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Effect of solution condition on the precipitation of nano-cupric oxide by using a high gravity process

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ABSTRACT

In order to find the optimum conditions to obtain nano-cupric oxide particles, the synthesis of CuO is carried out by feeding $CuCl_2$ (0.1–0.4 M) and NaOH (0.2–1.0 M) solutions simultaneously into a high gravity apparatus. The precursors obtained are calcined for three hours at 100 and 350°C in an oven prior to further characterization using XRD, SEM, UV, PL (photoluminescence) and BET instruments. The major precursors are found to be CuO, $Cu(OH)_2$ and $Cu_2Cl(OH)_3$. The specific surface areas after calcination are in the range of 7.45 to 58.21 m^2/g, corresponding to an average diameter between 16.4 and 127.2 nm. In addition, the yields obtained, 0–95.5%, are found to be strongly dependent on the operating conditions. The results show that the reactant concentration ratio, R=[NaOH]:[$CuCl_2$], plays an important role in influencing the product distribution. A roadmap of technology for the production of precursors is established. Finally, the effects of rotating speed and feed rate of the solutions are also discussed.

1. Introduction

Cupric dioxide, a narrow band-gap material, is an interesting material, which is found in numerous applications [1–10], such as field emissions, magnetic storage media, semi-conductors, superconductors, solar cells, catalysts, pigments, ceramics, nanofluids, gas sensors and Li ion batteries. It is also of importance for enzymatic glucose biosensors and solid-state gas sensors [11]. Compared with bulk materials, it has several special properties [12–15], such as anti-bacterial activity, magnetic properties, oxidation properties, optical properties, thermal conductivity properties and catalytic properties, due to its quantum size effect. Various strategies for the synthesis of CuO nanostructures with controlled morphologies, such as nanoplatelets, nanoleaflets, spherical nanostructures, nanostructures with nanoribbons, nanowhiskers and nanowires, have been reported in the literature [14,16–25]. Recently, chemical looping has become an important process in CO_2 capture, in which metal oxides, such as CuO, Fe_2O_3 and NiO [26], are used as the oxygen carriers. Other oxides (such as NiO and CoO) have been explored for many applications [27–29]. In order to extend the application of metal oxides, the fabrication of sensors using the CVD method has been explored [11,30,31]. In the synthesis of cupric oxide, two major classes are used: one is a chemical technique, the other a physical technique. In addition, the biotechnology synthesis of nanoparticles has been studied [10]. Most of these studies were performed using a chemical technique because of the lower energy consumption and costs, as compared with the physical technique and biotechnology method. Chemical techniques [32–36], including the hydrothermal method, sol-gel method, spray pyrolysis method and precipitation method, have been used to synthesize cupric dioxide. Recently, the molten method [37] and the metal-organic framework-assisted synthesis [38] were used to prepare CuO. In the chemical technique, the precipitation method is an attractive method for the preparation of cupric dioxide, not only for its ease of operation, but also for its lower cost as compared with other methods. With this method, the formation of nanoparticles can be obtained in several steps, including the generation of supersaturated solutions, the generation of clusters, the generation of nuclei and the growth of nuclei. Other methods have also been reported in the literature [39–41].

Generally speaking, the precipitation method is carried out by reacting two components to directly produce precursors (intermediates) or products. The precursors are further calcined to obtain the final products. During the operation, the mixing, reaction and precipitation steps occur in sequence before the formation of precipitates; therefore, it is important to control the precipitation mechanism and solution chemistry. In the reaction of $CuCl_2$(aq) with NaOH(aq), several different precursors can be obtained, depending on the stoichiometry and operating conditions, because the solution chemistry, including ion-pairs and complex, is very complicated and affects the formation of intermediates. It is important to control the precipitation step in order to obtain the desired intermediates, since the decomposition temperature is different for different intermediates.

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Nomenclature

d_{BET}	particle size defined in Eq.(5) (nm)
F	liquid flow rate (L/min)
N	rotating speed, rpm
R	reactant concentration ratio (-)
S_w	specific surface area (m^2/g)
W	weight of product (g)
W_0	weight of reactant at initial stage (g)
W_{Cu}	weight of copper in the product (g)
Y_{Cu}	yield of product defined in Eq.(6) (-)

Greek symbols

ρ	density of solid (kg/m^3)

In an aqueous solution, $CuCl_2$ dissociates into $[Cu(H_2O)_6]^{2+}$ and Cl^- anions, and then four water molecules surround the Cu^{2+} ion due to a solvating action [16,32]. The possible reactions are shown below:

$$Cu^{2+} + 4OH^- \rightarrow [Cu(OH)_4]^{2-} \quad (1)$$

$$[Cu(OH)_4]^{2-} \rightarrow Cu(OH)_2(s) + 2OH^- \quad (2)$$

$$Cu(OH)_2(s) \rightarrow CuO(s)H_2O \quad (3)$$

Alternatively, $Cu_2(OH)_3Cl$ can be obtained by the hydrolysis reaction, shown as follows [42]:

$$2CuCl_2 + 3NaOH \rightarrow Cu_2(OH)_3Cl(s) + 3NaCl \quad (4)$$

From Eqs. (1)–(4), it was found that the concentration of reactants becomes significant due to the different reactant ratios resulting in the formation of different materials. For example, the product is $Cu(OH)_2$ or CuO when the ratio of NaOH to $CuCl_2$ equals 4, while the product becomes $Cu_2Cl(OH)_3$ when the ratio is 1.5.

In addition, during precipitation, the competition which occurs between the mixing time and reaction time is one of the significant controlling steps. In order to produce nanoparticle of a particular size, the particles formed should not grow further after the formation of particles when the mixing time is less than the induction time. This can be achieved by a high gravity centrifugal packed bed (a HiGee process). The process has several advantages, such as high mass-transfer coefficient, rapid mixing, rapid separation and energy saving. Using the high gravity process, the mixing time can be adjusted to 10–100 μs, which is comparable to 10–1000 μs for the induction time. The segregation index is less than 0.05 when the rotating speed is higher than 500 rpm [43]. This indicates that better micromixing efficiency can be achieved with the high gravity process with the aid of centrifugal force. It has been found that the increased mixing intensity enhances the crystallization rate and reduces the particle size. Therefore, the use of this process makes it possible to control the size of the nanoparticles at a desired value. There are several reports available for nanoparticle synthesis using the high gravity process [44–45]. However, the products obtained depend on the reactant ratio, which cannot be effectively controlled by stoichiometry, only because the contact in the high gravity machine is a probability issue. In addition, a large amount of product can be obtained by using this process as compared with other processes. CuO has been found to be a very useful material for many applications. Therefore, the process is valuable for the mass production of cupric oxide.

In this study, a high gravity centrifugal packed bed reactor was used to synthesize nano-cupric oxide using $CuCl_2$ and NaOH solutions as the reacting materials. The purpose of this work was to explore the effect of operating conditions on the formation of CuO precursors and to characterize the properties of nano-cupric oxide. In order to control the desired products, a synthesis technology was established by integrating the experimental results.

Table 1
Operating conditions for the synthesis of precursor of cupric oxide.

Precipitation conditions	
Concentration of NaOH (M)	0.2, 0.3, 0.5, 0.6, 1
Concentration of $CuCl_2$ (M)	0.1, 0.2, 0.3, 0.4
Liquid flow rate (L/min)	0.25-0.60
Rotating speed (rpm)	500–2000
Calcination conditions	
Calcinations temperature (°C)	100, 350
Calcinations time (hr)	3

2. Experimental section

2.1. Materials and method

All the chemicals were of analytical purity and were used without further purification. The starting materials used for the synthesis of CuO were $CuCl_2$ and NaOH. The experimental apparatus of the high gravity process is shown schematically in Fig. S1 in the supplementary section. The apparatus consisted of a rotating packed bed, pumps, flow meters, speed controller, water bath and reservoir. The rotating packed bed contained wired packing with several layers. A known volume and concentration of reactants ($CaCl_2$ solution and NaOH solution) were taken and fed into the reactor at a desired rotating speed from the top of the reactor through the action of tubing pumps. The reactant temperature was controlled at 25° C. The reactant was pumped through the distributer into the rotating packed bed, where the primary step of reaction occurred. Then, the product slurry flowed out of the reacting chamber and was collected in the product reservoir. The time from the beginning of this process to the end is termed the reaction process time, which was fixed as 15 min. After the reaction operation, the slurry was filtered and rinsed with acetone, and the cake was dried in a hot air oven for one hour. The dried powders were analyzed by XRD to identify the composition of the product. The decomposition temperatures of the dried powders were determined by means of TGA/DSC analysis. Based on the TGA/DSC results, the dried samples were calcined for three hours in order to obtain nano-cupric oxide. Then, the cupric oxide powders were characterized further by means of XRD, SEM, UV, PL and BET analyses. A total of twenty-five runs were carried out in this work. The operating conditions are listed in Table 1. Most runs were carried out at a flow rate of 2.5 L/min and a rotating speed of 500 rpm [6,43].

2.2. Characterization

In order to identify the intermediates in the precursors and to analyze the samples after calcination, X-ray diffraction (XRD) analysis was performed. Powder X-ray diffraction patterns were recorded on a Regaku 2000 diffractometer operated at 40 kV and 30 mA using CuKα radiation with a wavelength of 1.5406 Å. The scanning angle was from 25 to 80° at a rate of 0.05°/s. To understand the decomposition temperature of the precursor samples, we examined the thermal decomposition of the precursors by means of TGA/DSC analysis. TGA/DSC measurements were made with the aid of differential scanning calorimeter equipment (Perkin Elmer DSC 7). The samples were heated from room temperature to 800 °C at a heating rate of 5°C/min in a steady flow of dry N_2 (20 mL/min). The morphology of the nano-cupric oxide samples was examined by means of SEM analysis, which was performed using a JEOL JSM-6500f instrument. The samples were first coated with carbon and then with gold before scanning. The BET surface area was measured by nitrogen adsorption-desorption at 77 K using a Micromeritics ASAP2010 instrument. Before each measurement, the sample was degassed at 423 K for 4 h to remove the adsorbed impurities.