



# Growth of giant silver dendrites on layer-by-layer assembled films



Jia Song<sup>a</sup>, Junxia Hou<sup>a</sup>, Lili Tian<sup>a</sup>, Ying Guan<sup>a,\*</sup>, Yongjun Zhang<sup>a,\*</sup>, X.X. Zhu<sup>b,\*\*</sup>

<sup>a</sup> Key Laboratory of Functional Polymer Materials, Institute of Polymer Chemistry, College of Chemistry, Nankai University, and Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300071, China

<sup>b</sup> Department of Chemistry, Université de Montréal, C. P. 6128, Succursale Centre-ville, Montreal, QC H3C 3J7, Canada

## ARTICLE INFO

### Article history:

Received 5 November 2014

Received in revised form

1 February 2015

Accepted 4 March 2015

Available online 11 March 2015

### Keywords:

Dendrites

Layer-by-layer assembled film

Silver

## ABSTRACT

Ag dendrites were previously synthesized, with limited success, via the chemical reduction of Ag<sup>+</sup> ions with a soluble reducing agent in homogeneous solutions. Here Ag<sup>+</sup> ions were first loaded in hydrogen-bonded layer-by-layer (LBL) films fabricated from poly(vinyl pyrrolidone) (PVPON) and poly(acrylic acid) (PAA), then reduced chemically using p-hydroquinone (HQ) as a reducing agent to afford Ag dendritic structures. The dendrites were characterized by SEM, TEM, XRD and optical microscope. Compared with the Ag dendrites synthesized in homogeneous solutions, the dendrites obtained here are much larger. The fully developed ones can reach a size over 600 μm, ca. 2 orders of magnitude larger than those synthesized in homogeneous solutions (~1–5 μm). In addition, the dendrites obtained here are 2 dimensional which grow along the surface of the LBL film, instead of 3 dimensional as those obtained in homogeneous solutions. A possible 3-step growth mechanism, which involves the rapid reduction of the Ag<sup>+</sup> ions in the film, formation of Ag seed particles on the film surface, and fractal dendritic structure formation as described by the diffusion-limited aggregation (DLA) model, was proposed.

© 2015 Elsevier Ltd. All rights reserved.

## 1. Introduction

The shape and size of noble metal particles strongly influence their physical and chemical properties, therefore control of their morphology is a crucial issue in material science [1,2]. Up to now, metal particles with various morphologies, such as nanospheres, nanoplates, nanowires, nanobelts, and nanotubes, have been synthesized [2]. Among all the morphologies, dendritic nanostructures are unique because their abundant edges and corners provide a large number of active atoms. These materials show many interesting properties and have found important applications. For example, silver dendrites show excellent surface enhanced Raman scattering properties [3–11] and high catalytic activity [12,13]. They can significantly enhance the emission of the adsorbed fluorophores [14,15]. As an ideal conducting matrix for enzyme immobilization, they can increase the sensitivity of an electrochemical biosensor by as much as 1–2 orders of magnitude [9]. They have also been used to create super-hydrophobic surfaces [16–19].

Several methods have been developed to synthesize Ag dendrites. Among them, electrochemical deposition, in which Ag<sup>+</sup> ions are reduced electrochemically, is facile and effective. The growth rate of the nanostructures can be controlled by the applied potential [11,20]. Ag dendrites have also been synthesized via galvanic displacement (or electroless deposition), by the use of heterogeneous or solid reducing agents such as silicon wafer [15], aluminum foil [4,21], and zinc microparticles [9] or plates [22]. Wet chemical routes, i.e., reducing Ag<sup>+</sup> ions in solutions with a soluble reducing agent, were also developed. Under proper conditions, Ag dendrites were synthesized by reducing AgNO<sub>3</sub> in solutions, using *p*-phenylenediamine [23], L-ascorbic acid [8], or NH<sub>2</sub>OH [3,5] as reducing agent. Although the wet chemical methods are powerful for the synthesis of Ag nanoparticles with various morphologies [24], such as spheres, cubes [25], and plates [26,27], for the synthesis of Ag dendrites, only limited success has been achieved [3]. Usually the obtained structure is not well-defined, and the size is relatively small [3].

A possible reason for the limited success of wet chemical routes may lie in the facts that dendritic structures usually form under non-equilibrium conditions, which is difficult to achieve and control in homogeneous solutions. In contrast, when the reaction occurs at an interface, for example when using solid reducing agents, it is much easier to build a non-equilibrium condition. With this in

\* Corresponding authors.

\*\* Corresponding author.

E-mail addresses: [yingguan@nankai.edu.cn](mailto:yingguan@nankai.edu.cn) (Y. Guan), [yongjunzhang@nankai.edu.cn](mailto:yongjunzhang@nankai.edu.cn) (Y. Zhang), [julian.zhu@umontreal.ca](mailto:julian.zhu@umontreal.ca) (X.X. Zhu).

mind, here we loaded  $\text{Ag}^+$  ions in layer-by-layer (LBL) self-assembled films. They were then reduced chemically using *p*-hydroquinone (HQ) as a reducing agent. (Scheme 1) Using this method, large, well-defined dendritic structures were successfully obtained. The dendritic structures prefer to grow along the film surface, resulting in a 2D structure, instead of 3D structures as those produced in homogenous solutions. In addition, the dendrites obtained here are about 2 orders of magnitude larger than those synthesized in homogenous solutions. It is noteworthy that similar approach was previously used to synthesize nanoparticles embedded in LBL films as nanoreactors [28–34]. Zhang et al. [16] synthesized gold dendritic clusters via electrochemical deposition onto an indium tin oxide (ITO) electrode modified with a polyelectrolyte multilayer.

## 2. Experimental section

### 2.1. Materials

Poly(vinyl pyrrolidone) (PVPON) (K30, Mw 58,000) was purchased from Guangfu Institute of Fine Chemicals (Tianjin, China). Poly(acrylic acid) (PAA) with a Mw of 100,000 was purchased from Aldrich. Silver nitrate, *p*-hydroquinone (HQ) and nitric acid of analytical grade were purchased from Tianjin Chemical Reagents Wholesale Company. The chemicals were used as received without further purification.

### 2.2. Film fabrication

The LBL films were fabricated on quartz slides or silicon wafers, which were cleaned in boiling piranha solution (3: 7 v/v  $\text{H}_2\text{O}_2$ – $\text{H}_2\text{SO}_4$  mixture) before use (Caution: this solution is extremely corrosive!). Aqueous solutions of PVPON and PAA with a concentration of 0.15 wt% were prepared and their pHs were adjusted to 3.0 using 0.1 M  $\text{HNO}_3$ . LBL films were fabricated by alternate dipping the substrates in PVPON solution and PAA solution, each for 3 min, washing in fresh  $10^{-3}$  M  $\text{HNO}_3$  three times (each for 1 min) in between. After the desired numbers of bilayers were reached, the films were dried in the air.

### 2.3. $\text{Ag}^+$ loading

To load  $\text{Ag}^+$ , the PVPON/PAA films were immersed in  $\text{AgNO}_3$  solution (0.01 M, if not otherwise specified) for 15 min, if not otherwise specified. After a brief wash in deionized water, the films were dried in air. The operations were performed in the dark to avoid light reduction of the silver ions.

### 2.4. Growth of Ag structures

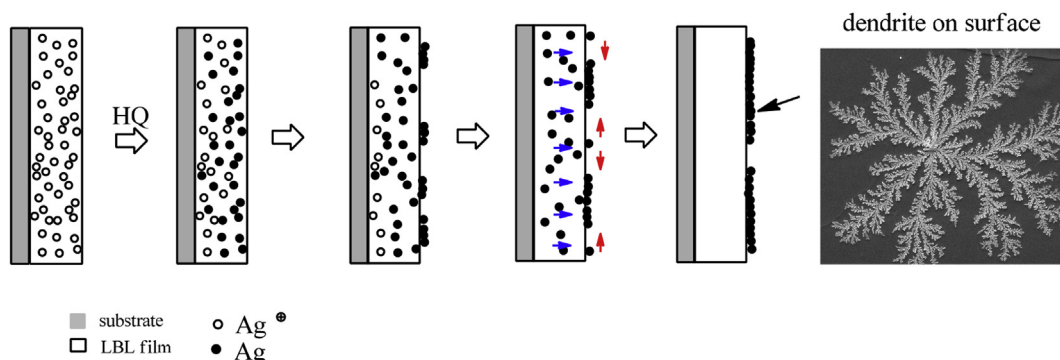
The  $\text{Ag}^+$ -loaded films were immersed in HQ solutions for a predetermined time. After rinsing in DI water thoroughly, the films were air-dried.

### 2.5. Characterizations

The UV–vis absorption spectra of LBL films fabricated on quartz slides were recorded on a Varian Cary 100 spectrophotometer. FTIR spectra of LBL films fabricated on silicon wafers (only one side was polished) were collected on a Bruker Tensor 27 FTIR instrument. The X-ray diffraction (XRD) patterns were recorded on a Rigaku D/max-2500 diffractometer with  $\text{CuK}\alpha$  radiation operated at 40 KV and 100 mA using the conventional symmetrical Bragg Brentano configuration. The sample was fabricated on glass substrate. The transmission electron microscopy (TEM) images and the corresponding selected area electron diffraction (SAED) patterns were recorded on a FEI Tecnai G2 F20 field-emission transmission electron microscope with an accelerating voltage of 200 KV. To prepare TEM samples, the films were soaked in ethanol. The Ag nanostructures were dispersed into the solution by ultrasonic. Then the suspension was dropped onto lacey film coated grids and dried in vacuum. The scanning electron microscopy (SEM) imaging and energy-dispersive X-ray spectroscopy analysis were performed on a FEI Nanosem 430 field-emission scanning electron microscope (FESEM).

## 3. Results and discussion

The polymeric films were fabricated from poly(vinyl pyrrolidone) (PVPON) and poly(acrylic acid) (PAA) using the so-called layer-by-layer (LBL) assembly method [35–38]. The main driving force is the hydrogen bonding between the two polymers as revealed in previous studies [39–44]. The film thickness was determined using Fabry–Perot fringes on their UV–vis absorption spectra (Fig. S1 in Supporting information 1) [44–47]. Typically, for a 40 bilayer film, the thickness was determined to be 1059 nm. The  $\text{Ag}^+$  ions were loaded by simply soaking the PVPON/PAA films in an aqueous solution of  $\text{AgNO}_3$  via an ion-exchange mechanism (Scheme 2) [48]. The films remain stable because the  $\text{Ag}^+$  ions bind with PVPON via coordination interaction and simultaneously bind with PAA via electrostatic interaction. The concentration of  $\text{Ag}^+$  loaded in the film, expressed as the percentage of carboxylic acid groups deprotonated, was estimated from the decrease of the intensity of the IR band at  $1725\text{ cm}^{-1}$  upon  $\text{Ag}^+$  loading (Fig. S2 in Supporting information) [48].



Scheme 1. Proposed mechanism for the growth of Ag dendrites on PVPON/PAA film surface.

Download English Version:

<https://daneshyari.com/en/article/5180500>

Download Persian Version:

<https://daneshyari.com/article/5180500>

[Daneshyari.com](https://daneshyari.com)