



Selective assembly of silver nanoparticles on honeycomb films and their surface-enhanced Raman scattering



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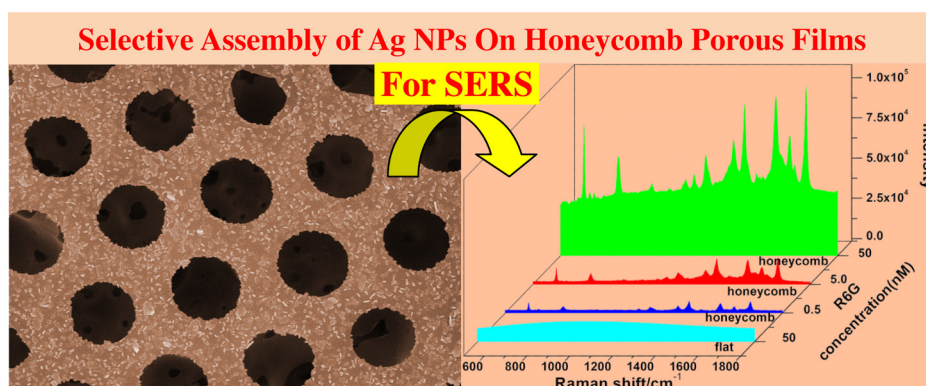
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HIGHLIGHTS

- Honeycomb films of PS-*b*-PAA were fabricated by breath figure method.
- Ag NPs were selectively assembled on the surface of honeycomb films rather than in the pores.
- The concentrations of precursors were important to the amount and uniformity of Ag NPs.
- The hybrid film decorated with Ag NPs exhibited strong SERS of R6G molecules.

GRAPHICAL ABSTRACT



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ABSTRACT

A facile approach to selective assembly of Ag nanoparticles on honeycomb film and their highly sensitive surface-enhanced Raman scattering of rhodamine 6G molecules were described. Honeycomb films were prepared based on amphiphilic block polymer (polystyrene-block-polyacrylic acid), by breath figure method. Key influencing factors to control micropore size and tune film surface properties, such as polymer concentration, solvent, relative humidity and substrate, were investigated. Ag nanoparticles were selectively assembled on the surface of honeycomb films rather than in the pores. The Ag nanoparticles on the hybrid films were applied in surface-enhanced Raman scattering of rhodamine 6G molecules to dramatically enhance signals. This proposed approach opens a new route for selective modification of honeycomb films and provides a facile and effective method for preparing surface-enhanced Raman scattering substrates.

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1. Introduction

As an important technology in modern testing field, surface enhanced Raman scattering (SERS) technique is widely applied in chemical industrial analysis, biological analysis, medical detection and many other areas due to its high sensitivity, good selectiv-

ity and nondestructive testing of samples [1–9]. Constructing SERS substrates with high activity is one of important subjects in SERS studies. It is believed that substrates with ordered structures are superior to disordered nanostructures [6,7,10–12]. Most of these attractive advantages are based on the periodic arrays of nanoparticles (NPs), which possess maximized specific surface density of hot spots and higher surface enhancement factors. Several methods have been applied to fabricate ordered SERS substrates including laser micro-nano processing, templating techniques, lithography and so on [6,12–15]. However, these commonly used SERS substrate preparation methods are time-consuming and high equipment costs. Therefore, the patterning technique known as “breath figure” method was also introduced due to its simple, inexpensive, and robust mechanism of pattern formation [16–19]. This method was first reported by Françoise et al. in 1994 [20]. By casting polymer solutions under humid conditions, the breath figure method makes use of the condensed water droplets as dynamic templates to produce ordered pores within a size range of 300 nm to 20 μm [21–23]. The versatility of this technique has also been demonstrated by the preparation of hybrid organic/inorganic structures [24–26]. For example, ordered honeycomb films containing Au NPs were prepared and presented a strong SERS of rhodamine 6G (R6G) [27]. Hirai et al. described a simple preparation method for silver pincushion films involving the breath figure method and vapor deposition processes and measurements of SERS on the silver pincushion films [15]. Raman spectra demonstrated that the obtained SERS substrate could detect R6G at concentrations as low as 0.5 nM. It was found that more ordered honeycomb films resulted in stronger SERS. Wan and co-workers also developed an approach to prepare highly sensitive SERS substrates with honeycomb films decorated by Ag NPs [28]. But Ag NPs in this method could be found both on the external surface and in the pores of honeycomb films, which meant selective assembly of NPs on patterned porous surface was not achieved.

As a versatile and efficient method of fabricating highly ordered pore arrays, the breath figure method has raised continuing concern in optical and optoelectronic devices, electrode materials, separation and biology over recent decades [29–36]. Amphiphilic block copolymers, which have a high segment density in some selective solvent, can be gathered in the interface layer of organic solvent and water so as to effectively stabilize the water droplets and prevent the mutual cohesion between the water droplets. Amphiphilic block copolymers as excellent candidates and functional materials are considered to be a kind of ideal materials for preparing ordered porous films. Honeycomb porous films have been employed as templates not only to fabricate patterned architectures but also for the assembly of nanoparticles. Sun et al. presented an elegant way to tune the localization of SiO_2 NPs inside a highly structured honeycomb film depending on the NPs surface functionalization [37]; A one-step procedure was also demonstrated for the preparation of nanoparticles-decorated films by casting a mixed solution of polystyrene and CdSe nanoparticles [38]. CdSe nanoparticles can self-assemble and segregate at the polymer solution–water droplet interface; Wu and co-workers described a facile approach for honeycomb structures of Mn-12 single-molecule magnets [39] and surfactant-encapsulated polyoxometalate complexes [40]. As for above mentioned strategies, NPs were successfully decorated in the pores of honeycomb films. As far as SERS substrates are concerned, only the NPs assembled on the surface can lead to the best effect. However, researches on selective assembly of NPs on the honeycomb patterned porous surface and their applications in SERS have not been reported.

In this paper, a typical amphiphilic block polymer, polystyrene-block-polyacrylic acid (PS-*b*-PAA), was selected to fabricate honeycomb patterned porous films by breath figure method. Several key influencing factors, such as the concentration of polymer,

the relative humidity of the atmosphere, the properties of solvent, the spreading volume and the substrates, were investigated for controlling micropore size and tuning film surface properties. Ag NPs with 20–100 nm were successfully assembled on the external surface of the porous films based on chemical deposition method. The hybrid films decorated with Ag NPs exhibited strong SERS effect of R6G molecules. To the best of our knowledge, it is the first report on the selective assembly of Ag NPs on the external surface of the honeycomb patterned porous film. This proposed approach opens a new route for selective modification of patterned porous films and provides a facile and effective method for preparing SERS substrates.

2. Experimental section

2.1. Materials

The synthesis of PS-*b*-PAA by atom transfer radical polymerization (ATRP) was described as reported [41]. The relative molecular weights of PS and PAA blocks were 12500 and 1000 $\text{g}\cdot\text{mol}^{-1}$, respectively. The PDI of such diblock copolymer was 1.09. Hydrogen peroxide (H_2O_2 , 30 wt%), sulfuric acid (H_2SO_4 , 98 wt%), formaldehyde (HCHO, 36 wt%), ammonia (17 wt%), silver nitrate (AgNO_3), and rhodamine 6G (R6G) and chloroform (CHCl_3) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). They were used as received without further purification. All the other reagents used were analytical grade. Deionized water was obtained by purification through a Millipore water system and was used throughout. All the experiments were conducted at room temperature.

2.2. Preparation of the honeycomb-patterned polymer films

The honeycomb-patterned films were prepared by the breath figure method and the schematic illustration including the set-ups for fabricating the porous polymer films was shown as Fig. 1. The glass substrate was immersed in a piranha solution (98% H_2SO_4 /30% H_2O_2 , volume ratio, 3:1) for 30 min, and then rinsed with deionized water and ethanol before film fabrication, respectively. PS-*b*-PAA was dissolved in CHCl_3 with a concentration ranging from 2 to 50 mg/mL. Then, 10 μL PS-*b*-PAA solution was dropped onto a clean glass substrate at room temperature in a chamber in which the relative humidity could be controlled by bubbling through distilled water and measured by a Humidity & Temperature Meter (AR-847, Smart Sensor). After the solvent evaporated completely, honeycomb films were obtained. For comparison, the flat films without pores were obtained using the same procedure under ambient condition.

2.3. Selective assembly of Ag NP on honeycomb-patterned films

The assembly of Ag NPs on the external surface of the honeycomb-patterned porous films was accomplished by chemical deposition onto the films. A piece of as-prepared film was first immersed into AgNO_3 aqueous solution with different concentra-

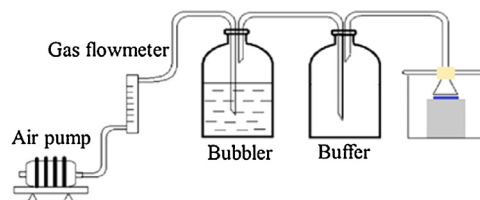


Fig. 1. Schematic illustration including the set-ups for fabricating the porous polymer films.

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