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Controlling the Geometry of Silver Nanostructures for Biological Applications

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Abstract

Noble metals nanostructures, particularly silver, have attracted much attention in the fields of electronics, chemistry, physics, biology and medicine due to their unique properties which are strongly dependent on the size and shape of metal nanomaterials. This study discusses on silver nanostructures with different geometries including wire, cube, sphere and triangle prepared using solution-phase method and applied for antibacterial activities. X-ray diffraction (XRD), Ultra Violet Visible (UV-Vis) spectroscopy, Dynamic Light Scattering (DLS) and electron microscopy studies of different types of silver nanostructures revealed distinct optical and structural properties of an individual silver nanostructure. We have also evaluated the antibacterial activity of different shapes of silver nanostructures against Escherichia coli (E.coli), Bacillus and Staphylococcus. Results presents shape dependent antimicrobial activity of silver nanostructures.

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Keywords: Silver nanostructures; Shape control; Characterization; Biological aplication

1. Introduction

Metal nanostructures, particularly silver, have attracted extensive research interest because of their specific optical, electronic, and catalytic properties [1]. These nanostructures have widely been investigated for surface enhanced Raman spectroscopy (SERS) [2], optoelectronics [3], catalysis [4], sensing [5], medicine and biological applications [6]. It is well-known that their properties and potential

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applications strongly depend on composition, size, shape, crystallinity and structure of metal nanostructures and various approaches have been developed to control them [7, 8]. These effects are the result of changes in surface plasmon resonance (SPR) of metallic structures. The optical properties of metallic nanostructures are determined by the collective oscillations of their conduction electrons with respect to the positive ion background, known as plasmon which relates the extinction coefficients to the size and geometrical properties of metallic nanostructures [9]. The unique advantage of this property is the ability of determining the geometrical properties of nanostructures during the synthesis process which causes their controlled production [10]. A large number of reports are available on the synthesis of silver nanostructures in solution with controlled morphologies. Xia and co-workers are one of the frontiers group in this field that synthesized a variety of silver nanostructures with different morphologies such as sphere, cube and truncated cube, tetrahedron and truncated tetrahedron, bar, rod, rice, bipyramid, polygonal plates and discs, branched and hollow structures based on polyol process [11]. In fact, they have shifted the plasmonic peak towards the visible and higher wavelengths by synthesizing different shapes or increasing the aspect ratio of the nanostructures which has a lot of applications in medicine, biology and especially in cancer therapy. Moreover Mirkin, Halas, Murphy and co-workers are another leading group in this field. They have also fabricated metal nanostructures with various shapes specially silver and gold for diverse applications [12-14].

In this study, we have prepared silver nanostructures with four different geometries by a solution-phase method and studied the effect of different morphologies on size distribution, optical properties and antibacterial activities.

2. Experimental details

2.1 Synthesis of silver spheres, cubes, wires and triangles

Briefly, for synthesis of cubic structures 5 mL ethylene glycol (EG) was kept in a three-neck home made vessel (two necks for simultaneous injection and one neck for thermometer) and heated under stirring in an oil bath at 150 ^{o}C for 1 h. Then 3 mL $AgNO_3$ (0.25 M in EG) and 3 mL polyvinylpyrrolidone (PVP) (0.375 M in EG) were simultaneously injected to the primary stirring EG solution through a double-syringe pump (Ascor AP 22) at a rate of 22.5 mL per hour. After finishing the injection process the reaction mixture was kept at 150 ^{o}C for 45 minutes. All samples were then centrifuged (at 4500 rpm for 10 min.) and washed two times with acetone and then water to remove the excess amounts of EG and PVP. For synthesis of silver nanowires the experimental procedure resembles the synthesis of cubic structures except the injection rate and concentration of precursors. Keeping the ratio between PVP and $AgNO_3$ unchanged, the concentration of $AgNO_3$ and PVP were 83 and 125 mM, respectively while the injection rate was 45 mL per hour. For synthesis of spherical silver, 20 mL aqueous solution of $AgNO_3$ (1 mM) was reduced with 2 mL of 40 mM aqueous sodium citrate solution at room temperature. Then 0.5 mL of 100 mM aqueous sodium borohydride solution was added dropwise to the previous solution under vigorous stirring leading to a light yellow color. After that 0.5 mL aqueous solution of PVP (40 mM) was added and the solution changed to a darker yellow color after the reaction had proceeded for 30 min, indicating formation of spherical silver NPs. For synthesis of silver triangles, the spherical NPs prepared in previous stage irradiated with a 90 W halogen lamp for 24 hours at room temperature. After one day of aging the yellowish spherical silver particles turned to green, indicating formation of silver triangular structures.

2.2 Characterization

The crystalline structure was characterized by a XRD diffractometer (X'pert Philips) with the wavelength of Cu Kα radiation being 1.5406 Å in 2θ range from 10° to 90° by 0.05° sec^{-1} steps operating at 40 kV accelerating voltage and 40 mA current. UV-Vis spectroscopy of the samples was taken out by a Lambda 950 spectrophotometer (Perkin Elmer) from 200 nm to 1100 nm wavelengths. Size distribution of nanoparticles was determined by a zetaseries Malvern instrument. SEM analysis was carried out by a SEM instrument (Philips XL30) at 15-20 keV accelerating energy. TEM analysis was performed by a LEO 912 AB instrument at 100-200 keV accelerating energy by deposition of nanostructures onto the copper grid at room temperature.

2.3 Antimicrobial Test

The antibacterial activity of four distinct silver shapes was studied against the E.coli, Bacillus and Staphylococcus bacteria. Before the microbiological experiment, all glass ware and samples were sterilized by autoclaving at 120 °C for 30 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 discussions

3.1 UV-Vis spectroscopy

UV-visible spectroscopy is one of the simplest and easiest ways to determine the geometrical properties of silver nanostructures including their size and shape. Fig 1 shows optical absorption spectroscopy of silver nanostructures with various shapes.

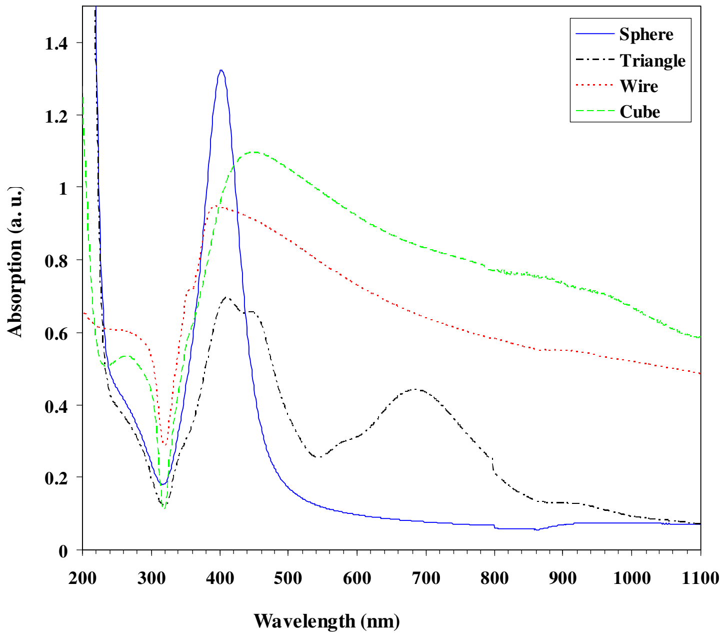

Fig. 1. Optical absorption spectroscopy of silver nanostructures with various morphologies.

It is well known that silver with spherical shape show a single surface plasmon resonance (SPR) around 400 nm while non-spherical samples reveal more than one SPR peak [15]. The symmetry of nanostructures determines the ways that they are polarized, and the number of these ways correlates to the number of plasmonic peaks. For example extinction spectra of small particles with the most symmetry shape (i.e. sphere) has just one peak because a small sphere could be polarized only in dipole mode, while cubic particles could be polarized both in dipole and quadrupole modes and that is why silver nano cubes shows two plasmonic peaks at 350 and 440 nm. One dimensional nanostructures such as silver nanowires have also two dipole plasmonic peaks, one belongs to oscillating charges along longitudinal axis (around 420 nm), and another belongs to oscillating charges along latitudinal axis (around 325 nm) [16].

3.2 XRD analysis of the products

XRD analysis was taken out to find the crystalline phase and structure of the produced structures. The results for different geometries are illustrated in Fig 2. Crystallographic data obtained from XRD demonstrates formation of metallic silver of face center cubic (fcc) lattice structure in all synthesized geometries. The peaks appeared at 2θ=38.1, 44.4, 64.7, 77.8 and 81.8 are corresponded to formation of silver phase according to 04-0783 standard card from JCPDS [17]. By orienting the structures in some specific directions and formation of cubic structures the intensities in some particular directions increases, indicating the preferential growth in those directions. This is more pronouncing for rod like structures due to Bragg reflection from crystalline planes along longitudinal axis of silver nanowires. Silver nanowires prefer to grow in (111) direction and consequently the XRD intensity in the main direction of wires is stronger than the other directions and also in cubic silver nanostructures [18].

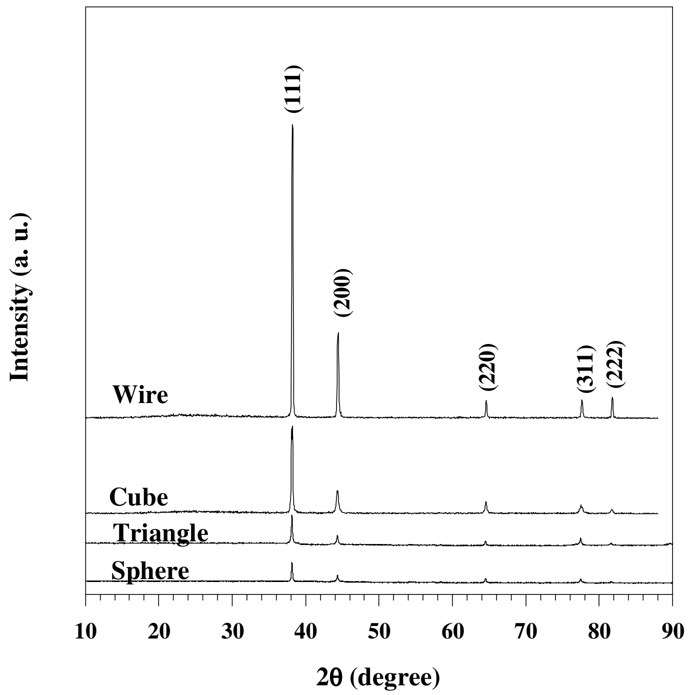

Fig. 2. XRD patterns of silver nanostructures with different geometries.

3.3 DLS Analysis

In order to find the particle size distribution we performed DLS analysis which is based on the scattering of the laser light in aqueous solution. Fig 3 exhibits the DLS results of silver nanostructures with four different morphologies. The average particle size of the silver wires and cubes were 92 and 450 nm, respectively. This is while the mean particle size for spherical and triangular silver was 17 and 50 nm, respectively. In this technique particles will be illuminated with a laser and by using the intensity fluctuations of scattered light arising from Brownian motion and the Stokes-Einstein equation the hydrodynamic diameter of the particles will be calculated. The diameter obtained by this technique is that of a sphere that has the same translational diffusion coefficient as the particle being measured. The translational diffusion coefficient will depend not only on the size of the particle (core), but also on any surface structure, as well as the concentration and type of ions in the liquid medium. This means that the size can be larger than measured by electron microscopy or other microscopic techniques, for example, where the particle is removed from its native environment.

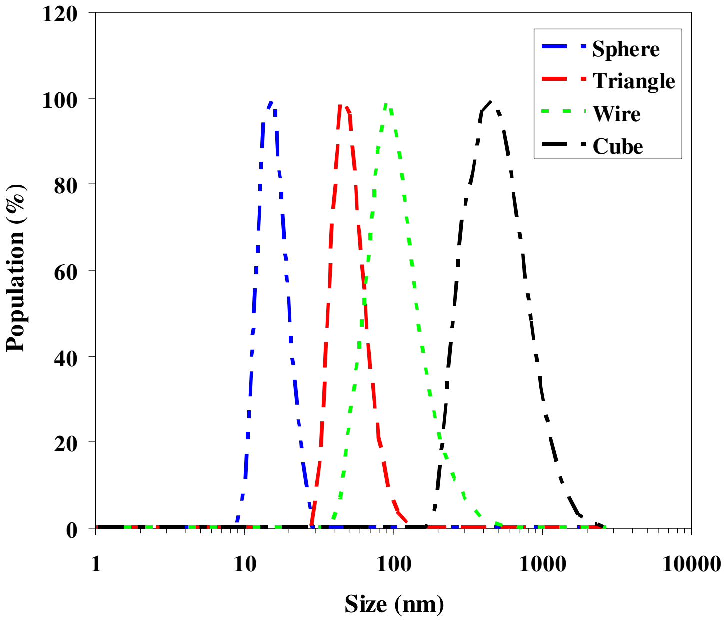

Fig. 3. Size distribution of silver nanostructures prepared with different geometries.

3.4 Microscopic Studies

The shape and size distribution of nanostructures were characterized using electron microscopy including scanning electron microscopy (SEM) and transmission electron microscopy (TEM). TEM analysis provides more insights to the specific details of nano scale systems (Fig 4(e) to 4(h), respectively). Due to large edge and high aspect ratio of silver nanocubes and nanowires they are clearly observable in SEM images (Fig 4(c) and 4(d), respectively). TEM images verify formation of nanocubes and nanowires, too. This is while silver spheres are hardly detectable in SEM analysis but they are so clear in TEM image.

SEM image of triangular silver is also unclear due to overlapping of silver plates but they are so vivid in corresponding TEM image.

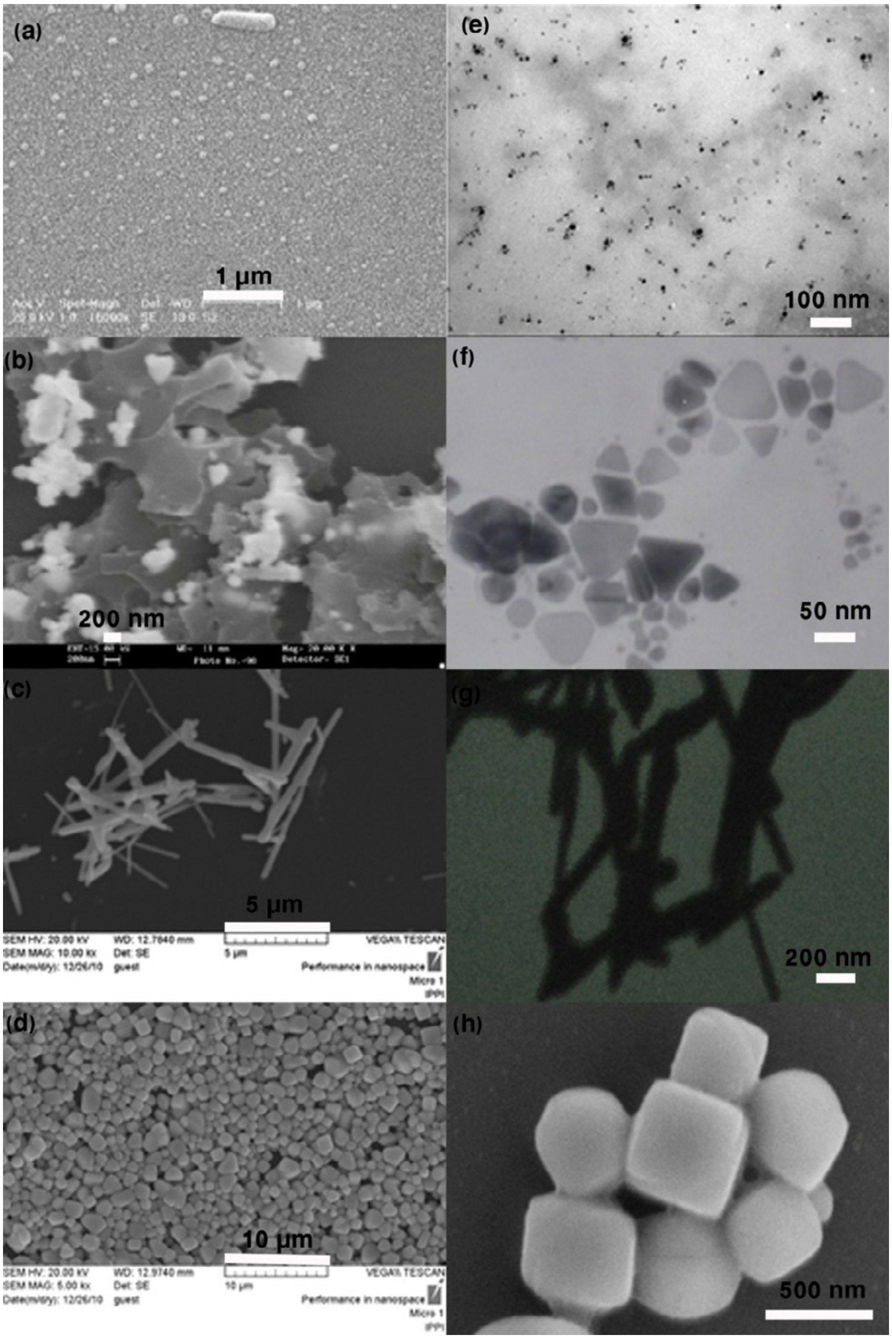

Fig. 4. SEM and TEM images of (a) and (e) spherical, (b) and (f) triangular, (c) and (g) wiry and (d) and (h) cubic silver nanostructures.

3.5 Antibacterial Activities

Antimicrobial measurements were performed on three different microorganisms (E-coli, Bacillus and Staphylococcus) as representatives. For all four shapes of silver nanostructures, the antibacterial activities were found to be different. Even though, we have found that the trends regarding interaction of all four shapes with E-coli and Bacillus were similar but the inhibition results were quite distinctive in the case of Staphylococcus bacteria. As presented in Fig 5, silver with spherical shape exhibited the most significant antibacterial activity among four shapes of silver nanostructures against E.coli and Bacillus bacteria. Cubic, wiry and triangular structures showed the most antibacterial activities against E.coli and Bacillus after spherical silver, respectively. This is while triangular, spherical, wiry and cubic structures have had the most antibacterial activity against Staphylococcus, respectively.

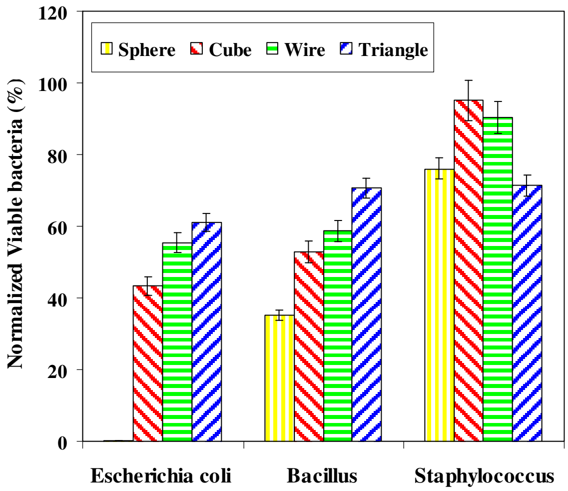

Fig. 5. Survival ratio of E-Coli, Bacillus and Staphylococcus cultured in the presence of silver nanostructures with various shapes.

4. Conclusion

In summary, various shapes of silver NPs were individually prepared via solution-phase method. XRD analysis exhibited formation of metallic silver with no impurity and oxide phase. Optical absorption spectroscopy revealed different plasmon resonances according to the symmetry and shape of the nanostructures. SEM and TEM analyses confirmed formation of cubic, wiry, triangular and spherical silver nanostructures. Antimicrobial properties of silver nanostructures with various shapes against three different types of bacteria were probed and the results confirmed shape and bacterial dependency of this property.

Acknowledgements

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