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Ultrasonic-assisted synthesis of starch-stabilized silver nanoparticles

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Well-dispersed and uniform starch-stabilized silver nanoparticles (Ag-NPs) with a relatively narrow size distribution are prepared via green chemistry method by ultrasonic procedure. Solutions containing silver ions and starch in water gave starch-capped Ag-NPs, which could be integrated into medical applications such as using in antibacterial wound dressing. Eco-friendly materials as bio-organisms in plant extracts contain polysaccharides, which act as both reducing and capping agents forming stable and size-controlled Ag-NPs. The size of the Ag-NPs decreases with the ultrasonic time. Ultrafine spherical Ag-NPs with a mean particle size of about 8.5 nm have been synthesized under ultrasonic process. X-ray diffraction (XRD), energy-dispersive X-ray analysis (EDX), UV–Vis spectroscopy, and transmission electron microscopy (TEM) are used to characterize the starch-stabilized Ag-NPs.

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1. Introduction

Normally, metallic nanoparticles can be fabricated and stabilized by physical and chemical methods; the chemical approach, such as the chemical reduction and the photochemical reduction is mainly applied [1-4]. Previous works have displayed that the size, stability, morphology, and properties -chemical and physical- of the metallic nanoparticles are strongly related to the experimental conditions such as interaction of metallic ions with reducing and stabilizing agents with metallic nanoparticles [5-7]. The design of a fabrication method in which the size, stability, morphology, and properties are controlled has become a most important and interesting field in nanotechnology. The interesting properties of nanomaterials strongly depend on size, shape of nanoparticles, their interactions with stabilizers and surrounding media, and also on the method of their preparation. Therefore, the controllable synthesis of nanoparticles is a key challenge to obtain their enhanced applied characteristics [8]. Nowadays, the inorganic antimicrobial agents have attracted interest for using in control of different microbes such as several ceramics and/or bioceramics which immobilized by antimicrobial metals (e.g., Ag and Cu) [9, 10]. Among the metallic nanomaterials Ag-NPs has been widely used for hygienic and medicinal purposes are times honored and prominent, though the mechanism is not yet fully understood [11].

Colloidal silver nanoparticles (Ag-NPs) with natural macromolecule can be fabricated by physical [12-15] and chemical reduction [16-19] methods. However, no literature is available on its preparation in starch by ultrasonic field. The sonochemical methods are follows: formation, development, and the implosion of the microcavities [20]. Starch which is a polymer of hexacarbone monosaccharide-D-glucose as a single helix structure [21] which it can cover the surface of the metallic nanoparticles by hydroxyl groups as a capping agent. This is due to the surface of many metallic NPs such as Ag, Au, and Cu which is negatively charged [22]. The sonochemical methods are follows: formation, development, and the implosion of the microcavities [23]. When solutions are exposed to ultrasonic irradiation, bubbles in the solution could be imploded by acoustic fields. Cavitations' bubble collapse can also induce a shockwave in the solution and drive rapid impact of the liquid to the surface of the particles [24]. The sonochemical method has been used to generate Ag-NPs [25], but for a long time (12h) $NaBH_4$ was used as reducing agent of hazardous materials. The obtained samples are not uniform and narrow in size. This work studied the effect of ultrasonic times on the size of synthesized Ag-NPs were studied.

2. Materials and methods

All the materials used were of analytical grade and were used without any purification. Silver nitrate (99.98%) was purchased from Merck (Germany). Soluble starch was purchased from the Sigma-Aldrich (USA). All glassware used in the laboratory experiments was cleaned with a fresh solution of HNO_3/HCl (3:1, v/v), washed thoroughly with doubly distilled water, and dried before use. Double distilled water was used in all experiments. Colloidal Ag-NPs were synthesized by reducing $AgNO_3$ with ultrasonic waves in the presence of starch. Briefly, 20 mL of $AgNO_3$ solution (0.1M) containing starch (1% wt.) was exposed to high-intensity ultrasound irradiation under ambient conditions at different periods of ultrasound irradiation (e.g., 5, 15, 30, 45, and 60 min). Ultrasound irradiation was carried out with an ultrasonic liquid processors (Misonix sonicator S-4000, USA, 20 kHz) immersed directly into the reaction solution. The colloidal Ag-NPs synthesized under the ultrasonic process were characterized by using X-ray diffraction (XRD, Philips, X'pert, Cu K_α), energy-dispersive X-ray analysis (EDX, Quanta 200F), ultraviolet-visible spectroscopy (UV-Vis, Evolution 300® Thermo Fisher Scientific, Germany), and transmission electron microscopy (TEM, Hitachi H-7100®, Japan). The particle size distributions of nanoparticles were determined using the UTHSCSA Image Tool® Version 3.00 program.

3. Results and discussion

Five aqueous solutions containing $AgNO_3$ (0.1M) and starch (1.0 %wt.) are irradiated at amplitude of 50 for 5, 15, 30, 45, and 60 minutes. Depending on the irradiation times, the reaction solutions display a spectrum of light yellow to dark yellow colors (Fig. 1).

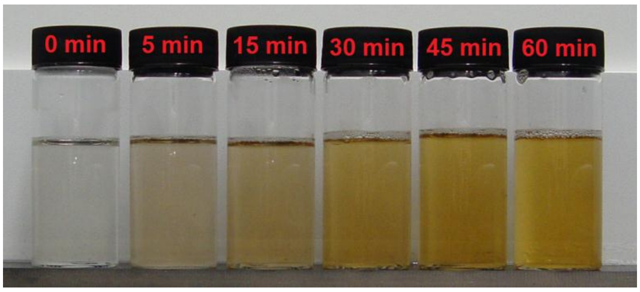

Fig. 1. Photograph of synthesized Ag-NPs.

The X-ray diffraction (XRD) patterns of the Ag-NPs synthesized via the sonochemical method using starch as the reducing and capping agent are shown in Fig. 2. All the reflections correspond to pure Ag-NPs with face centered cubic (fcc) symmetry. The reflections were indexed as [111], [200], [220], and [311] with the corresponding 2θ values of 38.1˚, 44.3˚, 64.4˚, and 77.4˚, respectively (JCPDS 07-0783). The intensity of peaks reflected the high degree of crystallinity of the Ag-NPs [26, 27]. However, the diffraction peaks were broad indicating that the crystallite size is very small [28].

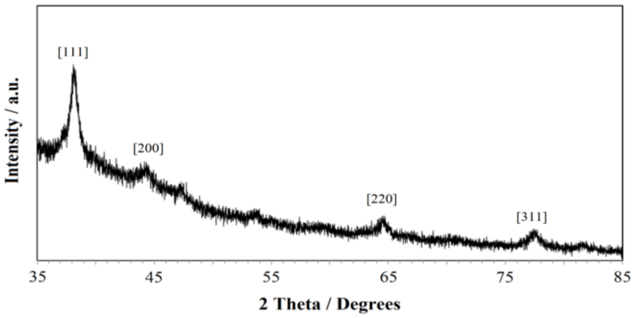

Fig. 2. XRD pattern of synthesized Ag-NPs/starch.

The elemental contents of the products were measured using EDX analysis. Fig. 3 shows the EDX spectrum of prepared Ag-NPs after 60 min by sonication. The emission peaks for Ag are clearly observed; similar results have been reported by Li et al (29) and Fayaz et al (30).

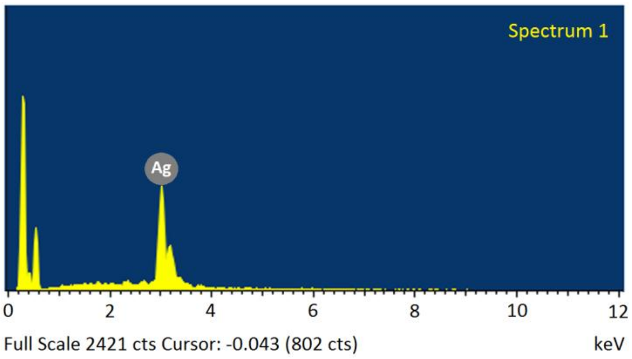

Fig. 3. EDX spectrum of prepared Ag-NPs/starch.

The dark yellow color indicates high Ag-NPs concentration which was confirmed by UV–Vis absorption spectra. The UV-Vis spectroscopy is a reliable route for displaying the presence of metallic nanostructures [25, 31]. Surface plasmon resonance (SPR) is a collective excitation of the electrons in the conduction band near the nanoparticles' surface [32]. While there is a weak characteristic UV–Vis absorption of Ag-NPs after 5 min sonic irradiation (Fig. 4), increasing in intensity of surface plasmon resonance (SPR) peak at 431 nm indicates as well as the formation of Ag-NPs (Fig. 4, 15 min). Gradually longer irradiation times, from 5 to 60 min, increase the corresponding peak intensities, with concomitant blue shifts from 431 to 416 nm. This suggests formation of smaller Ag-NPs [33].

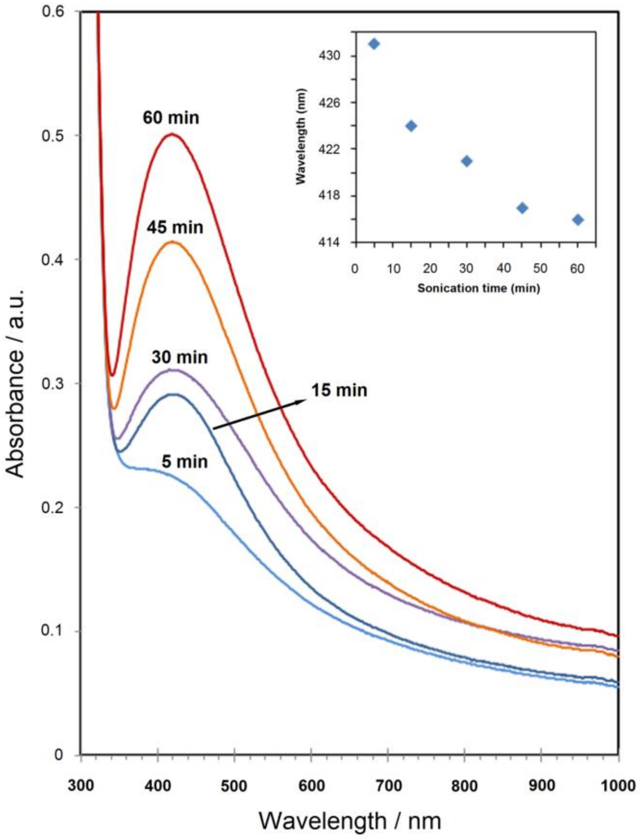

Fig. 4. UV-Vis spectra of synthesized Ag-NPs in starch solutions at different sonic irradiation times.

Based on Mie's theory [34], nanoparticles with different sizes should demonstrate different optical properties due to the difference in the SPR bands. As shown in Fig. 4, the SPR of starch stabilized Ag-NPs possessing different diameters. As such, when the particle diameter decreased from 14.1 ± 4.31 nm to 8.5 ± 2.31 nm (Fig. 5), the λ_{max} of SPR blue shifted from about 431 to 416 nm (Fig. 4; Inside). The absorption peak due to the SPR of metallic nanoparticles displayed the blue-shift with decreases in the particle diameter [35]. This result demonstrates that the larger Ag-NPs were obtained under shorter sonic irradiation time and disintegrated due to further sonic irradiation.

The sharp SPR band of starch-stabilized Ag-NPs (Fig. 4, 60 min), indicating the formation of uniform spherical nanoparticles. The TEM images also demonstrate the formation of Ag-NPs due to sonic irradiation after 5 and 60 min. Fig. 5 shows typical TEM images and the corresponding particle size distribution of the synthesized Ag-NPs at different sonic irradiation times. The TEM results confirmed the UV-Vis spectra and indicated that the samples obtained over a longer time period (Fig. 5c and d; 60 min) retained a narrower particle size distribution. The Ag-NPs are mostly spherical and exhibit a relatively narrow size distribution with a mean particle diameter of 8.5 ± 2.31 nm in longer sonic irradiation time.

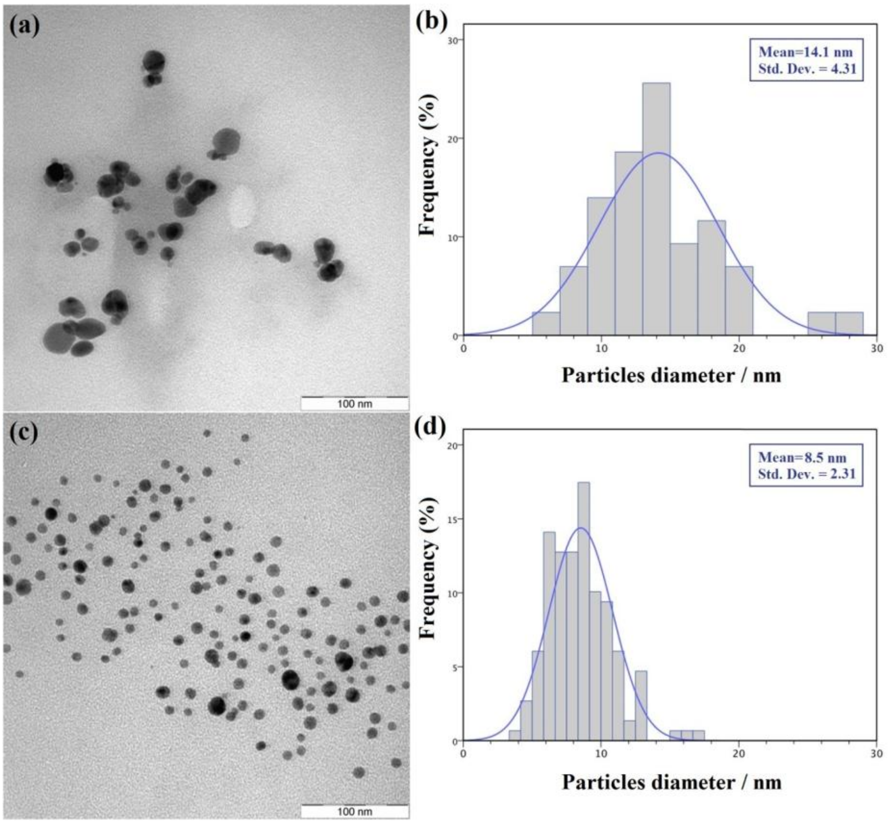

Fig. 5. TEM images and particle size distributions of synthesized Ag-NPs at different sonic irradiation times (a, b) 5 min and (c, d) 60 min.

4. Conclusions

In this study, a sonchemical method was applied for preparing Ag-NPs as a green chemistry route. In sonochemical route, colloidal Ag-NPs can be synthesized using $AgNO_3$ as silver precursor and starch as a reducing/stabilizing agent. Sonochemical reduction method demonstrates a remarkable potential for fabricating desired particle size and concentrations of colloidal Ag-NPs. The nanoparticles were characterized by UV-Vis spectroscopy, XRD, EDX, and TEM. UV-Vis spectra show the characteristic SPR peaks for the Ag-NPs between 416 and 431 nm. The studies of UV-Vis absorption spectra reveal that the SPR bands of Ag-NPs are clearly affected by the sonic irradiation times in starch media. Ultrasonic irradiation time is the main effective factor in size and yield of synthesized Ag-NPs. As ultrasonic irradiation time increase, initial synthesized Ag-NPs become smaller and their concentrations are enhanced. The EDX of the Ag-NPs dispersion confirmed the presence of elemental silver signal. No elemental impurity was detected. The XRD pattern confirmed the formation of fcc Ag-NPs. These results suggest that photoreduction methods such as sonic irradiation can maintain Ag-NPs in the presence of green stabilizers (e.g., starch at ambient temperature).

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