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Particle lithography-based patterning of polyelectrolyte template films and their application in fabrication of gold/silver nanoparticle assembly

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ABSTRACT

The site-specific deposition of polyelectrolytes (PEs) or PE/noble metallic nanoparticle (NP) composites at nanoscale is highly desirable owing to their diverse applications in nanodevices. Herein, we demonstrated a simple yet effective method to fabricate different types of surface micropatterns with PE/noble metallic NP composites via particle lithography. The positively charged PE of poly(diallyldimethylammonium chloride) and negatively charged NPs of gold/silver (Au/Ag) were used as a model system. The layer-by-layer self-assembly technique was employed as the fabricating strategy. The final nanostructures, consisting of Au NP films with inlaid circular vacant island microarrays or Au NP films with inlaid circular Ag NP island microarrays, were fabricated, respectively. Scanning electron microscopy and atomic force microscopy were used to investigate the structural morphology, microstructure, and the NP growth. Furthermore, the surface-enhanced Raman scattering performance has been obtained based on the as-prepared Au/Ag nanopatterns. Our method displayed an excellent opportunity for the simple and effective production of nanopatterns on the surfaces demonstrating significant advantages in designing novel nanodevices.

1. Introduction

The polyelectrolyte (PE) is a kind of polymer molecules whose main chain is composed by repeating units of the electrolyte. Because these molecules have some degree of charging, they have many applications in sol–gel chemistry, special in use to impart surface charges and thereafter assembly of nanoparticles (NPs) [1–4]. Modification of surfaces using PEs and NPs leads to numerous nanostructures displaying applications in the fields of materials [5], microelectromechanical systems [6], tissue engineering [7], solar cells [8], biosensors [9], surface plasmon resonance [10], and surface-enhanced Raman scattering (SERS) [11].

In general, the patterning technique is employed for the preparation of the desired surface nanostructures along with the deposition of PEs and the NP assembly processes [12]. For example, the patterned polymer brushes were synthesized for the selective adsorption of functionalized NPs and their bio-applications were anticipated [13–15]. Mohammed and McShane illustrated a micromachining method of photolithography to fabricate surface micropatterns, enabling high-resolution control over the composition and topography of surfaces [16]. Park et al. presented the multicomponent patterning of functional thin films, composed of PEs and NPs, with controlled alignment using the soft-lithography [17]; thus, demonstrating its application in practical device fabrication. Moreover, techniques such as microcontact printing [18] and lift-off methods [19] were also explored to exhibit the effective microfabrication on electronic components, optical devices, and bionanotechnology chips. Therefore, the fabrication strategy has attracted significant attention and its novel applications are still anticipated.

The particle lithography (or nanosphere lithography) is a simple, robust, cost effective, and powerful technique to fabricate precisely controlled periodic arrays of nanodots on the surfaces [20]. In a typical process, the self-assembled monolayers of polystyrene (PS) microspheres were used as evaporation masks and metallic vapors were deposited on the surfaces of the substrates through the microsphere masks [21]. Well-ordered two dimensional NP arrays with tunable sizes were produced by inexpensive high throughput synthesis that could rapidly help to achieve a high level of diversity in nanostructures. Recently, the capabilities of particle lithography has been extended toward construction of

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nanostructures by assembling PEs and NPs. Han et al. reported the assembling of PE multilayer-coated PS microsphere arrays and the performing reactions were restricted to the PE multilayers [22]. They suggested the innovative idea that the PE modified colloidal particles acted as excellent building blocks for the fabrication of microarray, instead of uncoated colloidal particles, leading to the formation of the patterns of interconnected well-ordered metal arrays. Inspired by Han's work, in this study, a different nanofabrication method was developed by directly depositing PE monolayers and NPs on the monolayers of PS microsphere arrays [11,23], that led to the formation of a novel patterned periodic microarray surfaces composed of continuous NP films. The difference of our method from the other particle lithography strategy is mainly in regard to the use of the monolayered PE film, which almost has no restriction when deposited on the extremely tiny space surfaces, and are very handy for the subsequently adsorption of NPs.

In this study, the possibility of constructing patterned surfaces by combination of particle lithography and PE/NP depositions was further explored. The basic strategy was to create patterned PE templates (PPTs) by particle lithography followed by the site-specific deposition of the NPs on the PPT films in a spontaneous process. Therefore, the obtained nanostructures replicated the precursor patterns of the PPT films. In this study, two synthesis routes were designed to achieve the desired synthetic transformation. First, very thin (one layer) PPT films were fabricated on the surfaces by particle lithography and were subsequently used to guide the deposition of Au NPs. Second, a more complicated pattern of Au NP films with inlaid circular PE dot microarrays was fabricated followed by the deposition of the Ag NPs on the PE dot microarrays via site-specific adsorption leading to the formation of the compound surface micropatterns with dual NPs. Thus, the above mentioned novel strategy created a platform for the fabrication of delicate nanostructures exhibiting significant potentials in nano-optoelectronics and nanomechanics. In the present work, the SERS property of the obtained nanostructures was investigated and good enhancement and excellent spectral homogeneity were achieved.

2. Materials and methods

Detailed information about the chemicals, pretreatment of the glass slides, synthesis of Au/Ag colloids and characterization of the samples is given in the Supplementary material. Herein, the methods of synthesis are summarized.

2.1. Preparation of PPT films by particle lithography

Two types of PPT films were fabricated through two synthetic routes, respectively, which are described as follows.

2.1.1. Route 1

An ordered monolayer of PS microspheres (650 ± 25 nm in diameter) was deposited on the pretreated glass slides by using the Langmuir–Blodgett (LB) self-assembly technique reported in our previous study [24]. These PS monolayer coated slides were immersed into a poly(diallyldimethylammonium chloride) (PDDA) solution (0.5 wt%) for 20 min to adsorb a layer of PE. The PS masks were removed by sonicating the entire sample in acetone for 2 min leading to the formation of patterned PE films.

2.1.2. Route 2

The materials used in route 2 and the experimental details were identical to that of route 1; however, the order of fabrication was different. First, the glass slides were immersed in the PDDA solution. Second, the PDDA modified slides were covered with a monolayer of PS microsphere arrays leading to the formation of a different type of patterned PE films covered with PS particles.

2.2. Assembly of Au/Ag NPs on PPT films

The Au/Ag colloids were synthesized according to the literature method [11,23]. The average diameters of Au NPs and Ag NPs were 17 and 45 nm, respectively. The NPs were assembled on the PPT films fabricated by routes 1 and 2, respectively. The description is as follows.

2.2.1. Route 1

The obtained PPT films were immersed in the as-synthesized Au colloid for 6 h. Subsequently, the samples were taken out, washed by water thoroughly, and dried.

2.2.2. Route 2

The obtained PPT films covered with PS microsphere arrays were first immersed in the Au colloid for 6 h. Second, the arrays of PS were removed by sonicating the samples in acetone. Third, the samples were immersed in the Ag colloid for 2 h. Thus, the patterned compound films of Au/Ag NP assembly were obtained after thorough washing and drying.

3. Results and discussion

Fig. 1 illustrates the fabrication procedure for the PPT films and the corresponding Au/Ag NP assemblies. Fig. 1a shows the schematic representation of route 1 involving a four-step synthesis process, in which a glass slide covered with an ordered monolayer of PS microspheres (650 nm) is used as a substrate for the deposition of a layer of PE (PDDA). The third step exhibits the formation of a PPT film after the elimination of the PS microspheres. Finally, the as-prepared PPT films are used for the deposition of Au NPs

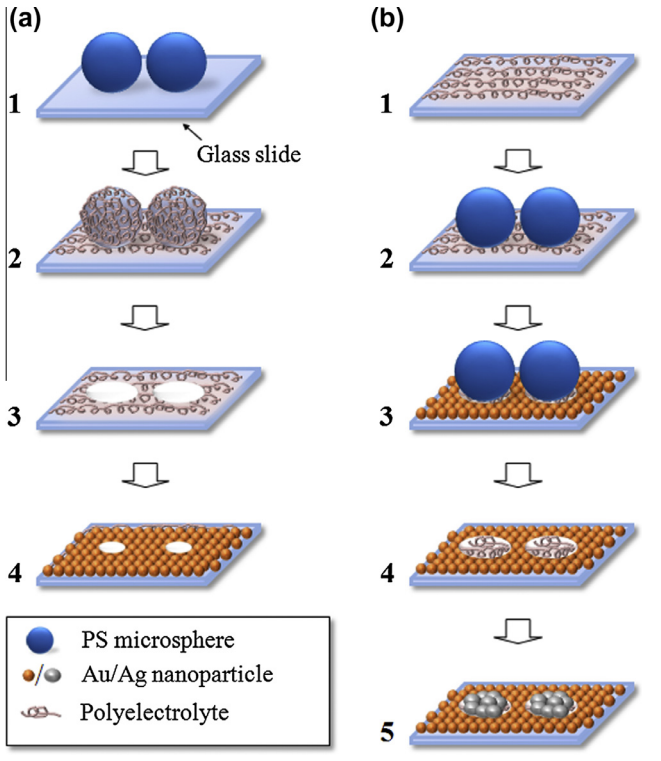

Fig. 1. Schematic illustration of the fabrication procedure for the PPT films and the corresponding Au/Ag NP assemblies.