

Direct, rapid synthesis of water-dispersed copper nanoparticles and their surface-enhanced Raman scattering properties



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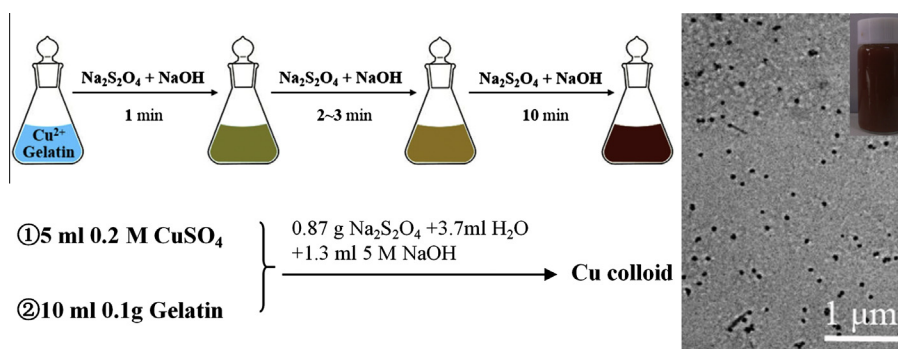
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HIGHLIGHTS

- Water-dispersed copper nanoparticles are rapidly synthesized under air atmosphere.
- Sodium hyposulphite works as reducing agent and gelatin as capping agent.
- High-purity copper nanoparticles are relies on the amount of NaOH and gelatin.
- The copper nanoparticles exhibit an excellent SERS activity.

GRAPHICAL ABSTRACT



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ABSTRACT

A facile synthetic method for monodisperse copper nanoparticles (CuNPs) has been reported, in which sodium hyposulphite works as reducing agent and gelatin serves as capping agent. Water-dispersed CuNPs have been produced without any protective atmosphere at room temperature. The as-prepared samples are characterized by ultraviolet-visible spectroscopy, transmission electron microscopy, X-ray diffraction and Raman spectra. The results show that the quasi-spheres and phase-pure crystalline CuNPs with a diameter of 32 ± 3 nm can be quickly obtained by adjusting the amount of NaOH solution and quantity of gelatin. The present work suggests a great potential of using obtained CuNPs colloidal as an efficient substrate for surface-enhanced Raman scattering signals.

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Introduction

Noble metal nanoparticles, such as Au and Ag, have been the most common subjects of research because of their novel physico-chemical properties and potential applications involving catalysis, biology, photonics, microelectronics, and as the substrate for surface-enhanced Raman scattering (SERS) signals [1,2]. However,

these noble metals are relatively expensive for the industrial applications. It has been well established in the literature that homologous elements show similar physical and chemical properties [3]. Thus, copper, an inexpensive material, has been an alternative candidate for the potential applications in a wide variety of areas such as the substrate for SERS, catalysis, optics, and antimicrobial actions [4–8].

As is well known, the unique properties of metal nanoparticles are highly dependent not only on the size, but also on the shape [9]. The ability to prepare copper nanoparticles (CuNPs) with well controlled sizes and shape is important in exploring their new application fields of SERS that are currently dominated by the

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use of gold and silver nanoparticles. To date, a few of preparation methods have been developed for CuNPs, such as thermal decomposition [8], dissociation the copper flakes into nanosized copper particles with ionic liquid [9], sonoelectrochemical method [10], photochemical reaction [11], laser ablation of pure copper or copper oxide [12] and liquid reduction method [13–15]. Among these methods, the chemical reduction of copper ions in aqueous solution is the most popular one because organic solvents are not used and the corresponding pollutants are absent. It is well known that CuNPs are easily oxidized to Cu₂O or CuO in air as well as in water. To avoid the oxidation, these methods were complicated, usually involving a number of steps or performed in nonaqueous media with low precursor concentration, and even under an inert atmosphere such as Ar or N₂.

Recently, much attention has been attracted to the preparation of water-dispersed CuNPs in the presence of various capping agent at room temperature, even under no inert atmosphere. However, until now, only few works have been done because Cu is easily oxidized. Wang et al. [16] prepared spherical- and rod-shaped CuNPs by reduction of copper ions with hydrazine in the presence of poly(allylamine) (PAAM) capping agent after 90 min reaction under atmospheric air. Wu et al. [17] reported the synthesis of high-concentration CuNPs (up to 0.2 M) by reduction of cupric chloride with hydrazine in aqueous cetyltrimethylammonium bromide (CTAB) solutions, and also the input of extra inert gases was not necessary. Wang et al. [18] proposed a solution-phase synthetic route to CuNPs by reduction copper ions with hydrazine in the presence of poly(acrylic acid)(PAA) as capping agent under air atmosphere. But hydrazine is used to work as reducing agent in the mentioned works. Therefore, there is a need for other reducing agent and more economic capping agent for the preparation of CuNPs. To the best of our knowledge, little information about the use of sodium dithionite as reducing agent has been reported.

In this paper, we report a facile, low-cost and fast method to synthesize monodisperse, high-purity colloidal CuNPs in aqueous solution at room temperature without any inert atmosphere. The CuNPs were prepared by reducing copper ions with sodium hyposulphite using gelatin as capping agent. The practical and economic advantages of the method include the use of atmospheric air and reaction at room temperature, even use of the cheaper gelatin as capping agent. The resultant nanoparticles were characterized by ultraviolet–visible (UV–vis) absorption spectroscopy, X-ray diffraction (XRD) and transmission electron microscopy (TEM). Their SERS properties were investigated in detail.

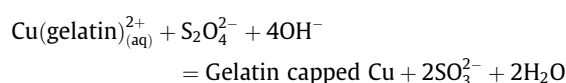
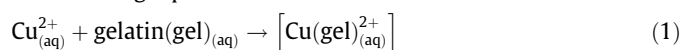
Experimental sections

Materials and reagents

Copper(II) sulfate pentahydrate (CuSO₄·5H₂O), sodium hyposulphite (Na₂S₂O₄) and Sodium hydroxide(NaOH) were obtained from Sinopharm Chemical Reagent Co. Ltd., China. Gelatin was purchased from Kermel, and CV was provided by A Johnson Matthey Co. All chemicals were used as received without further purification.

Synthesis of copper nanoparticles

The metallic CuNPs in this work were synthesized by chemical reduction of copper ions in aqueous solution at room temperature in air, and the chemical reduction reaction could be expressed by the following equation:



In a typical synthesis of copper nanoparticles, various amounts of gelatin were completely dissolved in H₂O (10 mL) at 80 °C for about 30 min under vigorous stirring with a magnetic stirrer, and then cooled to room temperature. At this time, 5 mL of CuSO₄·5H₂O (0.2 M) was added into the gelatin solution, giving a transparent light-blue solution. The quantities of gelatin varied from 0.05 to 0.25 g. Then another mixture of Na₂S₂O₄ (0.87 g) and various amounts of NaOH were dissolved in 3.7 mL H₂O. After that, the reducing solution was dropped into the oxidizing solution and the mixture was stirred for 30 min. The solution was centrifuged at 11,000 rpm for 15 min, then washed with deionized water and ethanol to remove any unreacted reactants, and dried under vacuum. It should be pointed out that the reactor was kept at room temperature without any inert atmosphere.

Characterization

The UV–vis absorbance spectra were recorded on a Shimadzu UV-2500 spectrophotometer in a 1 cm optical path quartz cuvette over a 200–800 nm range. The particle sizes from the TEM micrographs were carried out with a JEM-2000EX TEM operating at 160 kV, and the TEM samples were obtained by casting a drop of the as-prepared copper nanoparticle suspension on a carbon-coated copper grid and then drying them in air. The XRD measurement was performed on a Bruker D8 Advance X-ray powder diffractometer using Cu K α radiation. Raman spectra were done by the Renishaw Invia Raman microscope excited by an argon ion laser beam (514.5 nm, 20 mW). More details on the measurement can be found elsewhere [19].

Results and discussion

Synthesis of copper nanoparticles

Colloidal CuNPs could be quickly synthesized by reduction of copper sulfate with sodium hyposulphite using suitable quantities of gelatin and NaOH in the aqueous solution at room temperature without any inert atmosphere. The conversion of the copper ions to CuNPs was monitored by a set of color changes over different reaction periods, and the color changed from light-blue to deep green, then bright yellow, and finally wine-reddish gradually (Scheme 1). In our present study, we found that the size, purity and stability of the CuNPs were controlled by the amount of NaOH solution, quantity of gelatin and the reaction time.

Formation of copper nanoparticles by optimizing the amount of NaOH

The preliminary experiment indicated that the amount of NaOH was quite important for the synthesis of CuNPs, and the UV–vis spectra was recorded 30 min after addition sodium hyposulphite into Cu²⁺ solution in various amounts of 5 M NaOH in the presence of 0.005 g/ml of Gelatin. The typical UV–vis absorption spectra of as-prepared CuNPs and a graph of their absorption maxima versus molar concentration of NaOH are shown in Fig. 1.

As shown in Fig. 1a, the intensity of the absorption peak changed with the amount of NaOH. When the amount of 5 M NaOH varied from 1.0 to 1.7 ml, the UV–vis absorption spectra of the resulting nanoparticle solutions displayed a well-defined surface plasmon (SP) peak at around 575 nm corresponding to the plasmon resonance of CuNPs [16]. The intensity of this plasmon peak reached its maximum when the NaOH amount increased to 1.3 mL, indicating the increase in the number or yield of CuNPs (Fig. 1b). Also no clear absorption peak for copper oxide around 800 nm was observed [17]. These results further indicated that the formation of metallic CuNPs could be achieved quickly by reduction of copper sulfate with sodium hyposulphite in the presence of suitable quantity of NaOH.

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