



Semen cassiae extract mediated novel route for the preparation of silver nanoparticles

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ABSTRACT

In this study, we report a simple and environment friendly method for synthesis of well dispersed and stable silver nanoparticles using semen cassiae extract as both reducing and stabilizing agents in aqueous solution without employing any other reducing and capping agents. The formation of silver nanoparticles was observed by change of color from light yellow to red and the UV–vis absorption spectroscopy. The effect of reaction time and semen cassiae amounts on the synthesis of silver nanoparticles was studied. The morphology of the as prepared silver nanoparticles was examined by using HRTEM, which showed that the silver nanoparticles were spherical in shape with a size distribution from 2 nm to 30 nm. The crystalline structure of the silver nanoparticles was confirmed by XRD analysis. The as synthesized silver nanoparticles were tested against *Escherichia coli* and the obtained data were indicative of good antibacterial properties of the materials. The method presented in this paper provides a very promising approach to synthesize other noble nanoparticles using renewable materials as reducing and capping agents.

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1. Introduction

Recently, metallic nanoparticles have received considerable attention in engineering technology and nanoscale science because of their novel physical and chemical properties [1–4]. Among them, silver nanoparticles have aroused intensive interest due to the low-cost, high-efficiency and unique optical and electronic properties which lead to potential applications in industrial fields such as catalyst [5], antimicrobial agents, conductive coating and sensors [6,7]. Silver nanoparticles with various sizes, shapes and surface properties have been synthesized by a large number of strategies such as surfactant-assisted chemical, photoreduction, thermal decomposition, microwave-assisted synthesis, radiation chemical reduction and phase transfer method [8,9]. Among the various methods, the chemical reduction method is the most extensively used due to its simplicity, low cost, and the ease of size and shape control over silver nanoparticles [2,10,11]. Sodium borohydride, hydrazine hydrate and ethylene glycol are usually used as reducing agent to synthesize nanosize silver particles [12–14]. However, most of the current reducing agents cause serious environmental pollution and limit the applications of silver nanoparticles [15].

To address this problem, some non-toxic or green reducing agents, such as glucose, maltose and ascorbic acid, are used to

prepare silver nanoparticles in aqueous solution [15,16]. However, most of the reported green methods need a relative higher temperature and longer reaction time [3,15]. Hence, a more convenient method is desired to synthesize silver nanoparticles.

Plants extract has been widely used for the biosynthesis of metal nanoparticles. *Ixora coccinea* leaves extract has been used to prepare silver nanoparticles with size distribution from 13 nm to 57 nm [17]. The *I. coccinea* leaves extract acts as both the reducing and capping agents. Banana peels extract has been used to produce silver nanoparticles [18]. The as-synthesized silver particles displayed antifungal activity against the yeasts *C. albicans* and *Candida lipolytica* [18]. In this paper, we report the green synthesis of silver nanoparticles using semen cassiae extract as both the reducing and capping agents. Semen cassiae (the seed of annual plant *Cassia obtusifolia* L.) belongs to the Leguminosae family [19]. It is extensively cultivated in China and Korea, and easily grown. Semen cassiae was usually drunk as a roasted tea [19,20]. Furthermore, semen cassiae was generally used as a traditional Chinese medicine, which reduces inflammation in the liver, to improve eyesight and relax bowels [20,21]. To the best of our knowledge, it is the first time to use semen cassiae extract for synthesis of metal nanoparticles.

2. Experimental methods

Semen cassiae was obtained from local market in Wuhan, Hubei, China. Silver nitrate used in the experiment was purchased from Sinopharm Chemical Reagent Co. Ltd. Silver nitrate acted as

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the precursor in the formation of silver nanoparticles. Water used in the experiment was doubly distilled water. All chemicals and solvents were of analytical grade and were used as received without further purification. *Escherichia coli* was procured from School of Life Science and Technology, HUST.

The obtained semen cassiae was washed thoroughly in tap water and finally rinsed with distilled water until no foreign material remained. The cleaned semen cassiae was taken in a 250 mL flask, and 100 mL distilled water was added and boiled at 100 °C for 10 min. The semen cassiae extract was filtered through Whatman no.1 filter paper. The extract volume was adjusted to 100 mL by adding distilled water. This extract was stored at 4 °C and was used for further studies within 2 days.

In a typical reaction procedure, 10 mL of semen cassiae extract was added to 40 mL of 0.147 M silver nitrate solution (silver nitrate: 0.1 g) and kept at room temperature with continuous stirring (keeping in mind that the total volume of the reaction medium is 50 mL). Then the solution was maintained at room temperature and allowed to react for 24 h. The color of the reaction mixture was gradually changed from light yellow to red, suggesting the formation of silver nanoparticles. The green synthesis of silver nanoparticles in a solution was monitored by measuring the UV–vis spectra of the reaction mixture. The UV–vis spectra were recorded on a UV–vis Spectrophotometer (Cary 50 scan) from 300 to 800 nm at a resolution of 1 nm. Distilled water was used as a blank. The high magnification transmission

electron microscope (HRTEM) observations were performed using a Tecnai G2 F30 microscope at an acceleration voltage of 300 kV. The crystallinity and phase composition of the silver nanoparticles were characterized by using an X'Pert PRO X-ray diffractometer. The antimicrobial activity of the synthesized silver nanoparticles was evaluated against *E. coli* by the disc diffusion method [22,23].

3. Results and discussion

Biosynthesis of silver nanoparticles was prepared from the aqueous silver nitrate and semen cassiae extract at room temperature. In this reaction, semen cassiae extract acted as both the reducing and stabilizing agents. The reaction mixture changed with the progression of the reaction, from light yellow to deep yellow, and then red. To follow the reaction process, the color change of the reaction mixture was monitored by taking photographs and UV–vis absorption spectroscopy at different time intervals, as shown in Fig. 1. The color change and the surface plasmon resonance (SPR) peak at 415 nm obtained at 1 h reaction time confirmed the formation of silver nanoparticles (Fig. 1A(a–h) and Fig. 1B(a)). Gradually longer reaction time, from 1 h to 24 h, increased the corresponding peak intensities, with concomitant red-shifts from 415 nm to 426 nm (Fig. 1B(b–h)). The enhancement in intensities and small red-shifts indicated increase in the concentration and the size of the silver nanoparticles. We suggest

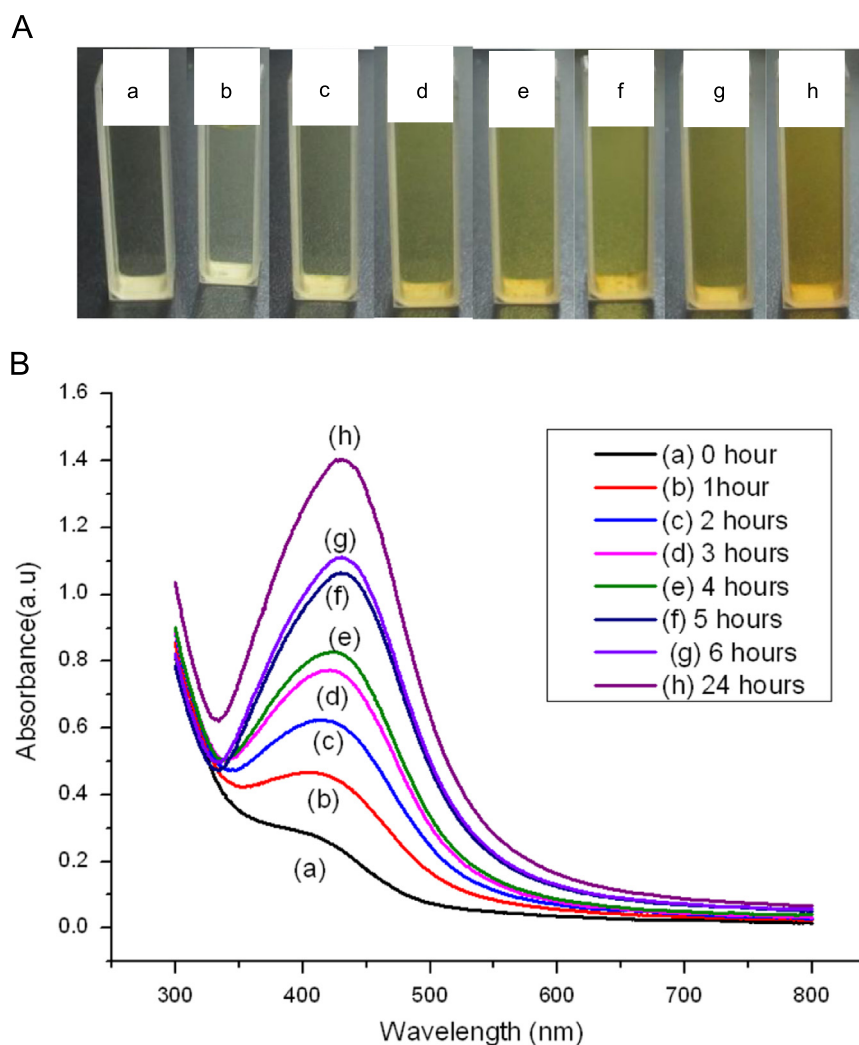


Fig. 1. Photographs and the UV–vis absorption spectra as the color change at different reaction time intervals.

that the color changes are related to the reaction that occurred in the solution: silver ions are first coordinated with semen cassiae extract, which are then reduced to zero-valent metallic silver nanoparticles. However, a more analysis is needed to explain the mechanism of reaction.

It is clear that the size, distribution, and dispersibility of the silver nanoparticles are influenced by the concentration of the capping agent and the reducing agent. Fig. 2 shows the UV–vis absorption spectroscopy and photographs of silver nanoparticles synthesized using different amounts of semen cassiae extract. It is

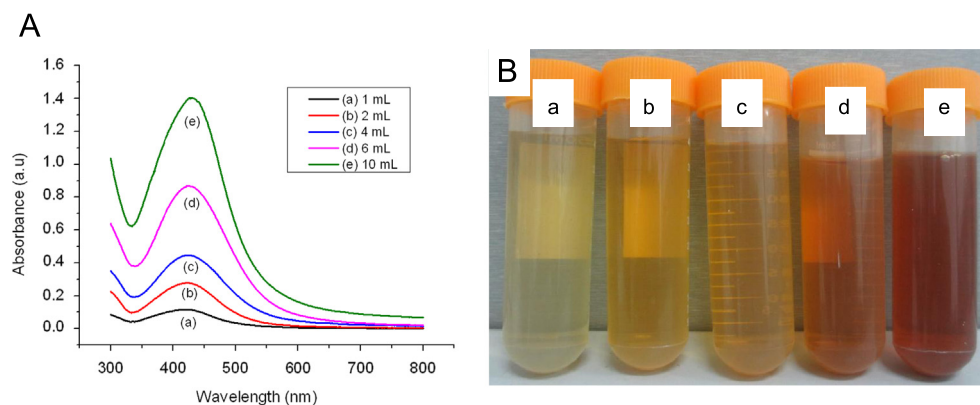


Fig. 2. Effects of semen cassiae extract amount on UV–vis spectra and photographs of as-prepared nano-silver sols.

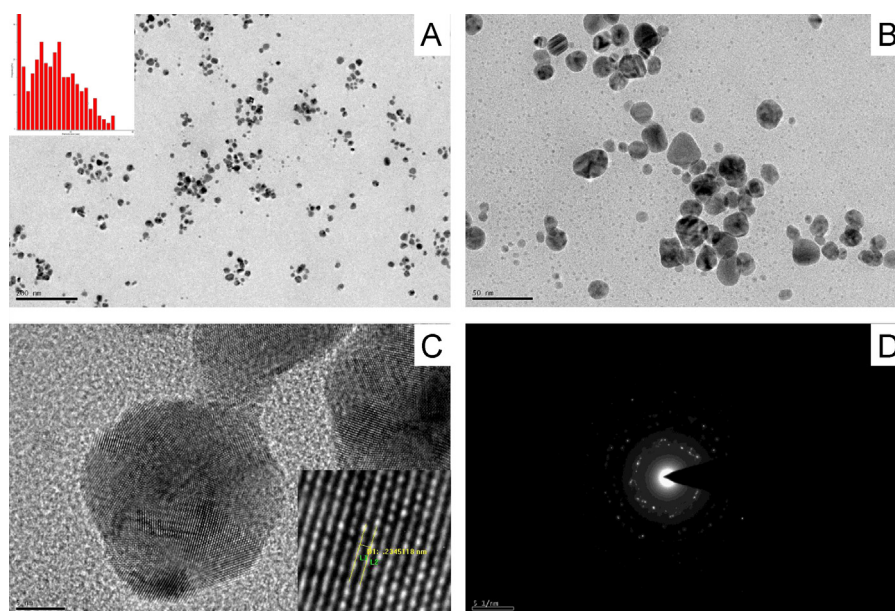


Fig. 3. Typical (a and b) TEM (c) HRTEM and (d) SAED pattern image for the synthesized silver nanoparticles. The inset in (a) is the corresponding size distribution. The inset in (c) is the corresponding lattice fringes.

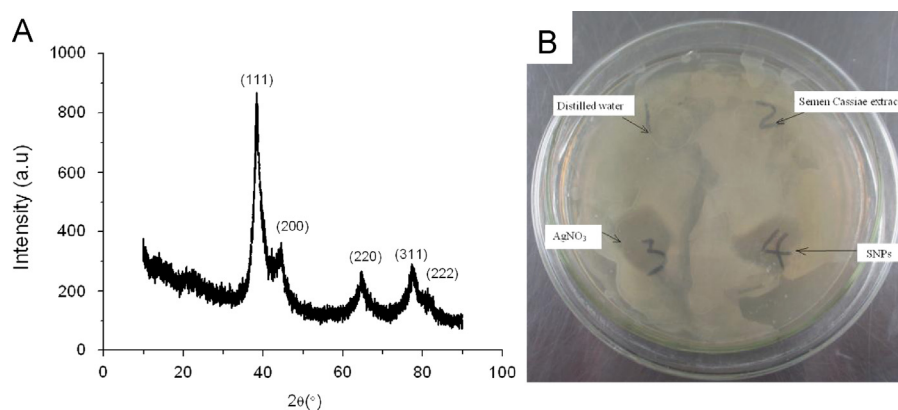


Fig. 4. (a) XRD pattern of silver nanoparticles. (b) Antimicrobial activities of silver nanoparticles against *E. coil*.

clearly seen that the color and UV–vis absorption spectroscopy of the as-prepared silver nanoparticles depend on the amount of semen cassiae extract. With increasing addition of semen cassiae extract into silver nitrate solution, the SPR bands were gradually increased and the color gradually changed from light yellow to red. It is obvious that the semen cassiae extract concentration played an important role in the synthesis and stabilization of the silver nanoparticles. Similarly, a gradual increase in absorption intensity was found when the concentration of pullulan was increased from 1.0% to 15% [24]. Furthermore, Pandey et al. also reported that the absorption intensity was increased as the concentration of guar gum was increased from 1.2% to 3.5% [25]. The higher concentration of pullulan and guar gum could be ascribed to increased stabilization of the prepared silver nanoparticles. We suppose that the semen cassiae extract plays a similar role by reducing silver ions to metallic silver nanoparticles and stabilizing the growth of silver nanoparticles.

The size and morphology of the semen cassiae stabilized silver nanoparticles were confirmed with the help of HRTEM and the results are shown in Fig. 3. Fig. 3a and b shows that the mono-dispersed silver nanoparticles are in the sizes ranging from 2 nm to 30 nm. The corresponding size distribution (the inset in Fig. 3a) displays that the silver nanoparticles are small with an average size of 18 nm. Further structural information was obtained from HRTEM image of the prepared silver nanoparticles as shown in Fig. 3c. The lattice fringes in the image are clearly seen (as shown in Fig. 3c) and consistent with the (111) planes of the FCC phase of metallic silver, with about 0.235 nm periodicity (as shown in the inset of Fig. 3c) [8,26,27]. The corresponding selected area electron diffraction (SAED) is shown in Fig. 3d, suggesting that the obtained silver nanoparticles are of single crystalline nature [23,28]. The crystalline nature of the obtained silver nanoparticles was also confirmed by XRD analysis. Fig. 4a reveals the XRD pattern of the silver nanoparticles with five distinctive diffraction peaks at 38.8° , 44.5° , 64.5° , 78.1° and 81.55° in the 2θ region, which correspond to (111), (200), (220), (311) and (222) lattice planes of silver nanoparticles. These data indicated that the as prepared particles were a face-centered cubic (FCC) crystal structure of silver nanoparticles (JCPDS no. 87-0717). According to the Scherrer equation, the average crystallite size of silver nanoparticles is about 20 nm based on the calculation using the width of (111), consistent with the result of TEM analysis. The as-synthesized silver nanoparticles exhibited significant antibacterial activity against *E. coli* while the semen cassiae extract, distilled water and silver nitrate were not active as shown in Fig. 4b. Furthermore, the as-synthesized silver nanoparticles were highly stable. There is no sign of sedimentation even after 1 month storage.

4. Conclusions

In summary, semen cassiae extract was used for the first time as capping agent and reducing agent to prepare silver nanoparticles. The semen cassiae plays an important role in the synthesis of

small size silver nanoparticles. The obtained silver nanoparticles were spherical in shape with an FCC structure. The size of the as-synthesized silver nanoparticles is less than 30 nm. The as-synthesized silver nanoparticles were highly stable and they exhibited significant antibacterial activity against *E. coli*.

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