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Preparation of Nanosized Cu_2O and Cu/ Cu_2O Mixture Using Disproportionation Reaction

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Abstract: In this study, copper (II) oxide and copper/copper (I) oxide mixture nanoparticles have been prepared via copper disproportionation reaction in non-aqueous solution. The disproportionation reaction in dimethyl solfoxide (DMSO) was used to synthesis a Nano metallic element without any modification for the first time. Copper (I) Iodide (CuI), DMSO and ethylene diamine (en) have been used as copper (I) ion source, solvent and ligand, respectively. In this investigation the experiments were performed at two conditions. The products were characterized using both X-ray diffraction (XRD) and scanning electron microscopy (SEM). The XRD analysis of the solids produced at ambient atmosphere depicts the formation of pure copper (II) oxide (CuO) phase. The results also indicate that the achievement of the process after removal of oxygen and at N_2 atmosphere yields a mixture of metallic copper (Cu°) and copper (I) oxide (Cu_2O). The SEM images of both products showed that the particle sizes are less than 100 nm and are spherical in shape.

Key words: Disproportionation · Non-aqueous · Dimethyl solfoxide · Ethylene diamine · Copper (I) Iodide · copper (II) oxide.

INTRODUCTION

Nanotechnology has been an extremely active area of science in the past decade due to its terrific applications in the field of catalysis, sensor technology and in the fabrication of contemporary electronic devices. Copper particles have been broadly studied because of their roles in electronic, resins, catalysts and thermal conducting. Copper oxides employed in sensors, microelectronic circuits, as catalyst, plus p-type semiconductors and luminescence sources [1]. Various training methods to ultrafine metal have been reported that some of them are mentioned here: 1- using reverse micelles [2-7], 2- Reduction: [8-13], 3-Irradiation [14], 4- Sonochemical approaches [15-17], 5- Electrochemical method [18], 6- Sonoelectrochemichal approach.[14] and 7- Synthesis Nanoparticles via microwave radiation [19, 20]. In this paper a chemical procedure to generate copper oxide (II) nanopowder and a mixture of copper/ copper (I) oxide nanopowder with similar shapes has been presented. Copper and Copper oxide has been obtained by direct precipitation from homogeneous solution in the presence of a ligand without any surfactant or coating agent. Because of performance of the disproportionation reaction in non- aqueous solution this method is different from the previous chemical approaches.

Methods

Materials and Techniques: Copper (I) iodide (analytical reagent) and DMSO have been purchased from Ried-de Haen and Ethylenediamine was from Merck. The scanning electron microscopy (SEM) images were obtained using Philips XL-30 scanning electron microscope. The X-ray diffraction patterns of the products were recorded by employing a Philips X-ray diffractometer (model PW-3040).

Preparation of Copper Oxide (II) Particles: The copper oxide (II) particles in DMSO (figure 1) were synthesized by following method: After dissolving 3 g CuI in 30 mL DMSO, the solution was heated above 80 °C under constant stirring rate. Then 4 ml ethylenediamine with 99 percent purity was added to CuI solution.

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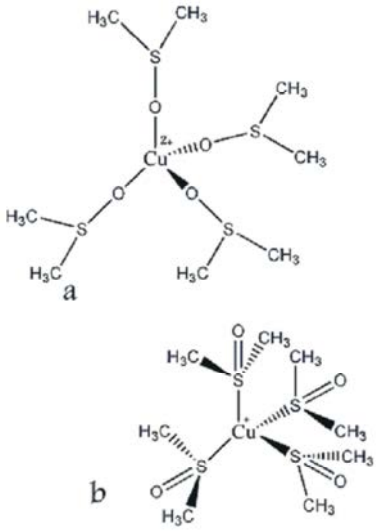

Fig. 1: Tetrahedral complex with DMSO molecules, a: Cu^{2+}, b: Cu^{+} [21].

The grey solution turned violet and after a few minutes copper oxide particles were precipitated at bottom of the experiment dish. The resultant black products were washed thoroughly with redistilled water and dried in an oven at about 327 K for above 4 h.

Preparation of Copper/copper Oxide (I) Particles: By repetition of the 2.2 direction after 1.5 hours passing of N_2 gas from 40ml solvent (DMSO) and at N_2 atmosphere produced mixture of copper and copper oxide (I) particles. These particles were dried via N gas.

RESULTS AND DISCUSSION

The Disproportionation reaction is a reaction in which the same elements are both oxidized and reduced. Some elements such as Ag, Au and Zn can perform disproportionation reaction. Carrying out of copper disproportionation reaction is needed Cu^{+} ion. This reaction in aqueous solution is rarely using to synthesis nano metals because of its hardly modification and preparation. In this study Cu_2O and Cu/ Cu_2O mixture tiny precipitation were produced in non-aqueous solution via disproportionation reaction. Simple and there by fast preparation are advantageous of this process. Because of simple preparation and using a few materials this method is very convenient. In this work after preparation of Cu^{+} ion at high temperature, in order to progress the disproportionation reaction, ethylenediamine added to solution as a ligand. Copper (I) ion is stable in DMSO so this solvent is appropriate for copper disproportionation

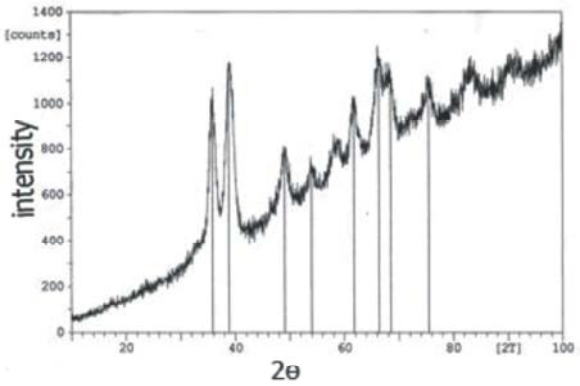

Fig. 2: X-ray diffraction pattern of the copper (II) oxide Nanopowder.

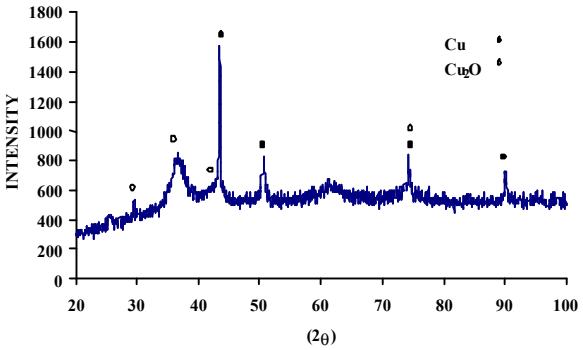

Fig. 3: X-ray diffraction pattern of the copper / copper (I) oxide mixture Nanopowder.

reaction. A DMSO molecule has three lone electron pairs, two of which are on the oxygen atoms and one is on the S atom. Cu^{+} (d^{10}) ion is a soft acid which prefers sulfur lone pair over than oxygen lone pairs. This ion is stabled by the bonds between DMSO lone pairs and its unoccupied orbitals. Cu^{2+} (d^{9}) ion is intermediate between hard and soft acid, therefore Cu^{2+} is less stable ion in DMSO environment than Cu^{+}. In fact, DMSO properties led to formation of Cu^{+} ion needed to disproportionation reaction. On the other hand, Cu^{+} ions are stabilized by the formation of a tetrahedral complex with DMSO molecules (Figure 1). Due to stability of complex, by adding the ligand (en) was failure to occur disproportionation reaction at room temperature, but product was produced after heating the solution over 80C. X-ray diffraction pattern Fig. 2 corresponds to the sample synthesized at ambient atmosphere. Figure 2 shows clearly that the solid consisted of all diffraction peaks of CuO phase. Figure 4 shows XRD pattern of mixture of Cu and Cu_2O that generated at N_2 atmosphere. It is seen also from Fig. 3 that the formed metallic copper phase is very well crystallized while Cu_2O phase exists as very poorly

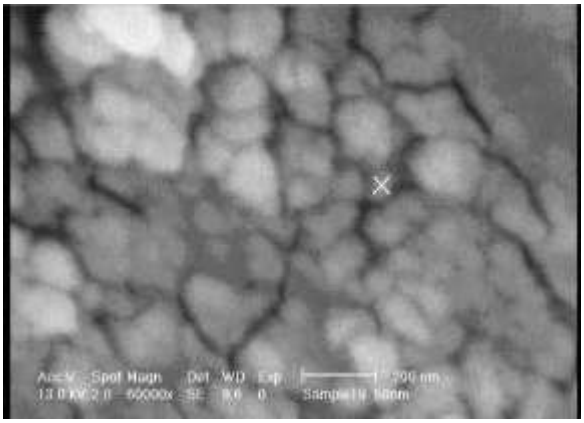

Fig. 4: SEM image of CuO particles

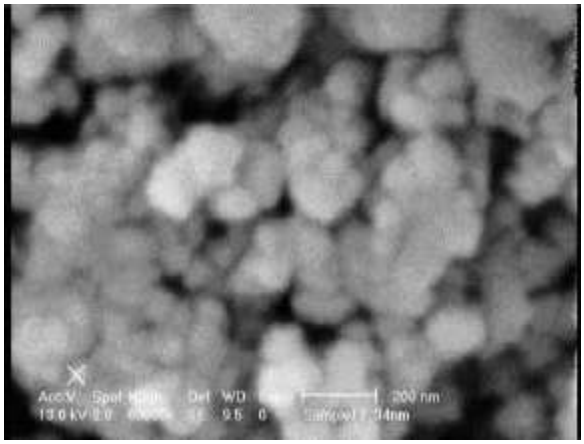

Fig. 5: SEM image of the copper / copper (I) oxide Mixture Nanopowder.

crystallized phase measuring nanosized crystallites. This XRD pattern (Figure 3) determines that the relative intensity of peaks of $Cu_{(s)}$ are bigger than that of Cu_2O, therefore the content of Cu in the sample is more than Cu_2O.The SEM images (Figures 4, 5) of both products in two conditions show that all particles are almost spherical in shape and measuring size smaller than 100 nm.

CONCLUSION

A simple novel chemical approach to preparation of copper (II) oxide and copper/copper (I) oxide mixture nanopowder is reported. The SEM images show that the shapes of the particles were spherical measuring size smaller than 100 nm. The results show non- aqueous solvent is suitable to performance of disproportionation reaction of copper. There are produced two kinds of materials via one method. This method may be used in industrial applications because of its rapid reaction and non- expensive used materials.

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