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A method for the preparation of silver nanoparticles using commercially available carboxymethyl chitosan and sunlight



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ABSTRACT

In this paper, a novel and useful method based on photolysis of silver chloride is presented for the preparation of silver nanoparticles. Silver nanoparticles can be prepared by using silver nitrate and commercially available carboxymethyl chitosan under solar irradiation. This method is based on the photolysis of silver chloride. The stabilizing effect of carboxymethyl chitosan allows for the stable storage of these silver nanoparticles in the reaction mixture for more than six months; further, nanoparticles of different sizes can be separated from each other just by centrifugation. The favorable properties of carboxymethyl chitosan facilitate the use of these nanoparticles without further purification.

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1. Introduction

Metallic nanoparticles have attracted great attention because of their size-dependent physical and chemical properties [1]. Silver nanoparticles are among the most widely studied metallic nanomaterials with applications in medicine [2], catalysis [3], biotechnology [4], etc. The conventional method for preparing silver nanoparticles, which is based on the chemical reduction of a silver salt, is simple and effective, but removal of the agents used is both cost- and time-intensive; furthermore, the residual agents show biological toxicity [5]. Thus, there is an increased interest in using dispersing or reducing agents based on biomaterial systems [6]. Over the last decade, polysaccharide based biopolymers such as, alginate [7], starch [8,9], and chitosan [10,11] have been used as “green” alternatives [12] to conventional agents due to their low cost, nontoxicity and environment-friendly processing. In most cases, the chemical dispersants for controlling growth of metallic nanoparticles was replaced by these biopolymers and toxic reductants were still used. Although some polysaccharides and their derivatives can act both as dispersant and reductant in some

processes [13,14], the reducing reaction is usually initiated by γ -rays [14], UV-rays [15], or heat [16]. It is necessary to create a “greener” and handier method.

Carboxymethyl chitosan (CMCS) is one of important derivatives of chitosan and shows good solubility in water over a wide range of pH. Since the carboxymethyl derivative is obtained by carboxylation of the hydroxyl and amine groups of chitosan using monochloroacetic acid, commercially available CMCS contains a small amount of chlorine. Thus, the suspension of silver chloride would be produced in the mixture of commercially available CMCS and silver nitrate. On the other hand, the photosensitivity of silver halide has been known for a long time and is exploited in photography. The photolytic decomposition of silver chloride generates silver atoms and chloride radicals. Zayat et al. found that glass films containing AgCl exhibited strong coloration upon exposure to sunlight, because of the reduction of AgCl to silver nanoparticles [17]. Obviously, compared to other methods, solar photolysis is more suited for use in the industry as it does not involve the use of any complex apparatus and low energy consumption. So, based on this research, we put forth a novel method for the preparation of silver nanoparticles. Silver nanoparticles were prepared by reducing silver nitrate in the presence of commercially available CMCS and sunlight. To the best of our knowledge, this is the first time that silver nanoparticles have been synthesized using such a simple method.

The CMCS polymer has been shown to be non-toxic both in vitro and in vivo [18]. Because of the biocompatibility of the starting reactants (commercially available CMCS and silver nitrate), the

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resulting nanoparticles can be used for downstream applications without further purification in some cases. Similar to other polysaccharides, the CMCS matrix can prevent the nanoparticles from aggregating [19,20]. The polymer can be used in diverse ways: as a gel [21], as a film [22], or as a sphere [23]. All these properties of CMCS make it a good candidate for use in the synthesis of silver nanoparticles.

In this work, the effects of the irradiation time and the molar ratio of the silver and chloride ions on the reaction were examined by UV–visible (UV–vis) spectroscopy, transmission electron microscopy (TEM), and X-ray diffraction (XRD).

2. Materials and methods

Materials: All compounds were used as received. Pharmaceutical grade carboxymethyl chitosan (95.1% substituted ratio) was obtained from Honghai Biotechnology Co. Ltd. (Qingdao, China). Silver nitrate (analytical reagent) and sodium chloride (analytical reagent) were obtained from Kelong Chemical Reagent Factory (Chengdu, China). Ultrapure water was obtained from a Millipore Milli-Q Plus filtration system.

Preparation of silver nanoparticles: An aqueous solution of commercially available CMCS (0.1% (w/v)) was prepared and stirred overnight. As determined by ion chromatography (ICS-3000, Dionex, USA), the concentration of chloride ions in the stock solution of commercially available CMCS was 14 mg/L (approximately 0.4 mM). Different amounts of a 0.6 M aqueous solution of AgNO_3 (1 mL, 400 μL , 200 μL , and 67 μL) were added dropwise under magnetic stirring into 100 mL of the CMCS stock solution. The reaction solutions were then irradiated by sunlight for different time durations. The mixtures were stirred with a magnetic stir bar during the irradiation. Control experiments in the absence of solar light (control A: 0.1% (w/v) CMCS polymer, 0.4 mM Cl^- , 6 mM Ag^+ and no solar irradiation), commercially available CMCS (control B: 0% CMCS polymer, 0 mM Cl^- , 6 mM Ag^+ and solar irradiation for 7 h) and only CMCS polymer (control C: 0% CMCS polymer, 0.4 mM Cl^- , 6 mM Ag^+ and solar irradiation for 7 h) were carried out under the same conditions.

Characterization: Before characterization, the nanoparticles were purified from the reaction solution by centrifugation. The precipitates were rinsed three times and re-suspended in ultrapure water.

The reactions were monitored using a UV-3600 UV–vis spectrophotometer (Shimadzu, Japan). TEM and selected area electron diffraction (SAED) experiments were conducted on a LIBRA 200 TEM (ZEISS, Germany) at an accelerating voltage of 200 kV. The TEM samples were prepared by slowly evaporating a drop of the nanoparticle solutions on a copper grid covered by a carbon-supported film at room temperature. XRD experiments were performed on a D/MAX-2500PC X-ray diffractometer (Rigaku, Japan) using $\text{Cu K}\alpha$ radiation. The tube voltage and current were 40 kV and 150 mA, respectively. The purified nanoparticle suspensions were coated on glass plates and dried. The obtained films were used for the XRD measurements.

3. Results and discussion

UV–vis analysis: Irradiation of the reaction mixture with solar light caused the extinction value to increase over time, reaching the peak value after 7 h (Fig. 1). Longer irradiation times resulted in a decrease in the peak extinction value (Fig. 1, green line). The reaction solution darkened with increasing irradiation time, because of the increased amount of silver nanoparticles (inset, Fig. 1). When the reaction solution was kept in the dark, no significant change in the extinction intensity or wavelength of the nanoparticles was

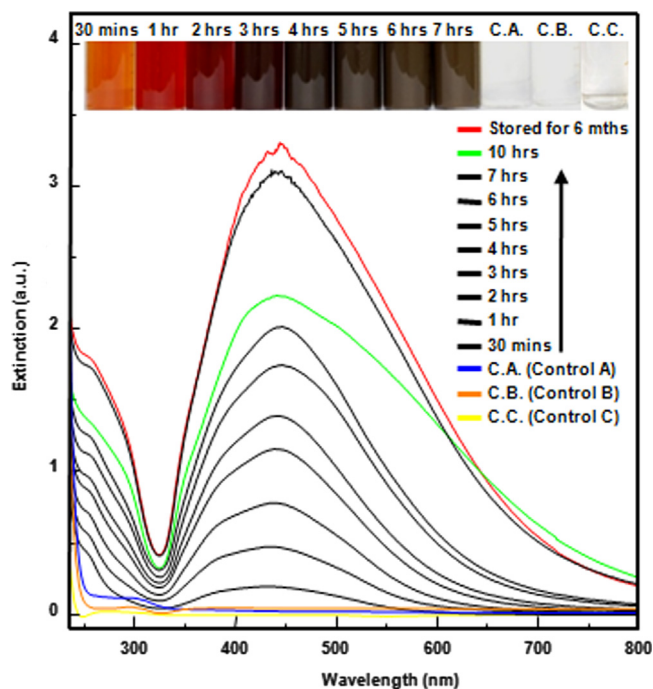


Fig. 1. UV–vis spectra of the reaction mixture at different time points. The reaction was carried out using commercially available CMCS (0.1%, w/v) and AgNO_3 (6 mM) in the presence of sunlight. In first control experiment, the solution of commercially available CMCS (0.1%, w/v) and AgNO_3 (6 mM) was kept in the dark for 7 h (C.A.). In second control experiment, an aqueous solution containing only AgNO_3 (6 mM) was irradiated by solar light for 7 h (C.B.). In final control experiment, an aqueous solution containing NaCl (0.4 mM) and AgNO_3 (6 mM) was irradiated by solar light for 7 h (C.C.). The inset shows the photograph of the solutions. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

observed even after six months (Fig. 1, red line). This stability of the nanoparticles can be attributed to the stabilizing effect of the CMCS matrix.

Control experiments carried out in the absence of solar irradiation or commercially available CMCS (C.A. and C.B.) do not show any extinction peak in the UV–vis spectra (Fig. 1, blue and orange line), suggesting that solar irradiation and commercially available CMCS were essential to the preparation of silver nanoparticles using this method. Furthermore, the control solution containing no CMCS polymer (C.C.) also does not show any extinction peak in the UV–vis spectra (Fig. 1, yellow line), and a little black precipitation was produced in the solution. It suggested that CMCS polymer helped to disperse the Ag nanoparticles in the reaction solution.

XRD analysis: The XRD patterns of the nanoparticles purified by centrifugation showed a total of ten peaks (Fig. 2a and b). In addition to the peaks corresponding to Ag ($2\theta=38.1^\circ$, 44.3° , 64.5° , 77.4° , and 81.4°), another five peaks ($2\theta=27.8^\circ$, 32.3° , 46.3° , 54.8° , and 57.5°) corresponding to the diffraction lines of AgCl were also observed. There was an obvious reduction in the intensity of the peaks corresponding to AgCl on prolonged irradiation (Fig. 2a) or on decreasing the molar ratio of silver and chloride ions (Fig. 2b, molar ratios of 15:1; 6:1 and 3:1). However, the photolysis reaction could not be pushed to completion even after irradiation for 10 h (Fig. 2a) or by further lowering the molar ratios of silver and chloride ions. Surprisingly, the reaction was hindered on using an equimolar ratio of silver and chloride ions (Fig. 2b). Thus, it was impossible to reduce all the silver chloride to silver nanoparticles, as evidenced by the presence of the silver chloride peak(s) in all the XRD patterns.

TEM and SAED experiments: The morphology of the nanoparticles could be easily observed by TEM. Most particles were around

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