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Synthesis of copper nanocolloids using a continuous flow based microreactor

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ABSTRACT

The copper (Cu) nanocolloids were prepared by sodium borohydride ($NaBH_4$) reduction of metal salt solutions in a T-shaped microreactor at room temperature. The influence of $NaBH_4$ molar concentrations on copper particle's diameter, morphology, size distribution, and elemental compositions has been investigated by transmission electron microscopy (TEM) and X-ray diffraction (XRD). The ultraviolet–visible spectroscopy (UV–vis) was used to verify the chemical compounds of nanocolloids and estimate the average size of copper nanocolloids. The synthesized copper nanocolloids were uniform in size and non-oxidized. A decrease in the mean diameter of copper nanocolloids was observed with increasing $NaBH_4$ molar concentrations. The maximum mean diameter (4.25 nm) occurred at the $CuSO_4/NaBH_4$ molar concentration ratio of 1:2.

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1. Introduction

Metal nanoparticles have widespread applications such as in catalysis, optoelectronics, photovoltaic technology, information storage, environmental technology, engineering, biosensor development, and medicine. The pressing need for synthesis of low-cost, scalable, and dispersible nanoparticles has generated much interest in the field of nanocrystal synthesis [1,2]. The preparation of copper (Cu) nanoparticles has been an active research area as Cu nanoparticles exhibit many excellent physical and chemical properties, such as high electrical conductivity and chemical activity. Due to their low costs, Cu nanoparticles compare favorably with silver (Ag) and gold (Au) nanoparticles in certain applications [1–6]. There are many existing chemical processes for Cu nanoparticle synthesis, including thermal reduction, microemulsion technique, sonochemical reduction, vacuum vapor deposition, metal vapor deposition, laser ablation, and aqueous reduction methods [5–12]. Among them, aqueous reduction method is most widely employed due to its simple operation, high yield and quality, limited equipment requirements, and ease of control. For example, application of $NaBH_4$ as reducing agent, Cu nanoparticles synthesized by reduction of metal salts aqueous solutions. Liu et al. prepared Cu nanoparticles with sodium borohydride ($NaBH_4$) by utilizing aqueous reduction method [5]. However, aqueous reduction method lacks precise control of mixing, nucleation, and growth processes, and thus yielding larger variation in the final particle size, size distribution, and the crystal structure. Sufficient mixing and rapid mass transfer can significantly improve the uniformity of these performance parameters, which in turn control both the physical and chemical properties of nanoparticles.

In recent years, microreactors have gained much attention in nanomaterials synthesis due to the possibility of precise control of reaction and mixing conditions. The advantages of microreactors are their high surface area to volume ratio, tunable inner-wall properties, versatile flow-orientation, and flexible-structural designs [13–21]. In addition, diffusive exchange of heat and mass can be achieved within small length scales. These features have prompted many innovative microreactor designs in improving reaction efficiency and controlling the synthesis and arrangement of the nanomaterials [22–29]. For example, Song et al. reported controlled growth of Cu nanoparticles by utilizing a tubular microfluidic

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reactor. Larger particle size was enabled through continued controlled growth of the initially formed Cu nanoparticle in a tubular microfluidic reactor [3]. Continuous synthesis has become one of the most promising advantages of microreactor technology as it proved to produce improved homogeneity of reaction solutions and yield more uniform products [22,30–32]. In a preliminary study, we used a PDMS microfluidic chip to synthesize copper nanoparticles, and studied the influence of flow rates on final copper particle diameter, morphology, and size distribution [33]. In the present work, we used the aqueous reduction method by using $NaBH_4$ as a reduction agent to synthesize copper nanocolloids in a continuous flow based T-shaped microreactor, and we investigated the effect of reactant concentration systematically.

2. Experimental methods

2.1. Materials

Copper (II) sulfate pentahydrate ($CuSO_4{\cdot}5H_2O$, purity 98%), Sodium borohydride ($NaBH_4$, purity 99%), Polyvinylpyrrolidone (PVP, average molecular weight of 360,000), Ammonium hydroxide solution ($NH_3{\cdot}H_2O$, 28.0–30.0%) and Sodium hydroxide (NaOH, purity 99%) were purchased from Sigma–Aldrich (St. Louis, MO, USA).

2.2. Synthesis of copper nanocolloids

Precursor preparation: 0.02 mol/L $CuSO_4{\cdot}5H_2O$ (Copper sulfate pentahydrate) solution and $NaBH_4$ solution (0.04 M, 0.1 M, and 0.4 M respectively) were prepared at room temperature, and argon was bubbled through both solutions for 30 min. A certain amount (2–3 mL) of ammonium hydroxide solution was added to the $CuSO_4$ solution as a complexant which changed the solution color from blue to dark blue. A 3.2 g/L of PVP was added into the $CuSO_4$ complex solution as a dispersant. The pH value of $CuSO_4$ complex solution and $NaBH_4$ solution was adjusted to 10–12 by adding proper amount of NaOH solutions.

Two aqueous solutions ($CuSO_4$ and $NaBH_4$) were pumped into a stainless steel T-shaped microreactor (IMM, Germany) with 1/16 inch diameter, at room temperature ($25 \pm 2\,^{\circ}C$), see Fig. 1. Two constant flow pumps (Yanshang Instrument Factory, China) were utilized to pump the $CuSO_4$ complex solution and aqueous $NaBH_4$ solution into the microreactor at the same flow rate of 10 mL/min, with the total flow rate being 20 mL/min. The average velocity U of the flow can be estimated by Eq. (1).

$$\text{Average velocity } U = \frac{\text{Flow rate}}{\text{Cross section area}} \tag{1}$$

Since the cross section area is 1.97 mm^2, the average velocity U can be estimated to be around 170 mm/s, and the average velocity of $CuSO_4$ solution and $NaBH_4$ solution is around 85 mm/s, respectively. The length of the microreactor outlet channel is 25 mm, with the average velocity of the flow in the outlet channel being ~170 mm/s, the residence time in the microreactor is estimated to be 0.15 s. The aqueous solution from the T-shaped microreactor was then flowed through a stainless steel tubular microchannel (i.d. 1/16 inch, i.e. 1.58 mm, provided by Dalian MICROCHEM Co. Ltd., China), the length of the stainless steel tubular microchannel is ~400 mm, with the average velocity of the flow ~170 mm/s, the residence time in the stainless steel tubular microchannel is estimated to be ~2.35 s.

The general chemical reaction to produce Cu nanoparticles is based on reaction equation below:

$$4Cu^{2+} + BH_4^- + 8OH^- = 4Cu + B(OH)_4^- + 4H_2O \tag{2}$$

Although the stoichiometric ratio of Cu ions to $NaBH_4$ is 4:1, $NaBH_4$ hydrolyzes to produce H_2 gas. In more details, the reduction of BH_4^- is strong, and its standard potential is about −1.24 V. BH_4^- can release 8 electrons in an alkaline medium such as

$$BH_4^- + 8OH^- \rightarrow B(OH)_4^- + 4H_2O + 8e \tag{3}$$

The standard potential of Cu is +0.337 V, and can obtain 2 electrons in solution,

$$Cu^{2+} + 2e \rightarrow Cu \tag{4}$$

Thus, it is feasible to use BH_4^- for Cu^{2+} reduction [34] as the reducing agent ($NaBH_4$) was added far in excess of stoichiometric requirement to promote sufficient reactions. The activation energy of $NaBH_4$ hydrolysis is about 56 kJ/mol at room temperature. However, in the T-shaped microreactor, the reaction activation energy is dependent on the fluid velocity, the concentration of reactants, the contact area of reactants, and reaction temperature. We intend to conduct systematic studies in the future to estimate the reaction activation energy in the microreactor.

2.3. Material characterizations

Transmission electron microscopy (TEM, 2100F, 200 kV, JEOL) was used to characterize the size and morphology of Cu nanocolloidal particles. A drop containing Cu nanocolloidal particles was deposited on a copper-grid coated with perforated, transparent carbon foil. The UV–vis spectrometry was used to verify the chemical nature of nanocolloidal particles and estimate the average size, by using a spectrometer (UV-2450, SHIMADZU), operated between 400 and 700 nm. Copper nanocolloids were centrifuged and rinsed with water and alcohol, dried in vacuum for 50 h at 40 °C. Samples were then analyzed by conducting XRD using an XRD-7000S diffractometer (Shimadzu, Ltd., Kyoto, Japan) with Cu K_α radiation (λ = 1.54060 Å).

3. Results and discussion

The nanoparticle formation via wet-chemical reaction includes four distinct stages: the formation of a supersaturated solution, its subsequent nucleation, growth, and aggregation [3,35]. The solutes consisting of ions in the solution are formed by chemical reactions (e.g., metal-salt reduction). When the solute concentration reaches a critical concentration, the formation of spontaneous nuclei occurs rapidly, which reduces the solute concentration till below the critical nucleation concentration, prevents further nucleation and hence controls the number of nuclei that are formed. The nucleation stage is then followed by the growth of the nuclei, until the complete depletion of the solute. The overall free energy of this reaction system is hence lowered and the reaction is irreversible. Therefore, in order to obtain a narrow particle size distribution, the nucleation time should be controlled to take place within a short time [33,36]. Copper nanocolloids were synthesized by using a T-shaped metal microreactor (Fig. 1) with two connection types (Fig. 2A and B). Flows of both aqueous solutions ($CuSO_4$ and $NaBH_4$) are laminar with the reaction layer apparent at the interface of the two reactants, while mass transfer between these two layers are dominated by diffusion. The residence times (both in the microreactor and stainless steel tubular microchannel) in case A and B are the same. However, in case B, the contact area between the two reactants is larger, which can promote both diffusion and mixing of the reactants with maximized surface areas, therefore enhance the reaction rate.

In this T-shaped microreactor, copper nanocolloids suspension was continuously synthesized and maintained stable up to 60 days (as shown in Fig. 3). To assess the effect of the reactant concentration, we fix the molar concentration of $CuSO_4$ solution at 0.02 M

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