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X-ray diffraction analysis of synthesized silver nanohexagon for the study of their mechanical properties

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HIGHLIGHTS

- PVP capped silver nanohexagons have been synthesized by chemical reduction method.
- HRTEM images show that the average size of the prepared nanohexagons is 45 nm.
- X-ray diffraction study confirms the crystallinity of silver nanohexagons.
- Elastic properties have been calculated by W–H analysis using different models.
- Further, the results from UDM, USDM, and UDEDM matches with SSP method.

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ABSTRACT

Silver nanohexagons have been prepared through the chemical reduction method using poly(vinyl pyrrolidone) (PVP) as a capping agent. High Resolution Transmission Electron Microscopic (HRTEM) study shows that average size of the prepared silver nanoparticles is 45 nm approximately with nearly hexagon shape. The peaks in the X-Ray Diffraction (XRD) pattern are in good agreement with that of face centered cubic structure. Williamson–Hall plots (W–H plot) have been analyzed to study the crystalline size and lattice strain considering the peak broadening of the AgNHs. The mechanical properties such as strain, stress and energy density of prepared nanohexagon have been calculated assuming uniform deformation model (UDM), uniform stress deformation model (USDM), and uniform deformation energy density model (UDEDM) and size–strain plot method (SSP). From all these results, it is found that the size and strain estimated from W–H analysis and SSP method are in good agreement.

1. Introduction

Nanostructures materials show unique optical, chemical, physical and mechanical properties compare to their bulk counter-parts [1–6]. These unique properties can be attributed to their large surface-to-volume ratio and applicable in different field. Many authors reported about the effects of mechanical strain on the different properties of nanomaterials [7–10]. Surface plasmon resonance (SPR) is an important optical property of noble metal nanoparticles [1], specially of silver and gold nanocrystals. There are many applications of silver and gold nanocrystals based on this important optical property. This Surface Plasmon Resonance is related to the electron density of the nanoparticles [7,11]. Again, it is reported that any change in size and shape of the nanocrystals, changes the SPR peak position [1,4,7] because a change in electron density takes place due to the change of size and shape.

As the lattice constant of nanoparticles is different from their bulk counterpart, it is obvious that the variation of lattice constants will result in a change of plasma frequency (ω_p) because ω_p depends on the lattice constant. Therefore, a change of the electron density in the nanoparticles occurs due to the change of the lattice constant, as electron density is related to the plasma frequency i.e. surface plasmon resonance frequency. Thus, the lattice constant plays an important role in the shift of the surface plasmon resonance peak position. Cai et al. reported that strain produced in a nanocrystals due to the variation of lattice constant results in a variation of the electron density in the nanocrystals [10]. Therefore, it is clear that variation of lattice constant takes place due to the change of size and shape of the nanocrystals and hence, the strain produced in a nanocrystals is obviously size and shape dependent [12,13]. Thus, the study of the mechanical properties of silver

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nanocrystals is very important as it is size and shape dependent [12,13] and it also effects the other properties of the metal nanocrystals such as surface plasmon resonance (SPR). For this reason, we are very much interested in the study of mechanical properties of silver nanohexagon.

X-Ray diffraction analysis has been widely used for the determination of crystal structures and lattice constant, and also for the determination of elasticity i.e. stress and strain of nanoparticles [14–25]. Various chemical synthesis methods have been employed by several workers to synthesize silver nanocrystals by different processes such as hydro-thermal, self-assembly and Sol–gel etc. [26–28]. In this work, Silver nanohexagons (AgNHs) have been synthesized by chemical reduction method using ethylene glycol (EG) as a reducing agent and poly-vinyl pyrrolidone (PVP) as a capping agent and mechanical properties of these prepared silver nanohexagon have been calculated by Williamson–Hall Plot (W–H plots) using XRD data.

The two main parameter that can be calculated from XRD peak width analysis are the crystallite size and lattice strain. Other sources of strain include the grain boundary triple junction and stacking faults [29–35]. W–H analysis is a simplified integral breath method, where size-induced and strain-induced broadening are deconvoluted by considering the peak width as a function of 2θ [36,37]. In this work, using W–H plots, the mechanical properties such as strain, stress and energy density of prepared nanohexagons have been calculated for all the peaks of XRD, assuming a uniform deformation model (UDM), uniform stress deformation model (USDM), and uniform deformation energy density model (UDEDM). Further, size and strain have also been calculated from the Size–-Strain Plot method (SSP), which are found in good agreement with the results obtained from W–H plots.

2. Experimental

2.1. Reagent

Anhydrous ethylene glycol (EG, 99.8%), silver nitrate ($AgNO_3$, 99+%), and poly (vinyl pyrrolidone) (PVP, MW ≈ 55 000). These chemicals were purchased from SRL.

2.2. Synthesis of silver nano-hexagons

Silver nano-hexagons (AgNHs) have been synthesized by reducing $AgNO_3$ with ethylene glycol (EG) in the presence of PVP [38]. In a typical synthesis of AgNHs, 0.45 g of PVP was dissolved in 15 mL of EG, which is served as a reductant and separately 0.45 g of $AgNO_3$ was dissolved in 15 ml of EG, which is served as a solvent. Both of these two solutions were immediately subjected in to a vigorous stirring at room temperature with magnetic stirrer. The $AgNO_3$ and EG solution after few minutes turned into a brown color during stirring, indicating that some silver nanoparticles had formed during this time. The PVP and EG solution colorless. A conical flask containing 15 ml of EG was heated ~ 50 °C with continuously stirrer. Both of these two solutions were simultaneously added in to the hot EG. Suddenly the clear EG solution turned into a bright yellow. The mixture heated with a fixed temperature ~150 °C for 8 h. In this way, capping these particles, PVP stabilizes them for one month. The sample, collected at the bottom of vessel after cooling to room temperature.

3. Results and discussion

3.1. TEM image analysis

HRTEM micrograph are the best way to investigate the nanoparticle's size and shape. Morphological studies of the silver nanoparticles have been obtained by HRTEM images, which were performed on a JEM-100 CX II model instrument with an accelerating voltage of 200 kV. A drop of silver nanoparticles solution is taken on carbon-coated copper grid and after evaporation has taken place, HRTEM image is recorded. HRTEM micrograph of the prepared PVP capped silver nano-hexagon is shown in Fig. 1(A), with the size distribution in Fig. 1(B), which indicates the narrow size distribution of silver nano-hexagons. The average diameter of the nanoparticles is found to be approximately 45 nm. Fig. 1(C) shows a single silver nano-hexagon with the Selected area electron diffraction (SAED) pattern as in Fig. 1(D).

3.2. XRD analysis

In solid state physics, material science and solid state chemistry, X-ray diffraction is one of the most important characterization techniques used [5,39] for the estimation of the average grain size as well as the elastic properties of the nanocrystals. Here, the structure of the prepared silver nano-hexagons have been investigated by Rigaku Corporation Japan/Model: Miniflex X-ray diffractometer (XRD). The XRD pattern of the prepared sample is shown in Fig. 2, which clearly indicates the crystallinity of the prepared sample.

All the detectable reflection peak could be indexed to the face-centered cubic (FCC) structure as found in the standard reference data (JCPDS file No. 04-0783). Further, XRD pattern does not show any impurity present in the prepared silver nano-hexagon. The high intense peak for FCC materials is generally (111), (222) reflection, which is observed in the sample. The XRD pattern also can be easily indexed for the respective peaks using the method as in the following Table 1.

3.3. Particle size and strain

3.3.1. Scherrer method

Peak broadening with crystallite size and lattice strain due to dislocation can be evaluated by XRD [40]. The particle size of the silver nanoparticles have been determined by the X-ray line broadening method using the Scherrer equation;

$$D = \frac{k\lambda}{\beta_D \cos\theta} \tag{1}$$

where 'k' denotes the Scherrer constant (shape factor) = 0.94 and β is broadening of diffraction line measured at half of its maximum intensity (in radian); λ = 0.1541 nm is the wavelength of the incident Cu-Kα radiation; and θ is Bragg diffraction angle (in degree). The average size has been calculated using the broadening of each peak separately. The combination of both instrument and sample dependent effect gives the breath of the Bragg peak [41,42]. Therefore the β_D (instrument corrected broadening) corresponding to the diffraction peak of silver nano-hexagons was estimated using the relation.

$$\beta^2_{hkl} = (\beta)^2_{measured} - (\beta)^2_{instrumental} \tag{2}$$

A standard silicon peak (111) has been used here to correct the instrumentation broadening effects for all calculations. From the calculation, the average crystallite size of the silver nanoparticles is obtained as 28 nm (approximately).

3.3.2. Williamson–Hall methods

The strain induced broadening in XRD due to crystal imperfection and distortion was calculated using the formula