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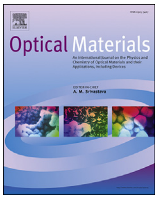

The effect of visible-light intensity on shape evolution and antibacterial properties of triangular silver nanostructures

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ABSTRACT

Triangular silver nanostructures represent a novel class of nanomaterials with tunable surface plasmon resonance (SPR). By controlling the size and geometry of these structures, their SPR peaks could be tuned from the visible to the near-infrared region with numerous applications in optoelectronic, sensors, nanomedicine and specially cancer diagnosis and treatment. In this study, triangular silver nanostructures were prepared by photoinducing of spherical silver nanoparticles (NPs) with an average diameter of 10 nm. Transmission electron microscopy (TEM) and ultra violet visible (UV–Vis) spectroscopy were used to characterize silver triangles. We have found that uniform triangular silver nanostructures can be obtained using an appropriate visible-light illumination to the primary spherical silver NPs. TEM images indicated that formation of triangular structures depends on the intensity of light source. The effect of intensity of visible-light source on the geometry and size distribution of silver triangles was investigated. It was found that formation of triangular structures in addition to their size and shape evolution strongly depends on the intensity of the light illumination. Furthermore, a comparative study on the antibacterial activities of silver triangles of different sizes reveals that silver triangles experience a size-dependent interaction with the gram-negative *Escherichia coli* bacteria.

1. Introduction

Over the past decade, silver nanostructures have been used in a variety of fields including biomedicine, catalysis, sensors and optoelectronics applications due to their specific physicochemical properties [1–4]. It is very well understood that physicochemical properties and potential applications of silver nanostructures significantly depend on their shape, size, composition and crystallinity which originates from changes in surface plasmon resonance (SPR) of metallic structures [5–8]. The most widely used application of silver nanostructures is in surface enhanced Raman spectroscopy substrates (SERS) which is strongly influenced by size and shape of the metallic nanostructures [9,10]. Among the various shape of silver, triangular structures have attracted much attention due to their sharp and tip edges [11]. It is well known that sharp tips create a large localized electric field enhancement around the sharp tips of silver triangle [12]. So SERS intensities increase and the position of localized surface plasmon resonance (LSPR) peaks change. Many methodologies have been reported for synthesis of silver triangles such as thermal routes, polyol method and photochemical synthesis [13–15]. Yugang Sun et al., have reported a thermal process to transform spherical colloidal silver nanoparticles (NPs) into triangular structures [16]. They have found that light illumination to the spherical silver NPs leads to the formation of triangular structures with sharper edges compared with thermal process [17]. Polyol method is also an appropriate procedure for synthesis of metal-containing compounds such as silver [18]. But, the problem is that controlling the concentration of O_2, which is a crucial factor in shape evolution, is difficult in the polyol method. In this regard, researchers have used oxidative etching to control the concentration of O_2 in the solution [19]. In this regard, photochemical synthesis is one of the best alternatives to overcome this drawback. In fact, light in photochemical synthesis provides a uniform distribution of the reducing agent in the entire medium and maximizes the absorption by chemical species in solution [20]. Therefore, by using of an appropriate intensity of light illumination during photochemical process, not only the size and shape of the particles can be controlled, but also LSPR absorption peaks of silver nanostructures, can be easily tuned [21].

In this paper, spherical silver NPs were first prepared using a wet chemical approach at room temperature. Then the role of light

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intensity on the photochemical transformation of spherical silver NPs to the triangular shapes was investigated. Furthermore, the effect of different light intensities on shape evolution of triangular silver nanostructures were probed. Moreover, the size-dependent bactericidal activities of silver triangles were probed against the gram-negative *Escherichia coli* bacteria.

2. Experimental details

2.1. Materials

Silver nitrate (AgNO$_3$), sodium borohydride (NaBH$_4$), polyvinyl pyrrolidon (PVP) and trisodium citrate (Na$_3$C$_6$H$_5$O$_7$) all were purchased from Sigma-Aldrich and were used without further purification. De-ionized (DI) water was supplied by a Human new power I water purification system with 18.2 MΩ cm (0.055 μs) resistance.

2.2. Synthesis of triangular silver nanostructures

Briefly, for synthesis of silver triangles, to 47.5 mL of DI water, 0.5 mL of 30 mM aqueous trisodium citrate was added, followed by 1 mL of 5 mM aqueous AgNO$_3$. Immediately, 0.5 mL of 50 mM aqueous NaBH$_4$ and 0.5 mL of 5 mg/mL aqueous PVP were added to the solution, respectively and kept under vigorous stirring for 30 min. Then, 50 mL of the final solution was irradiated for different periods of times using various visible-light halogen lamps with different intensities (50 W, 100 W, 150 W and 200 W).

2.3. Materials characterization

Analysis of the crystalline structures was performed by XRD diffractometer (Advance Bruker 8D) with wavelength of Cu Kα radiation in 2θ range from 10° to 80° by 0.04° sec^{-1} steps. UV–Vis spectroscopy of the samples was taken out by a double beam Optizen POP spectrophotometer (Mecasys Company, Korea) from 200 nm to 1100 nm wavelengths. The size distribution of NPs was determined with a zetaseries Malvern instrument. TEM analysis was performed by a TEM, PHILIPS EM208 instrument at 100–200 keV accelerating energy by deposition of nanostructures onto the copper grid at room temperature.

2.4. Antimicrobial test

The bactericidal activities of silver triangles with various sizes were studied against the *E. coli* bacteria. Before the microbiological experiments, all glass ware and samples were sterilized by autoclaving at 120 °C for 20 min. The microorganisms were cultured on a nutrient agar plate at 37 °C for 24 h. For the antibacterial test, each sample was placed into a sterilized Petri dish. Then 0.1 mL of the diluted saline solution containing a specific type of bacteria was mixed with the prepared sample. After that, the bacteria were washed with 5 mL of phosphate buffer solution in the sterilized Petri dish. Then 1 mL of each bacteria suspension was spread on a nutrient agar plate and incubated at 37 °C for 24 h before counting the surviving bacterial colonies.

3. Results and discussion

3.1. Crystal structure

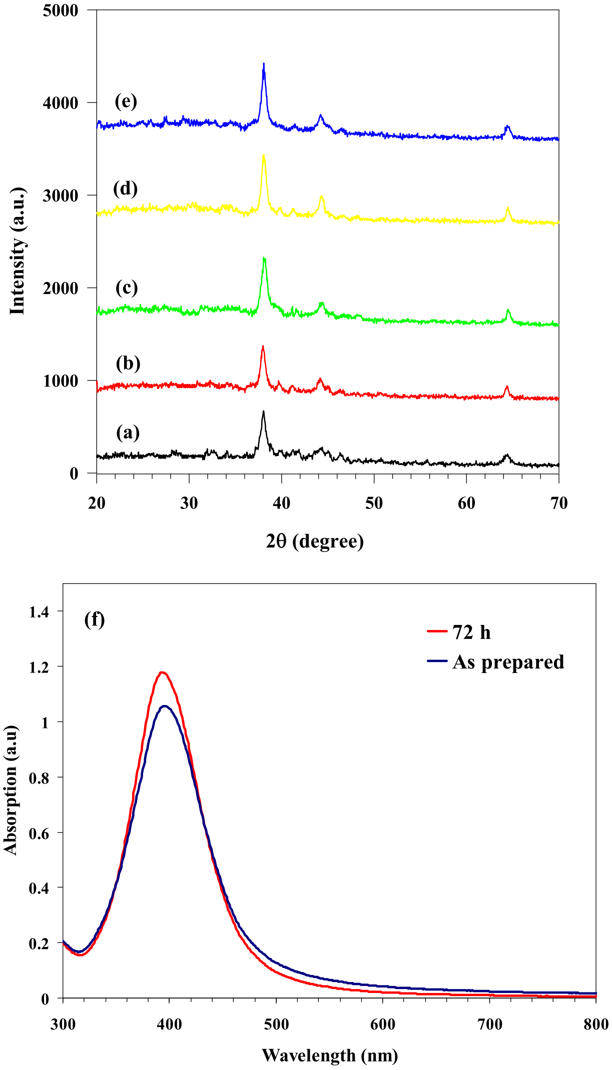

Fig. 1. XRD patterns of (a) spherical silver and silver triangles prepared under visible-light irradiation of (b) 50 W, (c) 100 W, (d) 150 W, (e) 200 W and (f) optical absorption spectroscopy of as prepared and after 72 h spherical silver NPs.

Crystalline phase of the produced structures was determined by XRD analysis and the results are depicted in Fig. 1. Crystallographic data obtained from XRD patterns of silver nanostructures prepared under different intensities of visible-light irradiation and various exposure times exhibits formation of pure face-centered cubic (fcc) silver crystals. Three individual diffraction peaks are observed at 2θ = 38.1, 44.4 and 64.7 which are correspond to the formation of silver phase according to 04–0783 standard card from JCPDS [22]. Fig. 1f also demonstrates optical absorption spectroscopy of as prepared and after 72 h silver NPs. The plasmonic peak around 400 nm corresponds to the dipole resonance of spherical silver NPs which remains stable after a couple of days.

3.2. Optical properties

UV–Vis spectroscopy is one of the most important methods for determination of metallic nanostructures. It is very well recognized that the position of the plasmonic peak of silver NPs strongly depend on size and geometry of nanostructures [23]. Fig. 2a–d show optical absorption changes of spherical silver nanostructures under different intensities of visible-light irradiation. After 12 h of visible-light irradiation the plasmonic peak of spherical NPs vanishes and three new plasmonic peaks appear which is due to the decrease in symmetry of NPs. In fact, the symmetry of nanostructures correlates to the number of plasmonic peaks [6]. Optical absorption spectrum of structures with the most geometrical