxidation during a certain time interval. The main advantage of the synthesis in micelles is fact that nanoparticles are formed in the core of the micelle, i.e., in a more organized environment. This process is called solubilization. In this case, the shell of the micelle is a certain limit of the growth of these aggregates, allowing to obtain the particles of small sizes. Ascorbic acid is a reductant with a weak reducing ability. As a result, the reaction driving force is low, and it is difficult for the Cu particles to aggregate and grow. Transition metal complexes representing an important class of compound that could be used as a precursor for the synthesis of metal nanoparticles. In literature many coordination complexes and alkoxides can be used as precursors of metal nanoparticles [22, 23, 24]. However, large scale synthesis requires the use of low cost precursor, a simple one step process and variable parameters for the tuning of the nanoparticles according to their size. Here we report a simple and one step method of the synthesis of copper oxide nanoparticles by in situ chemical reduction of synthesized copper isophthalate complex by ascorbic acid. Ascorbic acid is a reductant with a weak reducing ability. As a result, the reaction driving force is low, and it is difficult for the Cu particles to aggregate and grow. In this technique the shape and size of synthesized nanoparticles depend on the choice of precursor's i.e. metal salt, ligands and the presence of surfactant. Despite its simplicity and potential, this technique has not been widely explored.

MATERIALS AND METHODS

Materials: Copper nitrate hemihydrate $Cu(NO_3)_2.2.5\ H_2O$, isophthalic acid ($C_8H_6O_4$), octanoic acid ($C_8H_{16}O_2$), ascorbic acid ($C_8H_8O_6$) were purchased from Sigma-Aldrich and used as such without further purification for the synthesis of copper nanoparticles.

Preparation of the copper oxide nanoparticles: For the preparation of copper oxide nanoparticles, copper (II) isophthalate precursor was prepared by adding 60 mL solution of disodium isophthalate (2mM) to 40 mL of copper nitrate (1mM) in the ratio of 2:1 under magnetic stirring for 15 min. The resultant blue colour precipitate was further heated at 80^{o}C for 30 minutes. In this mixed solution 10 ml of 0.1 M ascorbic acid is added drop wise with constant stirring and heated for 60 min at 80^{o}C. As the chemical reduction proceeds solution turned to brown. The product is allowed to cool naturally and centrifuged. The resulting brown coloured powder was washed several times with distilled water and dried at room temperature. Experimental conditions are further modified by increasing the amount of ascorbic acid and the presence of octanoic acid as a surfactant. Details of the experimental conditions are given in Table.

Table 1: Ratio of precursor materials

Sr. No.	Copper Nitrate	Disodium isophthalate	Ascorbic Acid	Octanoic Acid
1	40 ml, 1mM	60 ml, 2mM	10 ml, 0.1M	NIL
2	40 ml, 1mM	60 ml, 2mM	20 ml, 0.1M	NIL
3	40 ml, 1mM	60 ml, 2mM	20 ml, 0.1M	2mM

Physiochemical characterization of nanoparticles: The copper oxide nanoparticles were characterized by X-ray powder diffraction (XRD). XRD measurements were performed using a Rigaku Smart Lab X-ray diffractometer with Cu Kα radiation in the range 2θ from 10 to 80 at room temperature. The size and morphology for the prepared copperoxide nanoparticles were determined by Transmission Electron

Microscopy (TEM) on a MORGANI microscope at 200KV. Samples for TEM were prepared by drying a drop of nanoparticles solution on a carbon coated copper grid.

RESULTS AND DISCUSSION

The XRD patterns of the prepared metal oxide nanoparticles are shown in Figure 1. The samples produced well defined diffraction patterns, indicating that they are crystalline, and the peaks match well with the standard JCPDS cards of the respective metal oxides (No.05-0661 for tenorite, CuO). The XRD graphs were treated with the software the system to reduce the background noise and to normalize the curves.

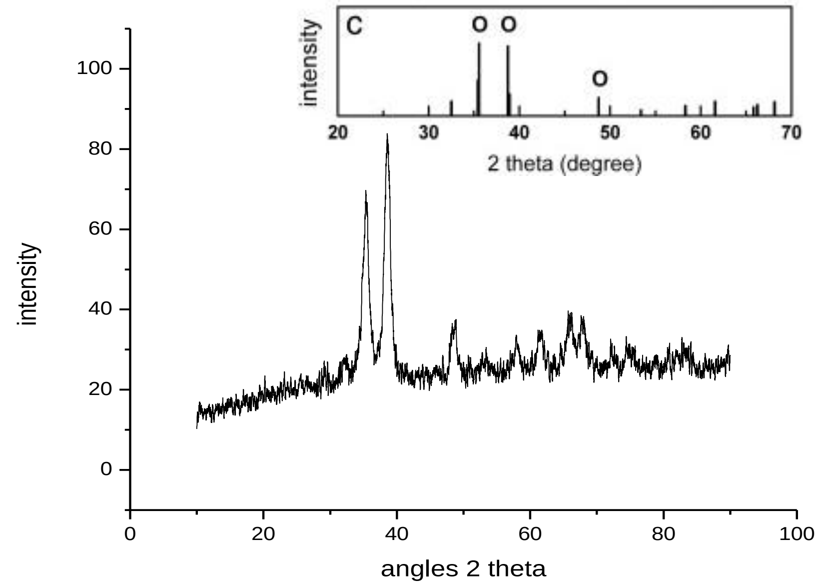

Figure 1. X-ray Diffractogram of copper oxide nanoparticles
(Inset shows the X-ray Diffractogram of CuO JCPDS 05-0661)

There are three sharps and well-defined peaks having 2θ values 35.6, 38.8 and 48.8 for copper oxide [11]. These values are in good agreement with those in JCPDS, card no. 05-0661 (X-ray diffractogram is shown in inset of Figure 1).

The morphology of the product was examined by TEM. TEM images of the synthesized copper oxide nanoparticles are shown in figures 2-4 at different experimental conditions.

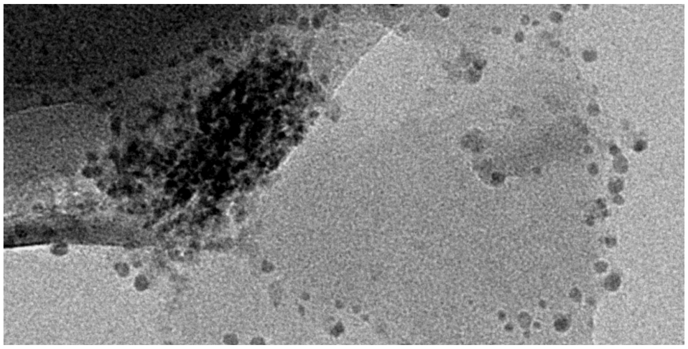

Figure 2. TEM image of copper oxide nanoparticles synthesized under the experimental condition given at sr. no. 1 in table 1

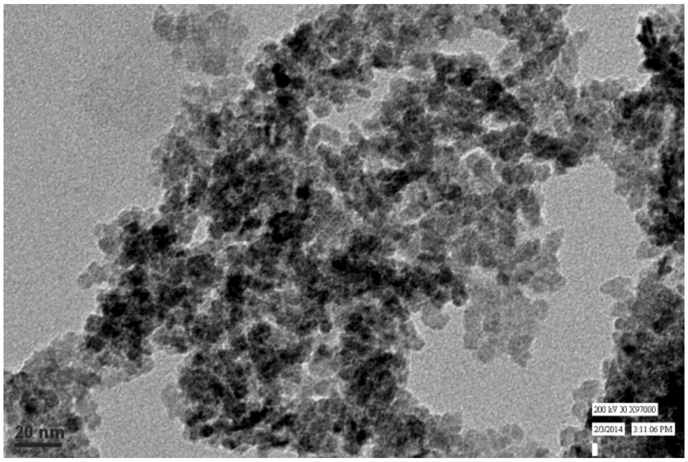

Figure 3. TEM image of copper oxide nanoparticles synthesized under the Experimental condition given at sr. no. 2 given in Table 1

Figures 2 and 3 shows the effect of the amount of ascorbic acid on the size of nanoparticles. As the amount of ascorbic acid increases, size of copper oxide nanoparticles increases. The nanoparticles synthesized under the experimental condition 1 are in the range of 5-20 nm (Figure 2) even though some larger nanoparticles are also observed. However, on increasing the amount of ascorbic acid, the size of nanoparticles was found in the range ≈ 10-20 nm (Figure 3). Herein, agglomeration of nanoparticles is also observed. The reason is that at higher concentration of ascorbic acid, rate of nucleation increases resulting in the high yield of nanoparticle nuclei which are agglomerated with each other leading to the formation of larger size copper oxide nanoparticles.

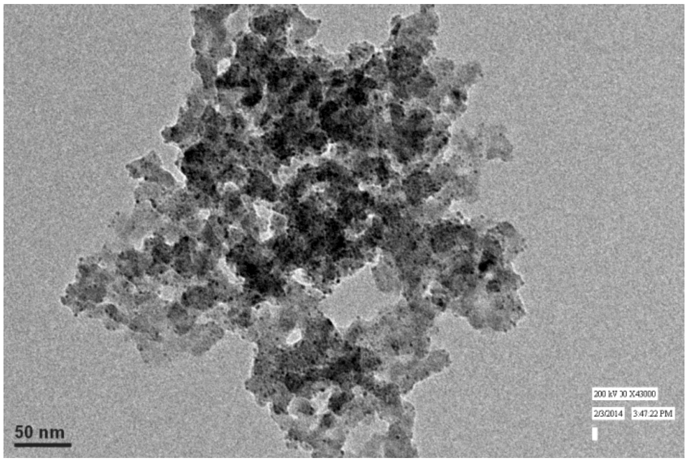

Figure 4. TEM image of copper oxide nanoparticles synthesized under the Experimental condition given at sr. no. 3 in Table 1

Figure 4 shows the TEM image of copper oxide nanoparticles synthesized in the presence of octanoic acid as surfactant. Result shows that the size of synthesized nanoparticles is much smaller (5 nm) as compared to other samples mentioned above. The stabilization of nanoparticles is due to the capping of nanoparticles by octanoic acid. It is noteworthy that the surfactant modulates the available surface energy of the particles so that the surface tension decreases, and preventing particles to agglomerate and lowering the mean particle size.

Highlights:

- Copper oxide nanoparticles has been synthesized by chemical reduction of copper isophthalate complex in aqueous medium using ascorbic acid as a reducing agent.
- Concentration of ascorbic acid affect the size of synthesized copper oxide nanoparticles.
- Ascorbic acid initiates the formation of spherical nanoparticles but the addition of octanoic acid along with ascorbic acid stabilizes the spherical copper oxide nanoparticles.
- Presence of surfactant checks the process of agglomeration and further reduced the size of nanoparticles under the same experimental conditions.

CONCLUSIONS

The present investigations show that it is the low cost one step method of the synthesis of copper oxide nanoparticles and samples can be prepared in simple laboratory equipment in ambient conditions. Copper oxide nanoparticles with narrow size distribution were prepared by the reduction of copper isophthalate complex into copper oxide nanoparticles. The stability of metal complexes is depending on the interaction between the metal ion and ligands. As a result, complexing agents have a profound effect on the reduction reaction. During the study, it was also found that the change of the volume of reducing agent affects the size of nanoparticles. In addition, the presence of surfactant checks the process of agglomeration and further reduced the size of nanoparticles under the same experimental conditions.

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