Applied Surface Science 258 (2012) 2368–2372

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

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

Depositing nanoparticles inside millimeter-size hollow tubing

Alexandra Friedman, Nina Perkas, Yuri Koltypin, Aharon Gedanken*

Department of Chemistry and Kanbar Laboratory for Nanomaterials, Bar-Ilan University Center for Advanced Materials and Nanotechnology, Bar-Ilan University, Ramat-Gan 52900, Israel

ARTICLE INFO

Article history:
Received 7 July 2011
Received in revised form
13 September 2011
Accepted 8 October 2011
Available online 14 October 2011

Keywords:
Sonochemistry
Nanoparticles
Coatings
Tubing

ABSTRACT

The inner and the outer walls of hollow tubing with an inner diameter of 0.4–0.9 cm and an outer diameter of 0.6–1.3 cm were coated with silver nanoparticles (NPs) by a one-step process using ultrasound irradiation. The structure and morphology of the nanoparticles (NPs) inside the hollow tubing and on the outer surface were characterized using methods such as XRD, TEM, HR-TEM, and HRSEM. The inner surface of the tubing was found to be coated with more silver than the outer surface. The coating was done on tubing made of rubber, PVC, Teflon and polyethylene. Sonochemistry is demonstrated as a method for depositing nanoparticles on the inner wall of a tube.

1. Introduction

Over the last 10 years the sonochemical method has been found to be an efficient method for coating nanoparticles on flat and curved surfaces, and a variety of materials were used as substrates for the deposition. Homogeneous coatings were formed on ceramics, metals, polymers, textiles, glass, and paper [1,2]. Various nanoparticles were coated on these surfaces, including metals, metal oxides [3], chalcogenides [4] and others. A good adherence to the substrate surface was found in all cases, and which was accounted for by the mechanism explaining how this coating is formed. Sonochemistry is known as a method in which chemistry occurs at 20 kHz as a result of the collapse of the acoustic bubble. This collapse creates very high temperatures and high pressures, conditions leading to the rupture of chemical bonds [5]. According to the interpretation suggested for the sonochemical coating process, after the collapse of the acoustic bubble near a solid surface microjets are formed. These microjets throw the newly formed nanoparticles at the solid substrate at such a high speed (>200 m/s) that the silver nanoparticles could penetrate glass to a depth of 60 nm [6]. This mode of coating is a one-step process containing the substrate and the precursor solution in the sonication cell, and the ultrasonic waves will conduct a well-known chemical reaction resulting in the desired nanoparticles. Subsequent to their formation, coating on the planned substrate takes place. However, in cases where sonochemistry does not lead to the desired nanoparticles, a two-step process is employed. The nanoparticles are either made by a different technique or are purchased from a chemical company, and the ultrasonic waves are used only for "throwing stones" at the substrate surface. For example, this was the case when trying to coat MgO on textiles such as cotton and polyester [7]. As the sonochemical hydrolysis led to the formation of $Mg(OH)_2$, and not to MgO, it was decided to purchase the MgO nanoparticles from Aldrich. The ultrasonic waves were then used successfully to form a monolayer of MgO nanoparticles on these textiles.

One of the properties that have already been demonstrated for sonochemistry is the ability to insert nanoparticles into small mesopores of mesoporous materials, as well as into the hollow part of carbon nanotubes [8–10]. The explanation suggested for this phenomenon is also related to the microjets. It was suggested that the shape of the collapsing asymmetric acoustic bubble (which is not spherical, but rather flask-like) is such that its sharp edge is aligned towards the opening of the pores or the cavity. Upon the collapse of the acoustic bubble, the formed nanoparticles are thrown into the hollow pore or tube and are attached to the inner walls, either by chemical interaction or by physical adsorption. For example, nanoparticles of Mo_2O_5 were inserted sonochemically into the mesopores of MCM-41 and catalyzed successfully the dehydrosulfurization of aromatic sulfur compounds [11].

Various techniques have previously been employed to coat the inner wall of tubing. For example, hollow-core glass waveguides (HCWs) with inner coatings of silver and polystyrene (PS) have been fabricated for the transmission of terahertz radiation. A

---

* Corresponding author. Tel.: +972 3 5318315; fax: +972 3 7384053.
E-mail address: gedankena@mail.biu.ac.il (A. Gedanken).

0169-4332/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2011.10.033

liquid-phase chemical deposition process was used to deposit silver and PS thin film coatings inside glass tubing [12]. Similarly, metal-coated hollow fibers for terahertz waves are fabricated with a conventional silver mirror-plating technique [13]. Most of the work reported in the literature on coating inner surfaces was devoted to wave-guide formation, and the coating materials were mostly metallic. However, the inner surface of hollow fibers and the tubing of extracorporeal membrane oxygenation (ECMO) were also coated by heparin [14]. Among the other techniques reported for inner tubing deposition we can mention pulsed laser deposition [15,16], flash dry deposition [17], plasma deposition [18], and chemical vapor deposition [19]. At the same time, it is clear that the spin-coating technique would not be an appropriate method for coating the inner surface of a tube.

In the current study we have investigated the possibility of depositing silver nanoparticles onto the inner walls of macro systems in a one-step process where the nanoparticles are formed and thrown onto the surface. The motivation for this study is to demonstrate that ultrasonic waves can introduce NPs not only into nanometer size pores, but also into larger hollow tubing. The paper does not deal with how parameters such as US power, US frequency, working temperature and time, reactor volume, and concentration of reagents affect the ratio of the deposition on the inner:outer wall. Such a study will hopefully be conducted in the future. The goal of this paper is to prove that the application of US waves provide an excellent technique for coating inner walls of hollow tubings.

The sonochemical reaction that was conducted in these studies is the reduction of silver ions, yielding metallic silver nanoparticles. This sonochemical reaction has been reported previously [20]. The hollow tubings that were coated in this study were made of Teflon, PVC, and rubber, and their inner and outer diameters varied from 0.6 cm to 1.3 cm. The hollow tubing was coated with silver NPs to impart antibacterial properties to the coated tubing [20]. We are currently involved in a different study on the introduction of metal fluorides into and on catheters, bearing in mind their potential application in inhibiting the formation of biofilms [21]. These results will be published elsewhere.

2. Experimental

2.1. Materials and chemicals

All the chemical reagents, of chemical grade, were purchased from Aldrich and used without further purification.

The hollow tubes were of Teflon, rubber, and PVC, with inner diameters of 0.4 cm, 0.6 cm, 0.9 cm, respectively, and outer diameters of 0.6 cm, 1.3 cm and 1.1 cm, respectively, and Pasteur pipettes with diameters varying from 0.2 cm to 0.7 cm. Silver nitrate was used as a precursor for silver coating and ethylene glycol (EG) was used as a polyol reducing agent. The EG reduces the silver ions to metallic silver. The addition of ammonia forms the $[Ag(NH_3)_2]^+$ complex. The equilibrium constant for the formation of $[Ag(NH_3)_2]^+$ is large ≈107, which dictates a small amount of Ag + 1 in equilibrium with the complex. Thus the reduction process is slowed down, enabling the creation of many seeds which eventually lead to the formation of silver nanoparticles.

2.2. Experimental details

The details of the process leading to nanosilver can be found elsewhere [20], it will be repeated here in brief. In the typical reactions leading to metallic silver, 0.02 M $AgNO_3$ in water–EG (10 vol% EG) were used as the starting solutions. The reducing agent was the ethylene glycol. The solutions were purged with Ar for 1 h in order to remove traces of O_2/air. The purging was done in the presence of the tubing to be coated. In the next stage, the solution was irradiated for 1 h with a high intensity ultrasonic horn (Ti horn, 20 kHz, 600 W at 70% efficiency) under a flow of Ar. 0.3 ml aqueous solution of ammonia (molar ratio $NH_3:AgNO_3 = 2:1$) was added to the reaction slurry during the first 10 min of sonication. The sonication flask was placed in a cooling bath keeping a constant temperature of 30 °C during the sonication. At the end of the reaction the coated tubing was first washed with water to remove traces of ammonia, then with ethanol, and then dried under vacuum. To determine the amount of silver on the outer circumference of the tubing, a layer of 0.1 cm was removed using a sharp scalpel. The removed layer was soaked in 5 M of HNO_3 and the silver concentration was then determined by ICP. The dissolution in HNO_3 was repeated for the tubing remaining after the removal of the outer surface. In this way we could get a measure of the relative coating on the inner and outer surfaces.

2.3. Characterization

The content of silver on the coated tubes was determined by Inductively Coated Plasma (ICP) analysis using an ULTIMEJY2501 instrument. The X-ray (XRD) patterns of the products were measured with a Bruker D8 diffractometer (Karlsruhe, Germany) with Cu Kα radiation. The particles' morphology and size were studied with a high-resolution scanning electron microscope (HRSEM), JEOL-JSN 7000F. The determination of the Ag particles remaining in the irradiated solution was conducted by Dynamic Light Scattering (DLS) measurements employing a Coulter particle analyzer (Malvern Zetasizer).

3. Results and discussion

Only the results related to the rubber coating will be presented in the current paper. The figures presenting the coating on the other substrates will be introduced in the supplementary information (index) to avoid repetition. Despite this, we present in Fig. 1 an example of all four materials before and after the anchoring of the silver NP. A change in color is evident from the figure and is observed on the inner and outer walls. Fig. 1 demonstrates the generality of the coating process, since even with the naked eye it is clear that all four surfaces were coated by metallic silver. We will introduce the results for rubber, PVC, and Teflon, but to prevent redundancy, we will not include the similar presentation for PE.

3.1. Structure and morphology of the coated Ag NP

Since identical diffraction peaks were obtained for nanosilver coating on all the tubing, only the XRD pattern of the rubber-coated tubing is presented. A typical XRD pattern of silver particles is shown in Fig. 2. The peaks fit well a face-centered cubic (fcc) structure (JCPDS, file no. 4-783) of silver. The peaks at $2\theta = 38.2, 44.4, 64.5$ and 77.5 correspond to the (1 1 1), (2 0 0), (2 2 0), and (3 3 1) planes of fcc Ag, respectively. No impurity peaks were detected in any of the coatings. The calculated size of the silver crystallites determined by the Scherrer equation is 19 ± 4 nm for the silver-coated rubber tubing. Very similar numbers were obtained for all other coatings.

The morphology of the tubing's surface area before and after the coating was studied by SEM and is presented in Fig. 3. The magnification for this SEM picture is 30,000.

Fig. 3a shows that the bare surface of the rubber tubing is rough and porous. On the other hand, in Fig. 3b it is possible to see spherical Ag particles anchored to the surface. The shape of the silver nanoparticles inside and outside the tube is similar, i.e., spherical. The average size of the Ag nanoparticles is 63 ± 27 nm, and we observe the aggregation of these spheres on both sides of the tubing. It looks that part of the Ag nanoparticles penetrated the surface