

Determination of intrinsic strain in poly(vinylpyrrolidone)-capped silver nano-hexapod using X-ray diffraction technique

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Poly(vinylpyrrolidone)-capped silver nano-hexapods (AgNHs) have been prepared by chemical reduction method using ethylene glycol as a reducing agent, for the study of their structural and elastic properties. HRTEM study reveals that the prepared nanocrystals are hexapod in shape with an average size of approximately 50 nm. From the analysis of the X-ray diffraction pattern, intrinsic strain produced in the nano-hexapod due to dislocation of silver atoms, has been determined from the W–H plot. The lattice constant of the AgNHs has also been determined from Nelson–Riley plot. Higher value of dislocation density confirms that there may exist intrinsic strain in the nanocrystals.

Keywords: Elastic properties, nanocrystalline materials, poly(vinylpyrrolidone), X-ray diffraction.

NANOCRYSTALS show different properties compared to their bulk counterpart, which are suitable for different applications^{1,2}. Elastic properties of nanocrystals are one among them^{1,2}. X-ray diffraction (XRD) is an important tool for the study of structural and elastic properties of different nanocrystals, specially intrinsic strain². Lattice imperfections in the nanocrystallites cause broadening of the XRD line profiles³. Larger crystallites produce sharp peaks in the XRD profile. When the crystallite size reduces, the peak width increases^{3–5}. Peak broadening also depends on the variations in lattice spacings, caused by lattice strain^{4,5}. So, XRD peak width is affected by crystallite size and lattice strain, which further affects the intensity and shift in the peak position⁵. Khan *et al.*³ studied the intrinsic strain using XRD and W–H plots, and further calculated the lattice constant. Biju *et al.*⁴ performed XRD analysis of silver nanocrystals. Bykkam *et al.*⁵ studied the elastic properties of silver nanoparticles using XRD analysis as well as lattice constant. In the present communication, a simple and low-cost preparation method of poly(vinylpyrrolidone) (PVP)-capped silver nano-hexapods (AgNHs) is presented with the study of their XRD pattern, for the determination of structural properties and intrinsic strain. Proper capping of nanoparticles is required for their stabilization as for AgNHs by PVP; otherwise the prepared AgNHs may begin agglom-

eration right after their preparation. It is reported that the intrinsic strain that gets produced in the nanocrystals during the synthesis process is size and shape-related⁶. As hexapod is rare shape, interest lies in the study of the intrinsic strain for AgNHs. Further, strain can induce a change in the lattice constant as well as in the dislocation density⁷. Therefore, along with the measurement of intrinsic strain, it is interesting to know about the lattice constant and dislocation density. Crystallite size and lattice strain increase the XRD peak width and also shift the peak positions. Considering this peak width, strain produced^{8,9} in the nano-hexapod has been calculated using Williamson–Hall (W–H) plots¹⁰. Further, the lattice constant of the AgNHs has been determined from Nelson–Riley plot for the determination of dislocation density. This plot gives the lattice constant of nano-hexapods with nearly zero error and the calculated lattice constant is further used for the determination of dislocation density. Strain that exists in the nano-hexapods depends on the dislocation density as dislocation of silver atoms creates the intrinsic strain.

A simple and cost-effective preparation of PVP-capped AgNHs is considered here, as this process produces uniform-sized nano-hexapods¹¹. For the synthesis process, 0.50 g of AgNO₃ and 0.50 g of PVP were dissolved separately in two beakers, each containing 16 ml of ethylene glycol (EG) solution. Both the solutions were then stirred continuously at 30°C. The AgNO₃ and EG solution gradually turned brown, indicating that some Ag nanoparticles had formed during the 30 min stirring¹¹.

However, the other solution containing PVP and EG remained clear and colourless. Now a flask containing only 16 ml EG solution was heated continuously under stirring by maintaining a temperature of 160°C. The two solutions mentioned above were injected slowly (dropwise) into the flask containing 16 ml colourless EG solution during heating and under stirring, keeping the reactant mixture at 160°C for 7 h. After addition of the reactant, the colourless EG solution suddenly turned bright yellow¹¹, which indicates the formation of silver nanocrystals and the solution after cooling to room temperature, is dispersed in water.

Size and morphology of AgNHs have been obtained using JEOL JEM-100 CX II transmission electron microscopy (TEM) operating at an accelerating voltage of 200 kV. XRD studies of the same have been carried out using a Rigaku Corporation Japan (model: Miniflex X-ray diffractometer). CuK α X-rays of wavelength (λ) = 1.54056 Å were used for the study.

The high resolution transmission electron microscopic (HRTEM) images give the morphology of the prepared nanocrystals as well as the proper size with the interplanar distances between the lattice planes of the prepared nanocrystals. From HRTEM image, the average size of AgNH has been obtained as 45 nm approximately with inter-planar distance of 0.12 nm. Figure 1 shows

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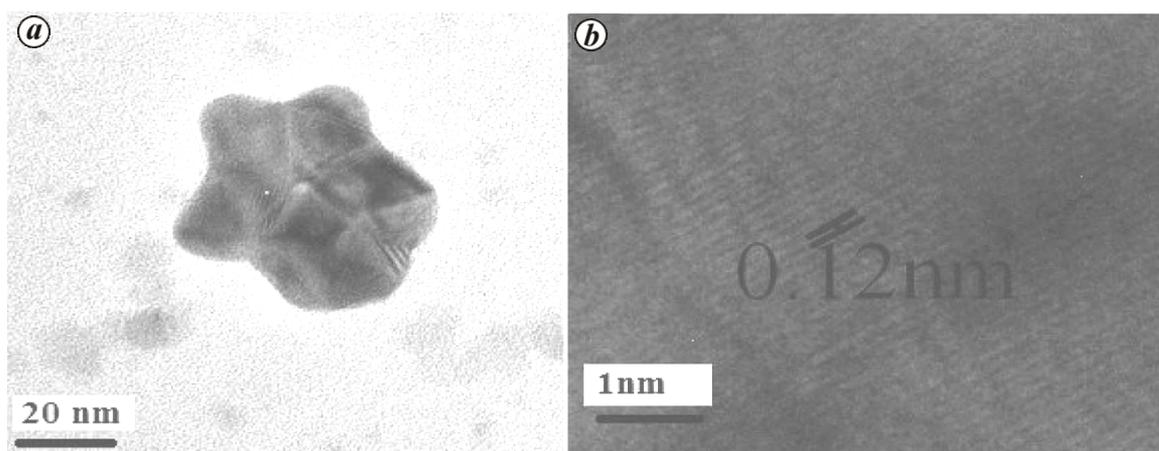


Figure 1. TEM photomicrograph (a) and HRTEM images (b) of silver nano-hexapods (AgNHs).

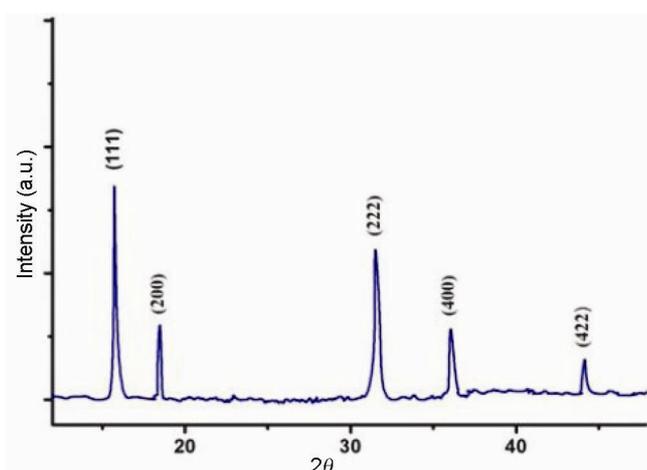


Figure 2. XRD pattern of AgNHs.

HRTEM photomicrograph of the prepared PVP-capped AgNHs.

XRD analysis is an important characterization technique for the study of the structure and size of the prepared nanocrystals along with the determination of intrinsic strain produced in them. XRD analysis is the only direct method for the determination of internal structure¹² and an indirect method for the determination of strain in the nanocrystals^{5,12}. Figure 2 shows the XRD pattern of prepared AgNHs. All evident peaks have confirmed the fcc structure on comparing with the standard JCPDS (Joint Committee on Powder Diffraction Standards, file no. 04-0783).

The average size of AgNHs has been determined by the X-ray line broadening method using the Scherrer formula¹³ as follows

$$D = (k\lambda/\beta_D \cos \theta), \quad (1)$$

where k is the Scherrer constant, λ the wavelength of the X-rays used (0.1541 nm), θ the diffraction angle and β_D is the full width at half maximum (FWHM; in radians).

Here FWHM has been obtained from the XRD data correcting the instrumental broadening for a standard silicon sample. The average crystalline size of AgNHs has been found to be 27 nm. The size calculated in this study does not match with that obtained from HRTEM analysis using the Scherrer method. XRD line broadening was considered due to crystalline size only. However, it takes place due to both crystalline size and strain broadening produced in the nanocrystals, which has been considered in the W–H method described below.

The contribution of strain to line broadening of the diffraction peak in addition to the crystalline size broadening with rearrangement can be represented as follows^{14,15}

$$\beta_{hkl} \cos \theta = (k\lambda/D) + 4\varepsilon \sin \theta, \quad (2)$$

where β_{hkl} is the FWHM (radians) corresponding to the respective $\langle hkl \rangle$ planes, D the size of the particle (nm), ε the strain, λ the wavelength (0.1541 nm) and k is the Scherrer constant.

The W–H plot (Figure 3) has been drawn according to eq. (2). The crystallite size and strain can be obtained from the intercept of the y-axis and the slope of the line respectively. The size and strain of AgNHs are found to be 43.43 nm and 1.63×10^{-3} respectively, with R^2 value 0.9878. This size matches well with the HRTEM analysis confirming the goodness of the W–H method over the Scherrer method. The value of strain obtained here matches well with the results reported by others^{3,4}. The value of strain depends on the dislocation density. For determination of dislocation density, lattice constant for AgNHs has to be determined using Nelson–Riley plot.

The lattice parameter for cubic crystals can be obtained using the equation

$$1/d^2 = (h^2 + k^2 + l^2)/a^2,$$

where d is the interplanar spacing determined using Bragg's equation and h , k , l are the Miller indices of the

lattice planes. The lattice constants calculated from the highest angle reflection data are reliable. However, it is found that the results are slightly different for different orientations of the same film of AgNH¹⁶. This difference can be attributed to the divergence of the X-ray beams as well as the refraction and absorption of X-rays by the specimens. This therefore involves a number of systematic errors in the measurement of θ and hence in the calculation of the lattice spacing d and lattice constants. Therefore, it is required to obtain the correct value of lattice constants free from all these systematic errors. This can be obtained from the intercept of the Nelson–Riley plots^{16–19}. These are plots of the error function versus calculated values of lattice constant for different planes. The values obtained from these plots are more or less free from systematic errors. Thus to determine the exact lattice parameter for AgNHs, the Nelson–Riley

method can be used^{16,18,20}. The Nelson–Riley function $F(\theta)$ is given as²⁰

$$F(\theta) = [(\cos^2\theta/\sin\theta) + (\cos^2\theta/\theta)]/2, \quad (3)$$

where θ is the Bragg angle. In Figure 4, the values of lattice constant a of all the peaks for AgNHs are plotted against $F(\theta)$, which is a straight line intersecting the Y-axis. In this method, the value of lattice parameter has been determined by extrapolating Nelson–Riley function $F(\theta) \rightarrow 0$. The value obtained is free from random errors and is determined as 0.930 nm with R^2 value of 0.7651, which is different from the bulk silver. Liu *et al.*¹¹ reported high value of lattice constant for silver nanocrystals. They also obtained a high value for lattice constant for silver nanoparticles (0.96193 nm)²¹, which matches with our result. The high value of lattice constant as obtained in the present study is due to the high strain that produced in AgNH^{11,21,22}. High strain is the result of lattice distortion or rearrangement of atoms in AgNH. That is, the means atoms get arranged in AgNH with more separation between them in the unit cell, in order to accommodate all the atoms in that particular AgNH of size around 45 nm.

In a crystal, if the periodicity of atomic lattice array is interrupted along certain directions, then the dislocation occurs. The presence of dislocation strongly affects many of the properties of materials. A larger dislocation density implies a larger hardness²³. It is well known that the strength of materials increases with decreasing size of the particles in the nanometre range²⁴. The dislocation density (δ) in the sample has been determined using the following expression²⁵

$$\delta = 15\beta_{hkl} \cos\theta/4aD.$$

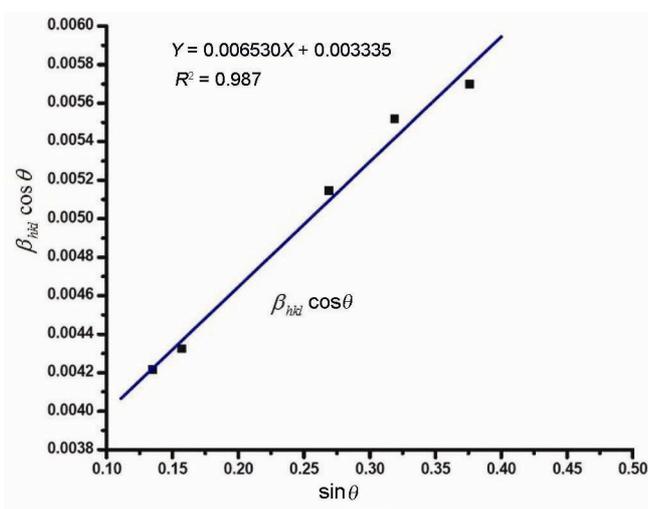


Figure 3. $\beta_{hkl}\cos\theta$ versus $\sin\theta$ of AgNHs.

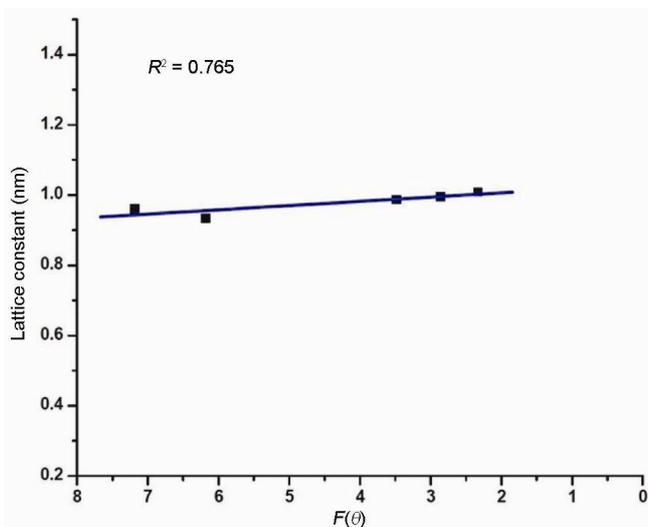


Figure 4. Lattice constant versus $F(\theta)$ for AgNHs.

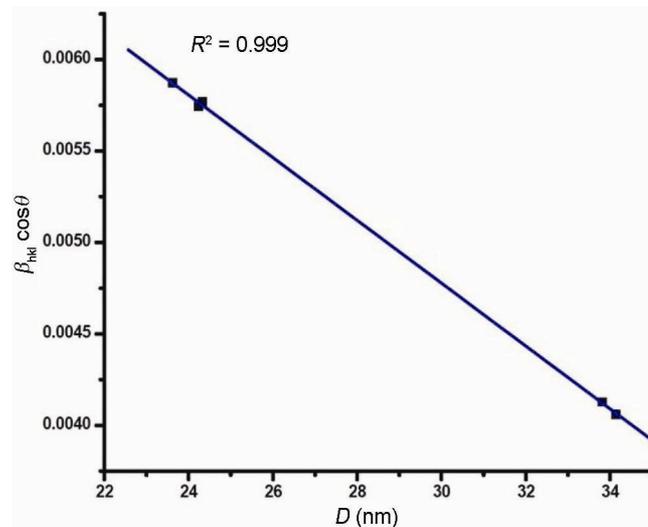


Figure 5. $\beta_{hkl}\cos\theta$ versus D for AgNHs.

This can be rewritten as

$$\beta_{hkl} \cos\theta = (4a\delta/15)D, \quad (4)$$

where a is the lattice constant (nm) calculated from the Nelson–Riley plot and D is the particle size (nm) obtained from Debye–Scherrer formula^{3,25}. In Figure 5, $\beta_{hkl} \cos\theta$ has been plotted along the y -axis with respect to the respective D values, and size along the x -axis. Dislocation density can be obtained from the slope of the fitted line. The dislocation density of AgNHs is found to be $7.31 \times 10^{14} \text{ m}^{-2}$ with R^2 value of 0.9997. This value of dislocation density directly confirms that intrinsic strain exists in the AgNHs. This high value dislocation density confirms the high value of the lattice constant; such high value of dislocation density has also been reported by others^{3,22}. The high value of strain as obtained in this study also confirms the high value of dislocation density.

AgNHs nanoparticles have been successfully synthesized by chemical route with an average calculated particle size of 48.43 nm using PVP as a stabilizing agent. The strain produced in AgNH has been determined as 1.63×10^{-3} from W – H plot. From the Nelson–Riley plot, lattice constant was found to be 0.930 nm. Further, dislocation density has been calculated as $7.31 \times 10^{14} \text{ m}^{-2}$, which also indicates the intrinsic strain that is produced in the nano-hexapods.

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