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Synthesis, characterization and stability of Cu_2O nanoparticles produced via supersaturation method considering operational parameters effect

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ABSTRACT

Cuprous oxide (Cu_2O) nanoparticles have been successfully synthesized using copper acetate as precursor via supersaturation theory as a facile rout. Synthesis parameters, such as the reducing agent concentration, reaction temperature, reaction time, type of the reducing agent and rate of adding reducing agent were investigated. The experimental results indicated that size of the Cu_2O nanoparticles is dependent on the above mentioned parameters. The Cu_2O samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and also by ultra violet visible spectroscopy (UV–vis). Results showed that temperature has unique influence on to the fabrication of Cu_2O nanoparticles which illustrate the higher the temperature of the synthesis the smaller the particles would be. Rate of reduction was specified as an influential factor in determining the particle size distribution. Particles with crystallite size of 74.01 nm were obtained among this study.

> In het rijk van de ideeën hangt alles af van het enthousiasme... in de echte wereld alle rust op doorzettingsvermogen. . .
> "In the realm of ideas everything depends on enthusiasm... in the real world all rests on perseverance. . ."
> J.W. von Goethe (1749–1832)

Introduction

Metal oxides play an inconceivable role and are of paramount importance in many rapidly developing research areas such as the intersection of chemistry and materials science [1]. Potential applications include sensors, microelectronics, corrosion protection coatings, fuel cells, nanotechnology in general or catalysis [1,2]. Focusing on the latter oxides are widely used either as supports for catalytically active noble metals or as catalysts themselves [1,2]. However, while the catalytic action of noble metal particles is widely understood, several drawbacks in the use of oxides exist; due to their inherently more complex chemical nature, the catalytic action might depend on a number of factors, such as oxidation state, surface termination, polymorphism or the presence of oxygen defects [1]. In this view, crystallization plays an incredible role to formation of the more qualified materials, especially in the scope of the synthesis of nanomaterials. Hence, the controlling of the crystallization process has a critical role on the properties of products and allows manufacturers to prepare materials with desired and reproducible properties. The recent interest in nanocrystals and other types of nanomaterials is a further illustration of the crystallization importance in the science and technology [3]. It is well known that at the nanometer scale, the optical, the electronic, and the catalytic properties of nanomaterials are highly sensitive to their size and shape [4]. Consequently, the crystallization process (nucleation and growth) plays an important role in determining the crystal structure, shape, size and size distribution of the nanomaterials. Therefore, a theoretical approach to understand the mechanism of nanocrystals formation provides a greater control over the size, shape, and composition of nanocrystals and results an ability to tune the above-mentioned properties simply by varying the crystallization conditions. Among the most widely used and characterized system is the copper, as well as its corresponding oxides [5–7]. Here, the complexity manifests itself by the presence of one important stable oxide with different

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properties for the copper system, which is cuprous oxide, Cu_2O (T_m = 1235 °C, ρ = 6 g/cm^3). As a representative p-type semiconductor with a band gap of about 2.2 eV, cuprous oxide (Cu_2O) nanomaterials have been widely used in solar energy conversion [8], gas sensors [9], photocatalysis [10,11], micro/nano electronics [12], lithium ion batteries [13], etc. To date, various well-defined Cu_2O nanostructures with different shapes and sizes, including hollow nano spheres [13,14], nano cages [15,16], nanowires [17,18], nano cubes [19,20], and octahedron [21,22] morphologies, have been synthesized. As is well known, shape, size and microstructures are the main factors that determine the chemical and physical properties of nanomaterials. Therefore, it is still of great importance to prepare single-crystalline cubic nanoparticles and to control the particle size in a narrow size distribution over a wide adjustable range with simple one-step additive-free solution method at room temperature. At present, hydrothermal method [23], template method [24], and solution-phase synthesis method [10,16,18–22,25] are the main wet-chemical methods developed for the synthesis of Cu_2O nanoparticles. In these methods, additives, including organic polymers, surfactants, and inorganic ions, are usually used to regulate the shape and size of the products. However, the additives are usually expensive or toxic, hard to wash and thus may affect the performance of the products. In contrast, an additive-free method is simple, of low-cost and environmentally benign.

Cu_2O due to the presence of vacancies and lack of Cu^+ cations is a semiconductor [26] and has a symmetric structure which its six oxygen atoms are in the BCC space lattice and copper atoms have occupied the position of the tetrahedral network [27,28]. Copper (I) oxide has been synthesized by various methods. In the reducing technique, salts containing copper (II) as $CuSO_4$ [29–35], $Cu(NO_3)_2$ [27], $Cu(CH_3COO)_2$ [30,36] and $CuCl_2$ [37] were utilized as a source of copper. In addition, presence of several reducing agents like hydrazine hydrate (N_2H_4) [38], glucose ($C_6H_{12}O_6$) [30,33,37], ascorbic acid ($C_6H_8O_6$) [31,32,34,36], sodium borohydride ($NaBH_4$) [29], plants contain aldehyde groups such as Tridax Procumbens [35] and γ-ray [39], Cu^{2+} will be converted to Cu^+ ions. In this procedure, stabilizers, complexing agents and surfactants due to improvement of the producing nanoparticles could be applied and supply the various particles in different sizes and morphologies.

Present work involves a facile additive-free and room temperature solution process for the synthesis of uniform cubic (lattice) Cu_2O nanoparticles. The size of the Cu_2O particles can be systematically tailored over a wide range simply through adjusting the concentration of the NaOH solution and changing the kind of copper salt. Effect of operational parameters on to the characteristics of the Cu_2O nanoparticles also has been considered.

Experimental

Materials

Copper acetate ($Cu(CH_3COO)_2{\cdot}H_2O$), sodium hydroxide (NaOH), ascorbic acid ($C_6H_8O_6$) and maltodextrin ($C_6H_{12}O_6$) were purchased from Sigma–Aldrich Co., Germany. All the chemicals were in analytical grade and used without further purification. Deionized water was used in the experiments.

General route for synthesis of Cu_2O nanoparticles

Synthesis of Cu_2O nanoparticles has been done using the following procedure; typically, 0.05 g copper acetate, 0.2 g sodium

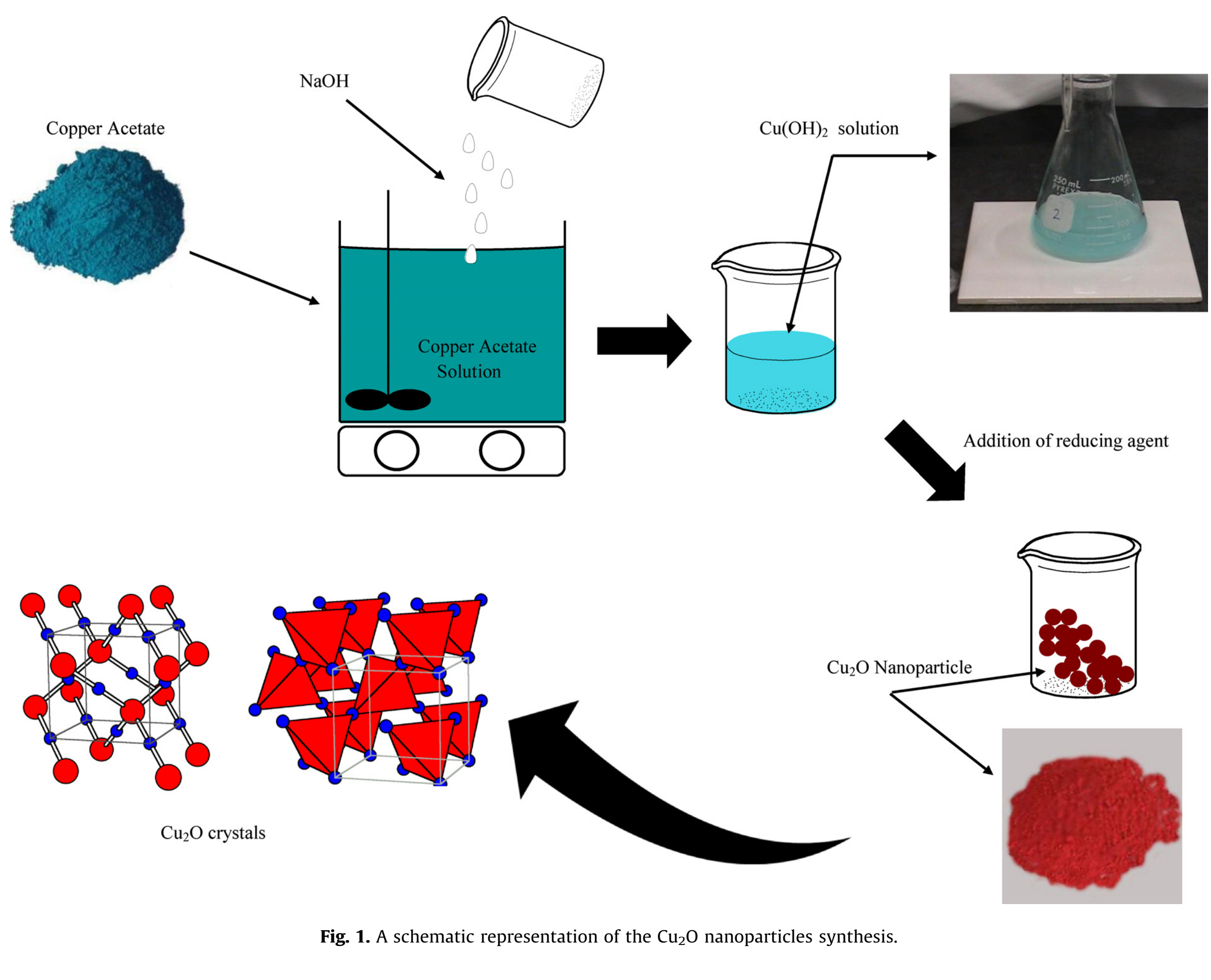

Fig. 1. A schematic representation of the Cu_2O nanoparticles synthesis.