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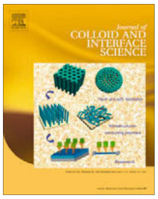

In situ synthesis of Ag nanoparticles in aminocalix[4]arene multilayers

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ABSTRACT

The layer-by-layer (LbL) assembled thin films containing tetraamino-thiacalix[4]arenes (**1**) and tetraamino-calix[4]arenes (**2**) were used as nanoreactor to synthesize *in situ* Ag nanoparticles (Ag NPs). UV–vis spectra and AFM images demonstrate that Ag NPs are included in the (**1**/Ag NPs)$_n$ and (**2**/Ag NPs)$_n$ multilayer films. The silver ions are absorbed through cation–π interaction and calix[4]arene-metal ion coordination interaction and are reduced into Ag NPs by calix[4]arenes. TEM images indicated that Ag NPs within aminocalix[4]arene multilayers were highly dispersed and uniform. Moreover, the mean size of Ag NPs is smaller than 10 nm.

1. Introduction

Metal nanostructures with size-dependent and shape-controlled properties are of interest for applications, including catalysis, magnetic information storage, biosensors, and surface-enhanced Raman scattering (SERS) [1–3]. In recent years, the preparation of thin films composed of metal nanostructures is one of the hot topics [4,5]. Among the metals, silver nanostructures are especially attractive because Ag nanoparticles (Ag NPs) have been known to have extraordinary inhibitory and bactericidal properties and surface-enhanced Raman scattering (SERS) [6–10]. As known, solution-phase synthesis is an effective method for producing inorganic metal colloid nanoparticles with controlled shapes and properties [11–15]. For example, in solution-phase synthesis, Ag ions can be reduced into Ag nanoparticles, nanobars, nanoprisms, nanorods and nanoplates in the presence of capping agents such as N, N-dimethyl formamide (DMF), poly(vinylpyrrolidone) (PVP), poly(ethylenimine) (PEI), polyacrylamide (PAM), and so on [6–18]. In contrast to solution-phase synthesis, the study on *in situ* nanoparticle synthesis within layer-by-layer (LbL) assembled films is limited [19–21]. LbL self-assembly method [22], which is based on alternately electrostatic adsorption of oppositely charged species from dilute solutions, has proven effective on constructing multilayer films. The effective and convenient method can fabricate the multicomponent films with good control over the layer composition and thickness. The *in situ* nanoparticle synthetic methodology was firstly reported by Rubner [19]. In brief, by utilizing LbL assembled thin films as nanoreactor, nanometer-sized metal particles have been synthesized *in situ* in the films. For instance, Rubner utilized PAH/PAA polyelectrolyte multilayer thin film as nanoreactor to synthesize *in situ* nanometer-sized metal Ag NPs in hydrogen atmosphere [19,20]. Moreover, Rubner prepared the antibacterial coatings based on hydrogen-bonded multilayer containing *in situ* synthesized Ag NPs on planar surfaces and on magnetic colloidal particles [21]. This *in situ* nanoparticle synthesis in LbL assembled films as nanoreactor afforded facile and precise control of the concentrations of the homogeneously dispersed nanoparticles. However, owing to the electroinactive polyelectrolyte multilayer films, the process requires the ion exchange and sequential reduction in hydrogen atmosphere. On the other hand, Kim reported that single-crystalline silver nanowires were synthesized inside the pores of self-assembled electrochemically active calix[4]hydroquinones (CHQs) nanotubes by electro-/photochemical redox reaction [23]. Ag ions were included in the cavity of CHQs through cation–π interactions.

Calixarenes, a fascinating family of cavity-shaped macrocyclic molecules, have attracted much attention in supramolecular chemistry due to the application in enzyme micmics, host–guest chemistry, selective ion transport, and sensors [24–27]. However, the application depends on the functionalization of calixarenes at the top and bottom rims. By functionalization of calixarenes at the upper and/or lower rims, many novel water-soluble calixarenes with interesting properties and potential applications were reported in the literature. In our previous work, we reported the multilayer films composed of single-component and positively-charged tetraaminocalix[4]arenes such as *p*-tetraamino-tetrathiacalix[4]arene (*p*ATC4) (**1**) and *p*-tetraamino-calix[4]arene (*p*AC4) (**2**) through hydrogen bonding between the amino groups and hydroxyl groups [28]. The two calix[4]arenes are modified at the up rim with amino groups [29,30]. Moreover, they are water-soluble and positively-charged macrocyclic ligands. However, the struc-

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tural differences between **1** and **2** are the bridging sulfur atoms instead of methylene units. Because of the presence of four sulfur atoms instead of the bridge methylene groups, **1** has many novel features such as excellent coordination abilities toward transition metal ions [31–33]. On the other hand, **1** and **2** are multifunctional and electroactive due to the presence of *p*-amino and hydroxyl groups. Therefore, we attempted to synthesize *in situ* Ag NPs in the combination of LbL assembly and calix[4]arenes.

2. Materials and methods

2.1. Materials

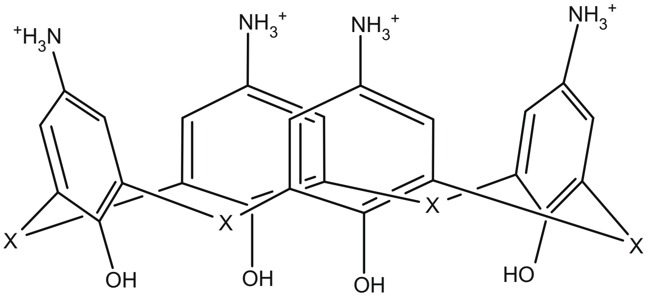
Poly(ethylenimine) (PEI, 50 wt.% aqueous solution) was purchased from Aldrich Chemical Co., $K_5BW_{12}O_{40}$ (BW_{12}) was prepared by published methods [34]. Both *p*-tetraamino-tetrathiacalix[4]arene (*p*ATC4) and *p*-tetraamino-calix[4]arene (*p*AC4), were synthesized according to the references [29,30]. The amino groups of *p*ATC4 and *p*AC4 were protonized with hydrochloric acid, abbreviated as $[H_4pATC4]Cl_4$ (**1**) and $[H_4pAC4]Cl_4$ (**2**) (see Fig. 1).

2.2. Layer-by-layer assembly (calix[4]arene/Ag NPs)$_n$ multilayer films (calix[4]arene = 1 or 2, nanopartilces = NPs)

The quartz slides (or single-crystal silicon slides) were cleaned with a "piranha solution" at 80 °C for 40 min, and thoroughly rinsed with distilled water. Further purification was carried out by immersion in a $H_2O/H_2O_2/NH_3OH$ (5:1:1) (V/V/V) bath for 30 min at 70 °C. The clean slides (or CaF_2 plates) were first immersed in PEI solution for 20 min. Then the slides were deposited into BW_{12} solution for 20 min. The slides pre-coated with PEI-BW_{12} were immersed in **1** or **2** (1.8 mM) aqueous solution for 20 min. Then, the substrates were dipped into 10 mM $AgNO_3$ for 25 min. Between each immersion step, the substrates were washed with water and dried with nitrogen stream. By repeating the two steps, PEI-BW_{12}-(**1**/Ag NPs)$_n$ and PEI-BW_{12}-(**2**/Ag NPs)$_n$ multilayer films were prepared.

2.3. Instruments and characterization

UV–vis absorption spectra were recorded on a quartz slide with a Lambda35 spectrophotometer (Perkin–Elmer, USA). High-resolution X-ray photoelectron spectra (XPS) were collected at a takeoff angle of 45° using PHI Quantum 2000 scanning ESCA microprobe (Physical Electronics, USA) with an Alα X-ray line (1486.6 eV). IR spectra were taken on films on CaF_2 plates, using a Spectrum One FTIR (Perkin–Elmer, USA). All AFM images were taken on a single-crystal silicon slide using a Veeco Multimode NS3A-02NanoscopeIII atomic force microscope with silicon tips. Height images of the films were recorded using tapping-mode AFM. Transmission electron microscope (TEM) images were performed on a JEM-2010 operated at 200 kV. The samples were prepared by alternately drop-coating calix[4]arene and $AgNO_3$ solutions on a carbon-coated copper grid. The copper grid drop-coated with (calix[4]/Ag NPs)$_3$ films was used for measurement.



1 X = S
2 $X = CH_2$

Fig. 1. Chemical structures of $[H_4pATC4]^{4+}$ (**1**) and $[H_4pAC4]^{4+}$ (**2**).

3. Results and discussion

3.1. Characterization of UV–vis spectra

PEI-BW_{12}-(**1**/Ag NPs)$_n$ and PEI-BW_{12}-(**2**/Ag NPs)$_n$ multilayer films were prepared by alternately immersing in aminocalix[4]arene and $AgNO_3$ aqueous solutions. In general, LbL self-assembled multilayer films depend on the conventional electrostatic interactions [35]. To date, the formation of LbL self-assembled multilayer films also includes hydrogen bonding and metal–ligand coordination interactions [36,37]. Hydrogen bonding plays an important role in supramolecular chemistry and life science. When applied to self-assembly at surfaces, hydrogen bonding opens up new possibilities for the uncharged components films. Moreover, transition-metal coordination chemistry provides new

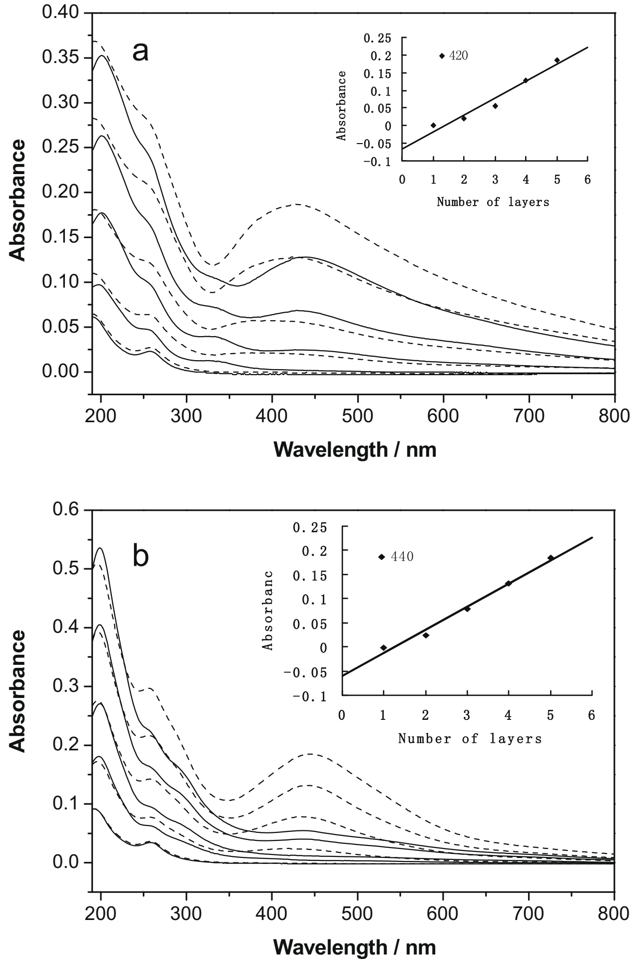


Fig. 2. UV–vis spectra of the multilayer films. a: PEI-BW_{12}-(**1**/Ag NPs)$_n$; b: PEI-BW_{12}-(**2**/Ag NPs)$_n$. The solid lines represent the spectra after the addition of calix[4]arenes layers. The dotted lines represent the spectra after addition of Ag NPs layers. Inset: increase in the absorbance at 420 nm (a) and 440 nm (b) as a function of the number of layers of calix[4]arene/Ag NPs.