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Self-assembly of silver nanoparticles: Formation of a thin silver film in a polymer matrix

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Abstract

A synthetic route is presented for the preparation of a silver film in presence of UV-radiation. Methoxy polyethylene glycol, a watersoluble polymer, was used as the reducing agent of the silver ions in the presence of an ultraviolet source to produce silver nanoparticles. During solution stirring, a centrifugal force was generated at the center of the solution. At this point on the surface of the solution, the nanoparticles coalesced to form a self-assembly of small subunits that ultimately develops into a film-like network. © 2005 Elsevier B.V. All rights reserved.

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1. Introduction

The combination of a polymer with quantum dots [1], fullerenes [2], redox molecules [3], metal [4-7] and metal nanoparticles [8-10] offers the potential of numerous and varied applications in the field of semiconductors, photovoltaic cells and molecular electronic fields. Thin films of gold and silver have been used in such diverse applications as in magnetic storage media [11-15], high temperature wear resistant [16] and anticorrosive coatings [16] as well as being able to influence electrochemical properties [17,18]. The deposition of thin metal films can be achieved by diverse and many well-established procedures. Most procedures are based on methods such as chemical vapor deposition [19,20] and metal evaporation or sputtering [21-24] that can be quite complex, require raised temperatures, plus a vacuum system for latter processes. Reports have also been published on conductive gold films [25] and

gold polymer composite films [26] being produced by a chemical synthesis procedure.

In this paper, we report on a new, simple synthesis route utilizing UV-irradiation for the preparation of silver films where silver nanoparticles are involved in the development of the film. Silver nanoparticles are produced from the ionic precursor, AgNO₃. Methoxy polyethylene glycol-5000, a water-soluble polymer, acts as in a dual role of a reducing agent in the presence of UV-irradiation as well as a stabilizer of the film.

2. Experimental

2.1. Reagent

Methoxy polyethylene glycol-5000 (MPEG) and silver nitrate (AgNO₃) were purchased from Union Carbide and Aldrich respectively. Ultra-pure water (resistivity >17 M Ω cm) was used to prepare the solutions of MPEG and AgNO₃. A stock solution of MPEG (0.5g MPEG dissolved in 1000 ml of water) was utilised in this work. AgNO₃ was used at a concentration of 10^{-2} mol dm⁻³.

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Fig. 1. TEM image of the silver nanoparticles after 3 min UV-irradiation.

2.2. Instrumentation

Photochemical reactions were carried out under a portable germicidal lamp (TUV 15W; G 15 T8 VU-C, Phillips, Holland). Transmission electron microscopy (TEM) studies of the particles were undertaken at an accelerated voltage of 200 kV using a Philips CM200. An ultra-thin windowed energy dispersive X-ray spectrometer (EDS) attached to the TEM was used to determine the chemical composition of the samples. Surface images were obtained utilising a JEOL JSM-840 scanning electron microscope (SEM) operating at 20 kV. The X-ray diffraction (XRD) patterns were recorded at 50 kV on Shimadzu XD-3A X-ray diffractometer using Cu-K_{\alpha} radiation (λ =0.1542 nm). The patterns were taken over the diffraction angle range 2θ =20° to 80°.

2.3. Procedure



In a typical experiment, 150 ml of polymer solution was mixed with 25 ml of AgNO₃ solution. The resultant solution

Fig. 2. UV–vis spectra of the colloidal silver particles after UV-irradiation was applied to the solution, 150 ml of MPEG-5000 (0.5 g of MPEG dissolved in 1000 ml of water) and 25 ml of $AgNO_3$ (10^{-2} mol dm⁻³), for (a) 3 min, (b) 5 min and (c) 6 min.



Fig. 3. XRD pattern from the silver film showing the predominant (111) oriented particles with minor contributions from (200) and (220) grains.

was then homogenized in a 250 ml beaker and purged with nitrogen gas for 15 min to remove the dissolved oxygen. The beaker was then placed on a magnetic stirrer and mild stirring applied for the rest of the procedure. The UV source was placed 10 cm vertically above the beaker. The solution became yellow after a 3 min period of irradiation indicating the formation of silver nanoparticles. TEM specimens were prepared by pipetting 2 μ l of colloid solution onto lacey, carbon coated, TEM copper mesh grids. After prolonged irradiation (30 min), the formation of shiny silver films (typically exhibiting a 'metallic silver' reflectivity) on the surface of the solution was observed, while the bulk of the solution became colourless. During stirring, a centrifugal force was generated at the center of the solution, and it is



Fig. 4. TEM image of the silver film. The inset is the diffraction pattern from the crystalline silver particles.

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