Fabrication of a Stable Polyelectrolyte/Au Nanoparticles Multilayer Film

Yu Fu,1 Hong Xu,1 Shilong Bai,1 Dengli Qiu,1 Junqi Sun,1 Zhiquang Wang,2 Xi Zhang*1

1 Key Lab for Supramolecular Structure and Materials, Department of Chemistry, Jilin University, Jiefang Road 119, Changchun, 130023, P. R. China
Fax: 0086-431-8923907 or -8980729; E-mail: xi@jlu.edu.cn
2 School of Material Science and Engineering, Beijing University of Chemical Engineering, Beijing, 100029, P. R. China

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Introduction
Organic/inorganic hybrid materials with fascinating properties stemming from their synergic activity have received increased attention.[1] Layer-by-layer self-assembly as a simple, fast and versatile technique has become an efficient strategy to fabricate multilayer hybrids with systematic control of both film thickness and structure.[2, 3] However, because the driving force for layer-by-layer self-assembly is generally electrostatic, the multilayer constructed by this technique is not stable enough when subjected to solvent etching, which limits its application range. Recently, Sun et al. have demonstrated a new method to fabricate a covalently attached film by the photolysis of a layer-by-layer self-assembled multilayer film containing diazoresin.[4] This method combines the advantages of the layer-by-layer assembly technique and the high stability of a covalently attached multilayer film, and provides an efficient way to fabricate stable multilayer assemblies. Au nanoparticles as attractive candidates of inorganic building blocks have been intensively investigated in recent years because of their wide applications in microelectronic devices, spectroscopy and sensor technology, etc.[5–7] Au nanoparticles were selected as a kind of model material and it was attempted to extend the above concept to fabricate a novel covalently attached organic/inorganic multilayer hybrid through UV irradiation of diazoresin (DAR)/Au nanoparticle self-assembled multilayers.

Experimental Part
DAR was kindly provided by Prof. Weixiao Cao (College of Chemistry and Molecular Engineering, Peking University,
Beijing), and its synthesis was reported previously.[8] The preparation of colloidal gold was similar to the procedure described by M. Giersig.[9] In brief, the Au nanoparticles synthesized using the citrate method were dialyzed to remove excess citrate. When the conductivity of the sol decreased to about 30 μS · cm⁻¹, 0.1 ml of an 0.01 M aqueous solution of 3-mercaptop-1-propanesulfonic acid sodium salt (Aldrich) was added to 10 ml of the stirred gold sol. After stirring for several hours, the Au nanoparticles were ready for use. Transmission electron microscopy (TEM) revealed a particle diameter of 26.5 ± 4.5 nm. A quartz wafer was immersed in fresh piranha solution (30% H₂O₂/98% H₂SO₄, 1:3 v/v) and heated until no more bubbles evolved. The substrate was then immersed in a 1 × 10⁻⁵ M solution of (3-mercaptopropyl)trimethoxysilane (MPTS) in benzene for 6 h to form self-assembled monolayers terminated with –SH functional groups at the exposed surface. After physically adsorbed MPTS was removed by sonication in chloroform, the terminal –SH functional groups were oxidized to sulfonic acid groups by immersing in a 30% H₂O₂/HOAc (1:5 v/v) mixture for 0.5 h. The mixture was heated in situ at 40–50°C.[10] The roughness (rms) of the resulting surface was about 0.6 nm, as determined by tapping mode Atomic force microscopy (AFM). The sulfonic-acid-covered quartz slide was then alternately immersed in aqueous solutions of DAR (1.5 mg/ml) and Au nanoparticles for 30 min each, with intermediate washing with water and drying under N₂. The above deposition steps were conducted in the dark to avoid decomposition of DAR. Exposing the as-prepared multilayer to UV irradiation for a given time is required to convert the ionic interactions between DAR and Au nanoparticles into covalent bonds. The thickness of the multilayer film was measured using an I-Elli2000 imaging ellipsometer (NanoFilm Technologie GmbH, Germany) at 532 nm laser at an incident angle of 50°. The film surface morphology was characterized by means of tapping mode AFM. Figure 4 shows the AFM images of an 11-layer DAR/Au nanoparticle multilayer film after 30 min of UV irradiation on a quartz slide. The rms calculated according to the AFM image of Figure 4A (4 μm × 4 μm) was about 9.2 nm, and the coverage of the Au nanoparticle was about 50%.

Results and Discussion

In order to choose an appropriate deposition time for Au nanoparticles, the deposition process was monitored by means of UV-vis spectroscopy. As shown in Figure 1, the absorption at 530 nm arising from the plasma resonance of the Au nanoparticles increased gradually with time for about 30 min. During this period, the peak value at 530 nm underwent no obvious shift, indicating that the intralayer aggregation of Au nanoparticles is very weak during the 30 min of deposition.[11] Alternating deposition was monitored by UV-vis spectroscopy and ellipsometry. Figure 2 shows the UV-vis spectra of 1, 2, 3, 4 and 5 layer pairs of DAR/Au nanoparticles assembled on a quartz slide. The absorption at 380 nm is attributed to the π-π* transition of the diazonium group.[12] The linear increase in absorbance at 380 nm with the number of layer pairs indicates a progressive deposition process of DAR/Au nanoparticles. The peak’s shift from 530 nm to 565 nm was assigned to a plasmon resonance caused by the aggregation between Au nanoparticles.[11] Figure 3 shows the ellipsometric thickness vs number of layers of the multilayer film after 30 min of UV irradiation on a quartz slide. Film thickness increased with each deposition cycle, which is in agreement with the UV-vis results. The film surface morphology was characterized by means of tapping mode AFM. Figure 4 shows the AFM images of an 11-layer DAR/Au nanoparticle multilayer film after 30 min of UV irradiation on a quartz slide. The rms calculated according to the AFM image of Figure 4A (4 μm × 4 μm) was about 9.2 nm, and the coverage of the Au nanoparticle was about 50%.
According to the section analysis of the AFM height image of the size 1 μm × 1 μm (Figure 4B), the average diameter of Au nanoparticles was calculated to be 30 ± 2 nm. The images reveal that Au nanoparticles in the multilayer film are partly aggregated, which is in accordance with UV-vis spectroscopy.

Owing to the well known photoreaction between diazonium and sulfonate groups, the above assembled multilayer containing 5 layer pairs of DAR/Au nanoparticle was irradiated with a 30 W medium power mercury lamp at a distance of 20 cm. Figure 5 shows the UV-vis spectra of the multilayer film after different irradiation times. The absorbance at 380 nm decreased dramatically due to the decomposition of the diazonium group. Meanwhile, the absorbance at 300 nm increased, and an isosbestic point at 344 nm could be observed.

The stability of the multilayers before and after UV irradiation was compared by sonicating the corresponding multilayers in a ternary mixture of H2O/N,N-dimethylformamide/ZnCl2 (3:5:2 w/w/w). This ternary system was chosen because of the high solubility of the DAR/Au nanoparticle complex in it. Film stability was estimated by the change in the fraction of the remaining film for different sonication time. The residual fraction was calculated from the absorbance at 380 nm and 300 nm, separately for multilayer films before and after irradiation. As shown in Figure 6, the residual fraction of the multilayer film before irradiation decreased continuously with time. For the multilayer after irradiation, the residual fraction only dropped rapidly during the initial 5 min, then remained constant. After about 90 min of sonicating the films in the ternary mixture, for the multilayer without irradiation, most of the film was scaled off; however, for the irradiated multilayer about 80% was remaining. The stability of the irradiated multilayer film thus was substantially improved as compared with that without UV irradiation.
Due to the changes of the UV-vis spectra of the multilayer films with different UV irradiation times and the enhanced stability of the UV-irradiated multilayer film, it is proposed that a photoreaction takes place between the diazonium groups of DAR and the sulfonate groups on the Au nanoparticles. According to the general reaction mechanism, the diazonium group of DAR is first converted into its phenyl cationic form after releasing N\(_2\) upon UV irradiation. An \(S_2\)\(1\) type of nucleophilic reaction by the sulfonate groups then occurs as shown in Scheme 1. The fact that the photoreaction not only changes the interactions between the neighboring layers, but also between the first layer of DAR and the modified substrate from ionic to covalent should be responsible for the improvement of the stability of the irradiated multilayer. However, still about 17% of the irradiated multilayer was dissolved. We speculate that not all the nanoparticles could react to form stable covalent bonds. Please keep in mind that the ternary mixture used for testing is a very strong solvent. In usual organic solvents or water, the stability of the resulting covalently attached DAR/Au nanoparticles should be satisfactory.

In conclusion, a new method to fabricate a stable polyelectrolyte/Au nanoparticles multilayer film has been developed exploiting the layer-by-layer self-assembly technique and a post-photoreaction that changes the ionic interaction between the layers into covalent linkages. Considering the large solubility difference in a selected solvent, multilayers without UV irradiation can be etched out while the irradiated part remains. A patterned multilayer surface consisting of organic/inorganic hybrid could thus be achieved. It is anticipated that this concept could be used to fabricate nanocomposites of differently modified nanoparticles and polymers, leading to advanced interfacial nanocomposite and nanopatterning materials.

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