



# Synthesis and characterization of Ag/PVA nanorods by chemical reduction method

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## ABSTRACT

Silver (Ag) nanorods with the average length of 280 nm and diameters of around 25 nm were synthesized by a simple reduction process of silver nitrate in the presence of polyvinyl alcohol (PVA) and investigated by means of scanning electron microscopy (SEM), X-ray diffraction (XRD), transmission-electron microscopy (TEM) and UV–vis spectrum. It was found out that both temperature and reaction time are the important factors in determining the morphology and aspect ratios of nanorods. TEM images showed the prepared Ag nanorods have a face centered shape (fcc) with fivefold symmetry consisting of multiply twinned face centered cubes as revealed in the cross-section observations. The fivefold axis, i.e. the growth direction, normally goes along the (111) zone axis direction of the basic fcc Ag-structure. Preferred crystallographic orientation along the (111), (200) or (220) crystallographic planes and the crystallite size of the Ag nanorods are briefly analyzed.

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## 1. Introduction

Metal or semiconductor nanostructures, in particular, nanowires and nanorods, may be used in the fabrication of nanodevices and novel nanocomposites due to their fascinating optical, electronic and magnetic properties [1–4]. Over the past decade, the synthesis strategy and mechanism of one-dimensional (1D) nanomaterials have been greatly developed [5]. As shown in a number of reported studies, 1D nanomaterials can be prepared by various chemical routes, such as the polyol-based process [6], wet chemical synthesis [7,8], hydrothermal method [9], ultraviolet irradiation photoreduction technique [10], electrochemical deposition technique [11], DNA or organic molecular template [12,13], porous materials template [14] and anodic alumina membranes (AAMs) [15].

Recent advances in soft synthesis of low-dimensional nanocrystals such as nanorods, nanowires, nanotubes, and more complex nanostructures, demonstrated that the “soft” approaches

are very promising alternative pathways for the synthesis of 1D nanocrystals under natural/mild conditions in contrast to traditional high-temperature approaches [16]. The soft synthesis routes, such as solvothermal/hydrothermal processes, solution–liquid–solid mechanism, capping agents/surfactant-assisted synthesis, bio-inspired approaches and oriented attachment growth mechanism, open alternative doorways to the low-dimensional nanocrystals and even more complex superstructures. Among these solution strategies, the solvothermal process shows the potential capabilities and versatilities for selective synthesis of various important semiconductor nanocrystals with controllable shape, size, phase, and dimensionalities under mild conditions.

In this work, following the solvothermal process, we employed polyvinyl alcohol (PVA, Mw = 72,000) as a protecting agent to synthesize silver (Ag) nanorods with an average length of 280 nm and diameter of 25 nm by reduction of silver nitrate using DMF as a solvent and reducing agent. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), powder X-ray diffraction (XRD) and UV–visible spectrum measurements were combined to investigate thus-obtained Ag nanorods, and further to elucidate the structure and the growth mechanism of them.

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## 2. Experimental

Materials containing a large yield of Ag nanorods were synthesized by reduction of silver nitrate in the presence of PVA. The procedure is briefly described as follows: Firstly, 5 ml *N,N*-dimethyl formamide (DMF) was refluxed in a three-necked round-bottom flask at 80 °C for 2 h, then 5 ml DMF solution of 0.02 M silver nitrate and 5 ml DMF solution of 0.05 mM PVA were simultaneously injected dropwise. When the first drops of silver nitrate and PVA/DMF solutions were added, the mixture turned yellow immediately. Continuing the injection, the solution became opaque gradually. By finishing the injection, the solution turned turbid with a gray color in about 15 min indicating the appearance of Ag nanoparticles. The reaction was continued at 80 °C for 16 h. After finishing the reaction and removal of the supernatant, a gray precipitate remained.

The XRD pattern was recorded on a Seisert Argon 3003 PTC using nickel-filtered XD-3a CuK $\alpha$  radiations ( $\lambda = 1.5418 \text{ \AA}$ ). The UV-visible spectrum, in absorbance mode was recorded on an UV-visible Hitachi spectrophotometer model U-2101 PC. The solution form of the sample was prepared by suspending a small amount of powder in ethanol. TEM was performed on a Philips EM208 and microscope operated at 100 kV. Samples were prepared by dispersing the powder in ethanol. Imaging was enabled by depositing few drops of suspension on a carbon coated 400 mesh Cu grid. The solvent was allowed to evaporate before imaging. SEM images of fabricated Ag nanorods were obtained using LEO 440i electron microscope. The samples were rinsed with distilled water, dried and coated with a thin layer of gold by evaporation at vacuum to form conducting film.

## 3. Results and discussion

A typical XRD pattern of as prepared Ag nanorods shows the presence of the diffraction peaks corresponding to the (111), (200), (220), (311) planes. All diffraction peaks in this XRD pattern (Fig. 1) can be well indexed as face-centered cubic (fcc) Ag with peak positions, indicating that the fcc structure of the Ag is preserved in these nanorods (JCPDS, File No. 4-0783) [17]. These results indicate a polycrystalline structure for Ag nanorods with an intense (111) preferred orientation. Secondary peaks at (200) and (220), corresponding to the high-angle XRD pattern ( $2\theta = 30\text{--}60$ ), supports the presence of Ag in nanocomposite form. The peaks appearing at ( $2\theta = 38.4$ ) and ( $2\theta = 44.6$ ) correspond to the (111) and (200) planes of the Ag lattice, respectively.

The dimensions of the crystallites of which the Ag nanorods are composed can be estimated from the Scherrer formula [18]. When the term “crystallite size” is used, we will be referring to the dimensions of the coherent diffracting domain. This equation is applicable to samples where lattice strain is absent. Nanorods can possess some strains, which could also be a factor contributing to the width of the peaks, thereby affecting the estimates of the crystallite size of the nanorods. Moreover, the grain size of the Ag nanorods estimated from the XRD peak width (and using Scherrer's formula), was greater than 40 nm. However, the Debye–Scherrer formula calculations were approximate, and more accurate for spherical particles. The results were not comparable with TEM results [19]. Thus, grain sizes were larger than the maximum critical acceptable values that can be deduced for these XRD measurements. Therefore, the size of the crystalline domains determined from the XRD peak widths will be used only as a comparative measure among samples.

The TEM images of the Ag nanorods as-prepared by the controlled-concentration and temperature are shown in Fig. 2(a, b), revealing the as prepared individual Ag nanorods and their constituent nanospheres. Fig. 2(c) exhibits the cross section of the prepared multiply fivefold twinned fcc Ag crystallite of the shape of rod and nanometer dimension nanorods. These pentagonal nanorods show aspect ratio between 3.3 and 12 with the length of their fivefold axis ranging from 45 to 280 nm.

The SEM images of the as-prepared Ag nanorods are shown in Fig. 3. The morphology of the resulting surfaces, indicates that the as-synthesized materials contain a high concentration of non-homogeneous Ag nanorods (Fig. 3(a)). Fig. 3(b, c) illustrates the presence of Ag nanorods with a random orientation in the samples.

Fig. 4 represents the UV-visible spectrum of as prepared Ag/PVA nanorods. This figure shows a broad absorption band at  $\lambda_{\text{max}}$  458 nm. This characteristic peak is due to the oscillation of conduction band electrons of Ag known as the surface plasmon

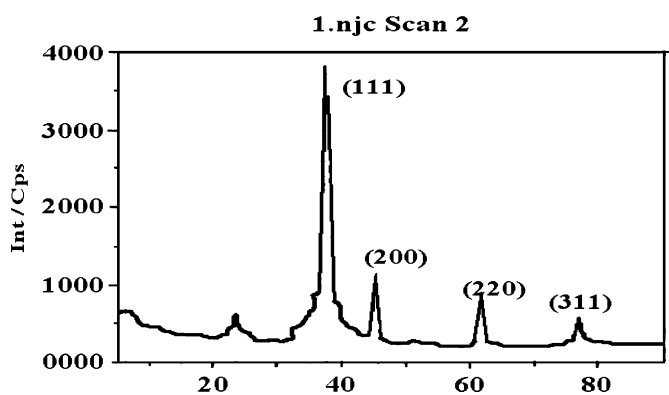


Fig. 1. XRD pattern of Ag/PVA nanocomposite indicative the fcc structure.

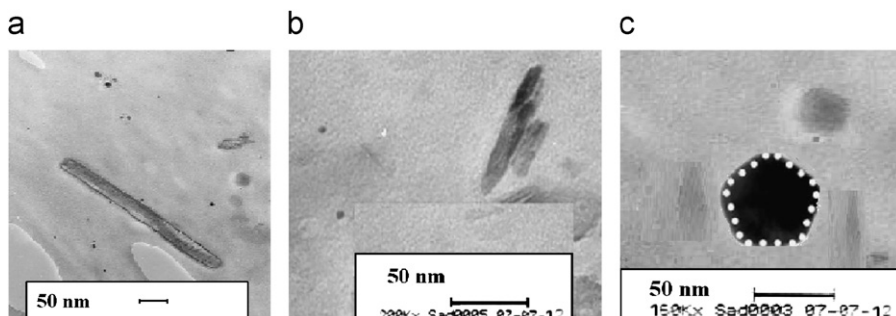


Fig. 2. Transmission electron microscopy (TEM) images of (a, b) individual and (c) cross section of Ag/PVA nanorods.

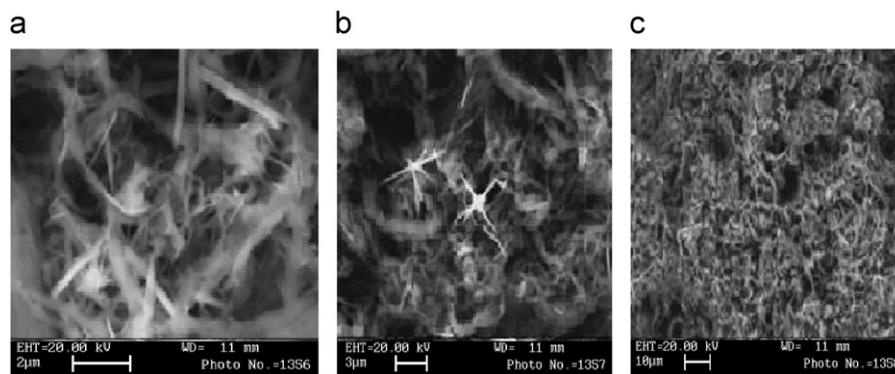


Fig. 3. (a, b, c) SEM image showing high concentrated distribution of Ag/PVA nanorods.

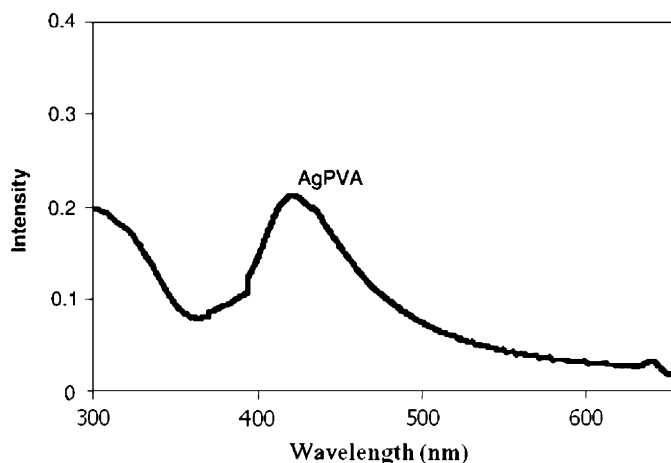


Fig. 4. UV-vis absorption spectrum of Ag/PVA nanocomposite prepared by using DMF solution.

resonance [20–24]. The position of plasmon absorption band depends on particle size, aspect ratio and diameter of nanorods or nanowires [25]. The broad nature of the absorption band in this case is indicative of the presence of both spheres and rods as reported in citrate reduction method [26].

As a result, we conclude that formation of Ag nanorods in this model is based on the reduction of Ag (I) ions by DMF. In this process, the DMF serves both as reductant and solvent. In the real reaction, two processes may occur simultaneously. At first, Ag nanoparticles are formed through homogenous nucleation and grow into multiply twinned particles (MTPs) with their surfaces bounded by the lowest energy {111} faces. Silver nanoparticles forming at the surface of the protecting agent or coming from the outer solution phase through Brownian motion aggregate into a 1D arrangement like a bunch of pearls, and then grow into nanorods through Ostwald ripening.

#### 4. Conclusion

It was concluded that PVA is a remarkably powerful capping agent for Ag ions. In this process, the DMF serves both as reductant and solvent [25,27]. The UV-visible spectra indicate well-defined absorption bands for Ag nanoparticles and nanorods due to the surface plasmon resonance phenomena. The XRD data confirmed that the Ag nanorod is crystalline with fcc structure having a preferred crystallographic orientation along the {220}

direction, and a straight, continuous, dense Ag nanorod has been obtained with a diameter 25 nm.

SEM and TEM observations along a series of relevant directions showed that the silver nanorods have an average length of 280 nm and diameters of around 25 nm. TEM observations from cross section of nanorods suggest that the transformation of Ag nanospheres to Ag nanorods is achieved by the oriented attachment of several spherical particles followed by their fusion. Resulting Ag nanorods have a twinned fcc structure, and they appear in a pentagonal shape with fivefold twinning. The fivefold axis, i.e. the growth direction, normally goes along the (110) zone axis direction of the fcc cubic structure.

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