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# Anisotropic growth of silver nanostructures from silver spheres by a simple chemical reduction route

M. Jose [a, *], R. Thanal [a], J. Prince Joshua [b], S.A. Martin Britto Dhas [a], S. Jerome Das [b]

[a] Department of Physics, Sacred Heart College, Tirupattur 635601, Tamilnadu, India
[b] Department of Physics, Loyola College, Chennai 34, India

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ABSTRACT

A well-designed two-step solution-based method has been proposed to switch isotropic silver nanospheres to anisotropic nanoprisms using sodium carboxy methyl cellulose as surfactant. This method has several clear advantages including simplicity and high stability. Silver prisms with a nanometer scale diameter could be judiciously prepared when the precursor concentration was slightly changed. The obtained samples have been characterized by X-ray diffraction, UV–Vis absorption spectroscopy, scanning electron microscopy, and transmission electron microscopy. The experiments show that the concentration of $AgNO_3$, is an important factor for controlling the morphology of the products.



## 1. Introduction

Fabrication of metallic nanostructures and controlled tuning of their optical properties by the modification of the shape and size is undergoing tremendous research activity due to their enormous potential in various industrial applications such as lead free interconnects in nanoelectronics, active components in nanophotonics and transparent conductors in addition to their fascinating applications in nanoscale electronic devices such as surface-enhanced Raman scattering and biological sensors [1–7]. Anisotropic metal nanostructures such as nanorods, nanodiscs, nanotubes, nanowires and nanoprisms attract significant technological importance due to their immense potential in diverse applications including enhanced fluorescence, nonlinear optical properties, optical resonances in the near infrared region and orientation-dependent plasmon excitation to name a few [8,9].

Among various metal nanoparticles, silver nanoparticles hereafter referred to as AgNPs find prospective applications and hence development of suitable routes for their synthesis are of paramount interest to be fully exploited for number of applications. Recently, much research and development efforts have been devoted to the synthesis and stabilization of nanoparticles using polymers [10,11]. The incorporation of metal nanoparticles into polymers has resulted in the development of new class of materials called nanocomposites that have found fascinating applications in biomedical, catalytic, optical and electronic sectors. Polymer-assisted or polymer template synthesis of metal nanoparticles have received significant attention due to the possibility of controlling the size and morphology of nanoparticles by varying the polymer/metal salt ratio as the

* Corresponding author. Tel.: +91 994 482 5036; fax: +91 4179 22 0553.
*E-mail addresses:* mjosh1231@gmail.com, jose@shctpt.edu (M. Jose).

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polymer containing appropriate functional groups serves both as reducing and stabilizing agent [12]. Moreover, polymers like Poly (vinyl alcohol), [poly(styrene)]-dibenzo-18-crown-6-[poly(styrene)], poly(N-vinylpyrrolidone) and poly (N-isopropyl acrylamide-co-sodium acrylate) have been used for the synthesis of small AgNPs [13–16].

The synthesis of metal nanostructures with non spherical shape requires a high control on the reaction parameters and the presence of external factors can favour the anisotropic growth despite the high symmetry and packing of Ag fcc lattices. To grow an asymmetric structure like rod or nano prism from a material with a high packing symmetry like metallic silver, one must judiciously minimize growth in two dimensions. Chemicals like surfactants PVP, polyols, citrate or ascorbic acid are used because they bind preferentially to specific crystal faces of the particles thus inhibiting growth on these faces. Much effort has been made to understand the mechanism, and many hypotheses have been proposed to explain the formation of such highly anisotropic structures. Interestingly, reports available in the literature indicate that photochemical conversion of AgNPs to nanoprisms is possible using multiple types of stabilizing agents. Poly(N-vinyl-2-pyrrolidone) has been used to stabilize the AgNPs [17,18]. AgNPs prepared using low molecular weight PVP (29 and 55 kg mol) underwent conversion from nanospheres to nanoprisms in the presence of fluorescent light whereas samples with high molecular weight PVP (1300 kg mol) did not underwent any such conversion [17].

Chemical reduction allows one to control the nanoparticles shape and one can obtain spheres, prisms, cubes, rods or wires by optimising reaction parameters such as the concentration of the metal ions or stabilizers, the temperature, the pH or using other simple tricks [19,20]. In this work, innovative sodium carboxy methyl cellulose (Na-CMC) based silver nano colloidal dispersions in aqueous medium were synthesized and the effect of precursor concentration on the morphology and size of the AgNPs is discussed. While Na-CMC acted as stabilizing agent for AgNPs and plays a critical shape directing role in determining the final morphology of the Ag nanostructures, ascorbic acid was added to the reaction medium to assist Na-CMC in establishing reduction of $Ag+$ to AgNPs. It is seen that the capping agent selectively adheres to a particular crystal facet of the growing nanocrystal and thus slows the growth rate of that facet relative to the others.

## 2. Experimental

### 2.1. Material synthesis

In the present work, silver nanoparticles of different morphologies were prepared by a simple yet cost effective chemical reduction route. Silver nitrate was taken as precursor, ascorbic acid as reducing agent and sodium carboxy methyl cellulose acting as capping agent. The samples of AgNPs with different precursor concentration from 0.01 M to 0.04 M were prepared according to the following procedure. The required amount of silver nitrate (0.01 M, 10 ml), Na-CMC (0.001 M, 10 ml) and ascorbic acid (0.01 M, 20 ml) were dissolved separately in double distilled water and stirred for fifteen minutes each. Na-CMC solution was poured into silver nitrate solution and this mixture was stirred for fifteen minutes and the resultant solution was colourless. Then ascorbic acid solution is added into this mixture while the stirring was continued. During this process, colour changes slowly from pale yellow to deep yellow to blackish green as stirring was continued for 15 minutes. The whole solution was centrifuged at 10000 rpm for ten minutes using a centrifuge machine and finally the blackish green precipitates were separated. The precipitate was washed several times with distilled water and acetone to ensure the removal of organic compounds and the product is dried at 70 °C for 1 hour using a hot air oven. The similar procedure was adopted to prepare the differently shaped silver nanoparticles at different precursor concentration. The whole reaction was performed at the room temperature. The AgNPs with different morphologies were obtained by adjusting the silver nitrate concentration to 0.02 M, 0.03 M, and 0.04 M while keeping other parameters unchanged.

### 2.2. Characterization

UV–visible absorption spectra were recorded at room temperature using a Varian Carey 5E UV–Visible spectrophotometer from 200 nm to 1000 nm. The powder XRD analysis was carried out by Enraf Nonius CAD4-F diffractometer with the CuK$\alpha$ ($\lambda = 1.540$) radiation with $2\theta$ ranging from $30^0$ to $70^0$. High resolution Scanning Electron Microscopy (HRSEM) studies were carried out using the instrument SEM quanta 200 at room temperature. The transmission electron microscopy (TEM) imaging was carried out on Tecnai using T30 G2-300 KV TEM instrument with $LaB_6$ electron gun at 250 KV.

## 3. Results and discussion

### 3.1. UV–Vis spectral analysis

Silver nanostructures exhibit interesting optical properties directly related to surface plasmon resonance (SPR), which is highly dependent on the size and morphology of the samples. Fig. 1 shows the UV–Vis absorption spectra of silver nanostructures synthesized with different precursor concentrations. It has been known that the SPR peak maximum shifts to a longer wavelength when the particle size becomes large [21].

As seen in the figure, when increasing the concentration of $AgNO_3$ from 0.01 M to 0.04 M, there is a red shift in the $\lambda_{max}$. In addition, it is found that the SPR peak becomes wider by increasing the precursor concentration indicating broad size distribution at higher concentration. When the concentration is 0.01 M, a symmetrical SPR peak is observed at 437 nm