Physica B 415 (2013) 44–48

Contents lists available at SciVerse ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

Gelatin-stabilized copper nanoparticles: Synthesis, morphology, and their surface-enhanced Raman scattering properties

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ARTICLE INFO

Article history:
Received 30 November 2012
Received in revised form
21 January 2013
Accepted 24 January 2013
Available online 9 February 2013

Keywords:
Gelatin
Copper nanoparticles
Hydrazine
SERS

ABSTRACT

Gelatin-stabilized spherical-shaped copper nanoparticles are synthesized by a simple chemical reaction. The synthesis is performed by the reduction of copper (II) salt with hydrazine in aqueous solution under atmospheric air in the presence of gelatin as capping agent. Advantages of the synthetic method include its production of water dispersible copper nanoparticles at room temperature under no inert atmosphere and making the synthesis more environmental friendly. The synthesized copper nanoparticles are investigated by UV–vis spectroscopy, scanning electron microscope (SEM), energy dispersive X-ray spectrometer (EDS) and transmission electron microscopy (TEM). The results demonstrate that the amount of gelatin is important for the formation of the copper nanoparticles. The resulting colloidal copper nanoparticles exhibit large surface-enhanced Raman scattering (SERS) signals.

1. Introduction

Metal nanoparticles (NPs) have attracted considerable attention for their unusual chemical and physical properties, such as catalysis, novel electronic, optic, and magnetic properties, and application in biotechnology [1]. The properties of nanoscale copper have found application in catalysis (e.g., water gas shift catalysts and gas detoxification catalysts) [2,3]. The synthesis of copper nanoparticles with controllable sizes, shapes, and surface properties is vital to explore copper-based catalysis. Such abilities will also lead to an increased use of copper in many other areas of nanotechnology that are currently dominated by the use of gold, silver, and platinum nanoparticles. Although there are a number of approaches to synthesize copper nanoparticles under specific conditions [4], few methods have been established to control the size and shape effectively. Because of the propensity of copper to surface oxidation [5], a key issue is whether copper nanoparticles can be produced with controllable sizes and shapes. To date, relatively limited attempts have succeeded in synthesizing copper nanoparticles with controllable sizes, shapes, and surface properties. In previous reports, copper nanoparticles have been synthesized using several methods that include polymer protected copper nanoparticles in an aqueous phase [5], the encapsulation of copper using a thiol as capping agent [6], and thermal decomposition [7]. The copper nanoparticles resulting from these methods had either limited size monodispersity or were susceptible to oxidation [8,9].

Recently, Cu NPs synthesized with polymers as stabilizing agent were reported to improve their stability and biocompatibility and enhance the capability for the immobilization due to the superior properties of the formed nanocomposites [10]. Gelatin is the thermally and hydrolytically denatured product of collagen, which has been extensively applied as the immobilization matrix for the preparation of biosensors [11,12]. It has a triple-helical structure and offers distinctive advantages such as good biocompatibility, nontoxicity, remarkable affinity to proteins, and excellent gel-forming ability [13]. To the best of our knowledge, there is no report on the use of gelatin as stabilizing agent to prepare Cu NPs-embedded gelatin nanocomposites (Cu NPs-gelatin). In this study, Cu NPs were prepared in the gelatin solution without using any other additional stabilizing agents. The major advantage of gelatin as a stabilizing agent is that it can be used to tailor the nanocomposite properties and also provide long-term stability of the nanoparticles by preventing particle agglomeration. This method did not introduce any environmental toxicity or biological hazards and thus was simple and "green".

Herein, we report a simple method to synthesize colloidal Cu nanoparticles by reducing copper ions with hydrazine using gelatin as a stabilizing agent. The advantages of this method is that the use of atmospheric air (or no use of inert atmosphere) for the synthesis of copper nanoparticles and its production of copper nanoparticles with reasonably uniform size and relatively higher yield. While changing the amount of gelatin used in the synthesis was found to help us to produce pure copper nanoparticles as opposed to copper oxide. Investigation of the SERS property of the

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http://dx.doi.org/10.1016/j.physb.2013.01.041

resulting copper nanoparticles showed that the nanoparticles gave a 10^3 times SERS enhancement for crystal violet (CV) adsorbed on the nanoparticles compared to bulk CV.

2. Experimental section

2.1. Materials and Reagents

Copper (II) nitrate trihydrate was obtained from Guangdong Chem. Co.; hydrazine hydrate solution (80%) and gelatin was obtained from Kermel; crystal violet was obtained from Shanghai Chem. Co. All chemicals were used as received, without further treatment.

2.2. Synthesis of copper nanoparticles

In a typical synthesis of copper nanoparticles, various amounts of gelatin were completely dissolved in H_2O (30 mL) under magnetic stirring at 60 °C for about 30 min, and then cool to room temperature. At this time, copper (II) nitrate trihydrate (0.05 M) were added in. After stirring for 30 min, 6 mL of hydrazine hydrate solution was dropped into the above solution under constant stirring. The reactor was kept at room temperature without any inert atmosphere (Scheme 1). It should be pointed out that hydrazine hydrate can also increase the pH of the solution. The reaction was monitored by UV–vis spectroscopy until no change of the absorbance spectrum was observed. The metallic copper nanoparticles in this work were obtained from the redox reaction between Cu^{2+} and hydrazine in the presence of gelatin as capping agent.

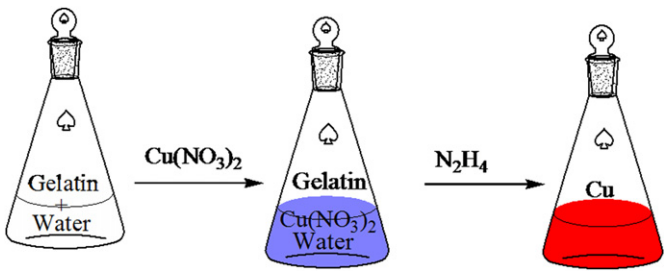
2.3. Instrumentation and instrumental methods

UV–visible spectra were recorded on a Shimadzu UV-1201 spectrophotometer in a 1 cm optical path quartz cuvette over a 200–800 nm range at room temperature. Nanoparticle size was analyzed by TEM using a JEOL 2100 transmission electron microscope operated at an accelerating voltage of 200 kV. The size distribution of the nanoparticles from the TEM micrographs was recorded digitally with a Gatan 794 charge-coupled device (CCD). Scanning electron microscope (SEM) images and energy dispersive X-ray spectrometer (EDS) analyses were preformed on a JEOL JSM-6380LV SEM. Raman spectra were obtained with a Renishaw 1000 model equipped with a CCD detector and a holographic notch filter. Radiation of 514.5 nm from an air-cooled argon ion laser (Spectra-Physics Model 163-C4260) was used for excitation.

3. Results and discussion

3.1. Synthesis of copper nanoparticles in aqueous solution

As in the synthesis of many types of colloidal nanomaterials, copper nanoparticles also require organic ligands to prevent them from irreversible aggregation in solution. Here, we used gelatin to prepare and stabilize small Cu nanoparticles. Besides providing long-term stability to the nanoparticles by preventing particle agglomeration, capping agents such as gelatin make the particles dispersible in aqueous solution. In our study, we found that the reaction time and the quantity of gelatin affected the formation of copper nanoparticles.



Scheme 1. Schematic illustration of the procedure used for the synthesis of gelatin-capped Cu nanoparticles.

3.1.1. Effect of reaction time

Fig. 1 displays the UV–vis absorption spectra that were taken at different stages of the continuous transformation of copper ions into gelatin-capped copper nanoparticles. After 15 min of reaction, a dark red solution, which displayed an absorption peak at 572 nm corresponding to the plasmon resonance of Cu nanoparticles, was observed (Fig. 2). Furthermore, after 180 min of overall reaction time, the solution turned red and showed a well-defined absorbance band still at ~572 nm corresponding to the plasmon resonance of Cu nanoparticles. This clearly indicated that the Cu nanoparticles started to form at the beginning of the reaction. In Fig. 1, we can see that the position of SPR band and

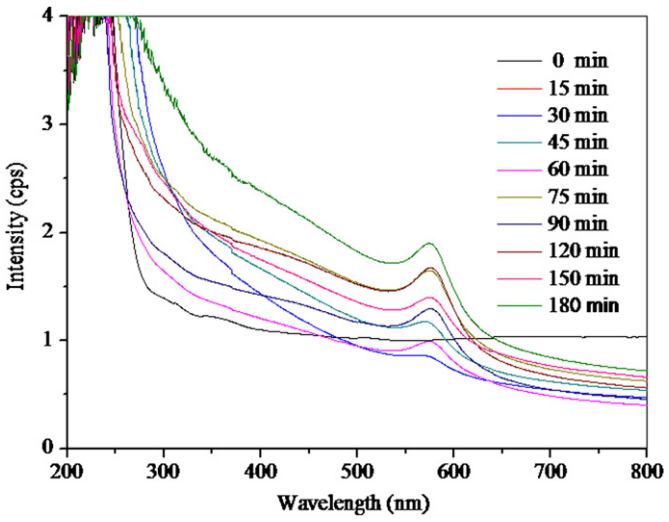


Fig. 1. UV–vis absorption spectra of copper hydrosol formed at different time intervals.

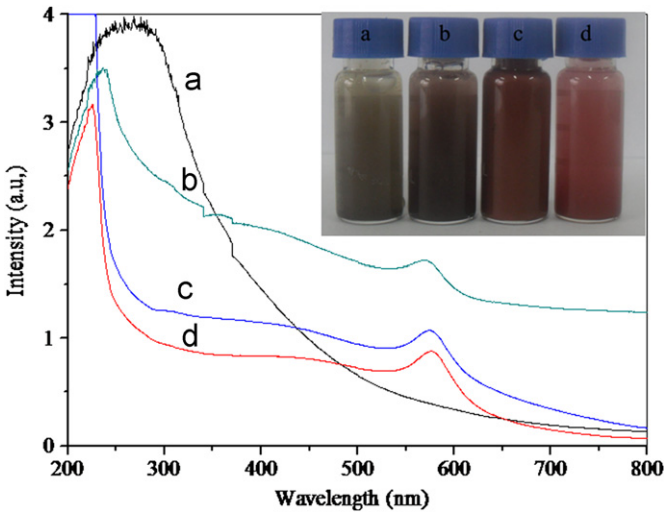


Fig. 2. UV–vis absorption spectra and the visible observation of solution color of copper hydrosol formed with different quantities of gelatin. (a): 0.1 g (b): 0.25 g (c): 0.5 g (d): 1 g. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)