Journal of Non-Crystalline Solids 354 (2008) 5515–5520

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Synthesis and characterization of starch-stabilized Ag nanostructures for sensors applications

D. Manno *, E. Filippo, M. Di Giulio, A. Serra

Dipartimento di Scienza dei Materiali, Università del Salento, Via Monteroni, 73100 Lecce, Italy

ARTICLE INFO

Article history:
Received 26 October 2007
Received in revised form 3 March 2008
Available online 22 October 2008

PACS:
81.07.Bc
68.37.Lp
78.67.Bf

Keywords:
Nanocrystals
Sensors
Electron diffraction/scattering
X-ray diffraction
TEM/STEM
Nanoparticles

ABSTRACT

Silver nanostructures were successfully synthesized through a simple and 'green' route using starch as a capping agent. High resolution electron microscopy (HREM), X-ray diffraction (XRD), UV–Vis absorption suggested that Ag nanocrystals, having a size lower than 10 nm, were obtained, in addition a self-assembly into ribbon-like structures was been also observed. The silver nanostructures were electrodeposited onto suitable substrates with gold interdigital electrodes realizing amperometric sensors that showed a high sensitivity to hydrogen peroxide.

1. Introduction

During the past decade, scientists have developed techniques for synthesizing and characterizing many new materials with at least one dimension on the nanoscale, including nanoparticles, nanolayers, and nanotubes [1]. Still, the design and synthesis (or fabrication) of nanoscale materials with controlled properties is a significant and ongoing challenge within nanoscience and nanotechnology.

Metal nanoparticles have attracted extensive interest because of their unique size-dependent optical [2,3] and electronic properties [4,5]. In addition, a growing number of applications of nanoscience/nanotechnology are being developed that promise environmental benefit, including new catalysts for environmental remediation [6], cheap and efficient photovoltaic [7], thermoelectric materials for cooling without refrigerants [8], lightweight (and thus energy-conserving) nanocomposite materials for vehicles [9], miniaturized devices that reduce material consumption, and sensors that eliminate the need for (often) wasteful wet-chemical analyzes. Nanoscale sensors [10] can also offer faster response times and lower detection limits, making on-site, real-time detection possible.

Many preparations of the building blocks of nanotechnology involve dangerous chemicals, low material conversions, high-energy requirements, and difficult, wasteful purifications; thus, there are multiple opportunities to develop greener processes for the manufacture of these materials.

Some progress toward greener nanosynthesis has already been made. The synthesis and assembly of nanoparticles would benefit from the development of clean, non-toxic and environmentally acceptable 'green chemistry' procedures, probably involving organisms ranging from bacteria to fungi and even plants [11,12].

Efforts have also been made for the synthesis of nanoparticles of different chemical composition, sizes and controlled monodispersity [13], as for example synthesis of biominerals, which are composite materials and consist of an inorganic component and a special organic matrix (proteins, lipids, or polysaccharides) that controls the morphology of the inorganic compound. In particular it is well known the DNA-template construction of polycrystalline nanowire and nanorod arrays [14].

Recently, starch has been used as 'green' capping agent [15] in the synthesis of silver nanoparticles. Starch is a renewable polymer, and it adopts right-handed helical conformation in aqueous solution, in which the extensive number of hydroxyl groups can

* Corresponding author. Fax: +39 0832 297069.
E-mail address: daniela.manno@unile.it (D. Manno).

0022-3093/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnoncrysol.2008.04.059

facilitate the complexation of metal ions to the molecular matrix. In fact, starch has been found to be not only an effective reducing agent but also a new morphology-directing agent [16].

A means of producing size and shape controlled nanoparticles and controlling their subsequent organization into super structures amenable to practical applications, are two of the primary goals of nanotechnology. Much efforts have been made and indeed progress has been achieved in providing reproducibility and control over the size and shape distribution of metal nanoparticles [17]. Recently, electrodeposition of silver nanoparticles has been realised [18] and an interesting high porous structure has been evidenced. Because the assembled nanosized particles have a large number of surface atoms that results in extremely reactive surface energy, it is reasonable to use such material for application in sensor devices.

In this work, we propose a preparation method of silver nanoparticles based onto hydrothermal synthesis that uses water as solvent medium, β-D-glucose as reducing agent, and starch as capping agent that are all environmentally benign and non-toxic material. The resulting nanocomposites were investigated by using structural, optical and morphological methods. XRD spectra confirmed the presence of nanostructured silver (cubic phase) in the matrix. High resolution transmission electron microscopy (HREM) methods showed that the nanoparticles are self-assembled into nanoribbon. Then, the silver nanostructures were electrodeposited onto suitable substrates with gold interdigital electrodes giving rise to interesting amperometric sensors that showed fast and high sensitivity to hydrogen peroxide.

2. Experimental

UV–Vis spectra were recorded in the range between 320 and 800 nm using a Varian Cary-5 double-beam spectrophotometer. Solution spectra were obtained by measuring the absorption of the prepared nanoparticle dispersions in a quartz cuvette with a 1 cm optical path. The experimental data were all corrected for the background absorption of the silverless solution.

X-ray diffraction (XRD) measurements were carried out in the reflection mode on a Mini Flex Rigaku diffractometer operated at 30 kV voltages and a current of 120 mA with Cu Kα radiation (λ = 0.154056 nm). Samples for XRD were prepared by casting the silver solution on glass substrate.

High resolution transmission electron microscopy (HREM) and electron nano-diffraction patterns were performed using a JEOL 2010 transmission electron microscope operating at 160 kV, representing the suitable acceleration voltage to obtain a good resolution and minimal radiation damage of the material. The diffraction patterns were recorded by selecting a suitable spot size, convergence angle and condenser aperture to get the diffraction patterns from chosen areas of about 100 nm in diameter with an approximately parallel beam (the convergence angle of the incoming beam was about 5×10^{-5} rad). The specimens for electron microscopy analysis were prepared by placing small droplets of freshly prepared solutions onto standard carbon supported 600-mesh copper grid and drying slowly in dry air flow.

The preparation of starched silver nanoparticles was quite straightforward. In a typical preparation, aqueous starch dispersions containing Ag^+ ions were prepared by adding 10 ml of a 0.1 M solution of $AgNO_3$ (Sigma) and 25 ml of a 0.1 M solution of D-glucose (Fluka) to about 2 ml of 0.20 wt.% aqueous solution of soluble starch (Sigma). The mixture was kept on boiling under vigorous stirring for about 60 min.

An electrochemical deposition technique was employed to obtain a solid-state device. A standard three-component electrochemical cell was used as the electrochemical reactor for the silver nanostructures depositions. A saturated calomel electrode was used as reference electrode. Gold patterned alumina plates were employed as counter electrode (anode) and working electrode (cathode), respectively. These electrodes were fabricated using a conventional lithography, gold evaporation, and lift-off processes on Al_2O_3 slides. The height difference between the electrodes and substrate was less than 100 nm. An insulating gap between the opposite electrodes of about 200 μm was obtained.

A colloidal solution of 'starched' silver particles at pH 5.4 was used as growth solution. The distance between cathode and anode was kept at 0.2 mm. The potential difference applied between the anode and cathode was kept nominally at 0.5 V. The depositions were carried out at a stabilized temperature of 21 °C.

All electrochemical experiments for sensors test were carried out in a conventional electrochemical quartz cell holding 10.0 ml at 21 °C temperature, manufactured in our laboratory. The electrodes of the sensors were connected to an electrometer Keithley 6517A in order to monitor the sensors resistance.

3. Results and discussion

3.1. Structural and morphological analysis

The transmission electron microscope image of the silver nanoparticles synthesized using this method is presented in Fig. 1. It is

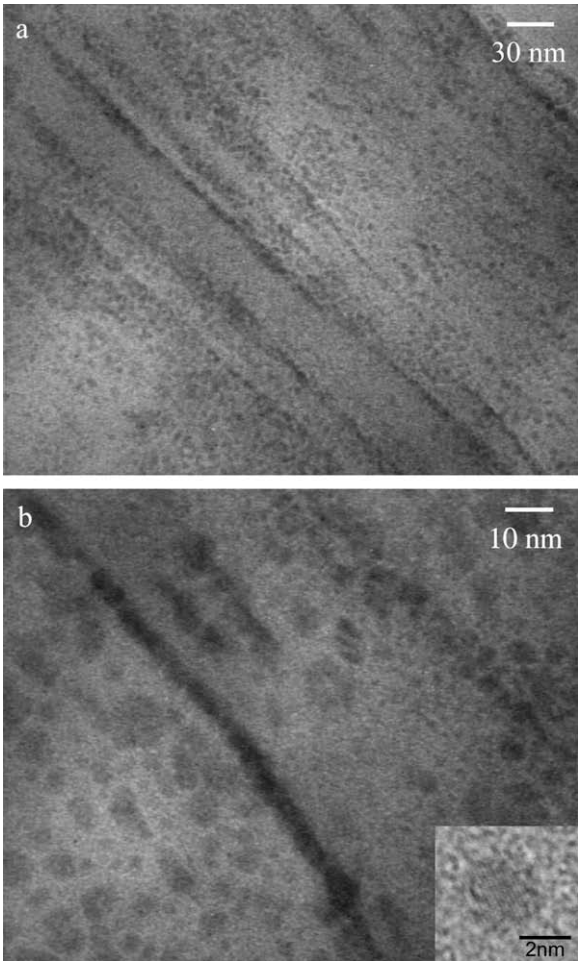

Fig. 1. (a) A typical TEM image showing the silver nanoparticles that, in some cases, assembled into elongated and well-aligned structures. (b) HREM image evidences isolated nanoparticles and nanoparticles aggregated into nano-ribbon, in the inset, the lattice image clearly evidences the crystalline nature of the nanoparticle.