Size-Controlled Synthesis of Cu₂O Nanoparticles via Reaction-Diffusion

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Copper (I) oxide nanoparticles are synthesized by a simple reaction-diffusion process involving Cu⁺ ions and sodium hydroxide in gelatin. The mean diameter and the size dispersion of the nanoparticles can be controlled by two experimental parameters, the percent of gelatin in the medium and the hydroxide ion concentration. UV-visible spectroscopy, transmission electron microscopy and X-ray diffraction are used to analyze the size, morphology, and chemical composition of the nanoparticles generated.

Introduction

The use of nanoparticles of characteristic size and narrow dispersion to form hybrid materials is gaining increasing interest in the biomedical^{1,2} and electronics³ industries. Among various metal oxide particles, copper (I) oxide has received much attention because of its distinctive characteristics and its low cost compared to silver and gold oxide nanoparticles. In particular, its electrical properties due to its low energy band gap (2.18 eV), enhanced nonlinear optical properties, photocatalytic and catalytic power⁴, and antibacterial activity⁵ make it an attractive material for many applications. Methods developed for the preparation of copper (I) oxide nanoparticles utilize ultrasound⁶, chemical curing⁷, gas-phase reduction⁸ and other techniques that involve the reduction of copper (II) oxide to copper (I) oxide^{9,10}. In the methods proposed to date, the extent of the reduction is not easy to control; thus the nanoparticles produced may not be very pure. Careful selection of surfactants or organic additives to protect the particles from aggregation is also required. The approach we propose here is unique in the sense that it uses mild reagents and ambient experimental conditions. The problems of reduction and aggregation are circumvented by the preparation method, where the initial reaction takes place between monovalent Cu⁺ ions and hydroxide ions in a gel medium to produce the Cu₂O nanoparticles. In addition, our approach allows the design and synthesis of nanoparticles with particular size characteristics simply by varying the gel composition and the concentration of sodium hydroxide. The diffusion-controlled reaction technique employed in our method has been widely used to prepare Liesegang patterns^{11,12}. The Liesegang phenomenon is the dynamic formation of self-organized rhythmic precipitate patterns. The proposed scenarios for the explanation of the Liesegang phenomenon can be classified as either prenucleation or postnucleation, depending on the sequence of elementary steps^{13,14}. The prenucleation models are descendants of Ostwald's supersaturation theory and assume that the formation of bands is the result of a supersaturation wave. Postnucleation models assume that before bands form, the precipitate forms a homogeneous solution of solid particles, which loses its stability and arranges into periodic bands. Walliser *et al.*¹⁵ employed a diffusion-controlled reaction technique to grow various size silver dichromate nanoparticles and microparticles in one step. In their study, they found a linear

correlation between the size of the particles and the position of the band measured from the interface. In another set of Liesegang-type experiments, Al-Ghoul *et al.*¹⁶ found that the average size of CdS nanoparticles at the front is smaller than the average size left in the wake of the pulse as the single band of the system propagates, and that both of these average sizes increase in time until they reach a constant limiting value. We note our experiments do not result in any banding, because the time of our experiments is short and the initial concentration of Cu⁺ ions is too small to result in observable bands. For the characterization, the synthesized copper (I) oxide nanoparticles are investigated by UV-visible spectroscopy and X-ray diffraction (XRD) and analyzed for size and morphology by transmission electron microscopy (TEM).

Materials and Methods

All chemicals were used as received, without further treatment. Gelatin and sodium hydroxide were purchased from Fisher and copper (I) iodide, 98% from Acros Organics. Solutions of 0.0042 g of CuI in 100 mL water were prepared, and 10 g, 12.5 g, 15 g, 17.5 g, and 20 g gelatin were added to obtain 10%, 12.5%, 15%, 17.5%, and 20% gel solutions, respectively. Each solution was heated until the gelatin dissolved and then filled to 2/3 in 30 cm long tubes of diameter 4 mm. The tubes were left to cool and gelify overnight. On the second day, NaOH solution of the appropriate concentration was added on top of the gel and allowed to diffuse overnight. On the third day, the samples were collected from the gelatin/NaOH interface up to the diffusion front for analysis.

The UV-visible spectra were obtained using a Shimadzu spectrophotometer, model UV-1650 PC. TEM images of particles were obtained using a Morgagni 268 instrument. The samples for imaging were prepared on carbon-coated 400 mesh copper grids. The size distribution and the average particle size were determined from at least 300 particles for each experimental system. Sample identification was done on a Rigaku Miniflex 600 X-ray diffractometer using nickel-filtered Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$) over a 25° to 90° angular region, with step size and rate of 0.02° and 5°/min, respectively.

Results and Discussion

Metal oxide nanoparticles undergo absorption of visible electromagnetic radiation due to the collective oscillation of electrons at the surface. This surface plasmon effect can be qualitatively checked using UV-visible spectroscopy to identify the presence of particles. UV spectra for a system with 10% gelatin and 2 M NaOH are shown in Figure 1. The distinct peak at 500 nm confirms the existence of nanoparticles. Furthermore, Figure 1 shows that there is only a slight variation in the spectra once the reaction is stopped. This indicates that the particles and their sizes are quite stable and no further aggregation takes place, since the electron scattering enhancement at the surface is constant. This stability can be attributed to the adsorption of polar functional groups of the gel on the surface of the nanoparticles^{17,18}, which inhibits further growth and aggregation of nanoparticles by repulsion of the surface charges.

To study the effect of varying [NaOH] on the size of the nanoparticles, we prepared systems with 0.0042 g CuI in 100 mL water, 10% gelatin, and 1.4 M, 1.6 M, 2 M, and 2.4 M sodium hydroxide. Figure 2 shows sample TEM images of the synthesized nanoparticles for different NaOH concentrations. The images show that the particles have spherical morphology. Image analysis was performed on at least

300 particles for each system. The results shown in Table 1 and Figure 3 demonstrate that the mean particle diameter increases from 10.18 nm to 22.20 nm and the standard deviation increases from 4.41 nm to 11.14 nm as [NaOH] is increased. The Cu^+ concentration and gelatin percentage in all four experiments are the same, so the difference in the nucleation rate in the 1.4 M, 1.6 M, 2 M, and 2.4 M NaOH systems stems mainly from the difference in the NaOH concentration and not from the effect of the medium on the rate of diffusion of hydroxide ions. At the start of the experiment, the nucleation rate is fastest for the system with the largest difference in the Cu^+ and OH^- concentrations. When the nucleation happens quickly, more time is left during the 24 hour experiment time for the particles to grow, thus the mean diameter of the nanoparticles increases as the concentration of NaOH is increased.

We next investigated the effect of changing the gelatin percentage on the size of nanoparticles by allowing 2 M NaOH to diffuse into 10%, 12.5%, 15%, 17.5%, and 20% gel media containing the same concentration of Cu^+ ions. TEM images for the nanoparticles obtained were collected, and image analysis was done for each gel percentage. Figure 4 shows the particle size distribution for the different gel percentages. As the gel percentage increases from 10% to 15%, the mean diameter and the standard deviation of the nanoparticles do not change significantly (Table 1). However, as the gelatin percentage was increased further, a bimodal size distribution was obtained, particularly for the 20% gel system. This result is an indication of two nucleation and growth cycles¹⁹ in analogy to postnucleation models of Liesegang patterning, but before the formation of patterns, since our systems were investigated for nanoparticles before any visible patterning. As OH^- diffuses in the gel medium, the first nucleation and growth cycle results in the size distribution with the larger particle size. A second nucleation and growth cycle starts at a later time and location along the tube, as the hydroxide ions diffuse further in the gel medium, yielding a distribution of smaller particles size during the 24 hour experiment time.

The particles synthesized using 10% gelatin and 2 M NaOH were used for composition analysis. The XRD result is shown in Figure 5. The characteristic peak observed at 34.6° can be assigned to the crystalline phase of Cu_2O in a (111) cubic structure (JCPDS 34-1354). No characteristic peaks of CuO and Cu were observed in the XRD pattern, which indicates that the Cu_2O prepared is pure. Other not very well resolved peaks at around 43° and 63° can be assigned to (200) and (220) cubic Cu_2O .

Conclusion

We have prepared pure copper (I) oxide nanoparticles by diffusion of hydroxide ions into a gelatin medium containing copper (I) ions. The presence and stability of the nanoparticles were checked using UV-visible spectroscopy, and a constant peak at 500 nm was found. We investigated the effect of changing two experimental conditions, [NaOH] and [gelatin], on the mean size and the size distribution of the nanoparticles. At smaller sodium hydroxide concentrations the mean diameter and the standard deviation are small. Bimodal histograms were obtained as the gel percentage was increased to 20%, reflecting two distinct nucleation-growth cycles. The identity of the nanoparticles was characterized using XRD, where the spectrum revealed that the particles synthesized were pure Cu_2O . The dispersion of particle sizes obtained by our method is narrow compared to other synthesis methods^{6,20}, especially for the 1.4 M NaOH/10% gelatin system. In addition, our method opens the way for studies of nucleation and growth processes, since the synthesis is based on reaction-diffusion kinetics, in which the

reaction is limited by the diffusion of the sodium hydroxide solution into a gel network containing Cu^+ ions.

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<i>[NaOH]</i>	<i>% gelatin</i>	<i>Mean diameter (nm)</i>	<i>Standard deviation (nm)</i>
1.4 M	10%	10.18	4.41
1.6 M	10%	15.98	6.57
2 M	10%	19.37	7.98
2.4 M	10%	22.20	11.14
2 M	12.5%	17.06	7.20
2 M	15%	20.65	7.38
2 M	17.5%	13.94*	7.74
2 M	20%	14.77*	7.42

* bimodal distribution

Table 1 – The mean diameter and the standard deviation of the nanoparticles' sizes obtained for the different NaOH concentrations and gelatin percentages prepared.

Figure Captions

Figure 1 – UV-visible spectra of the 10% gelatin/2 M NaOH system taken at various times after the reaction is stopped.

Figure 2 – TEM images of copper (I) oxide nanoparticles synthesized using (a) 1.4 M, (b) 1.6 M, (c) 2 M, and (d) 2.4 M NaOH.

Figure 3 – Particle size distribution of copper (I) oxide nanoparticles synthesized using different NaOH concentrations.

Figure 4 – Particle size distribution of copper (I) oxide nanoparticles synthesized using different gelatin percentages.

Figure 5 – XRD pattern for Cu₂O nanoparticles.

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Figure 1

Figure 3

Figure 4

Figure 5

Cu_2O Nanoparticles