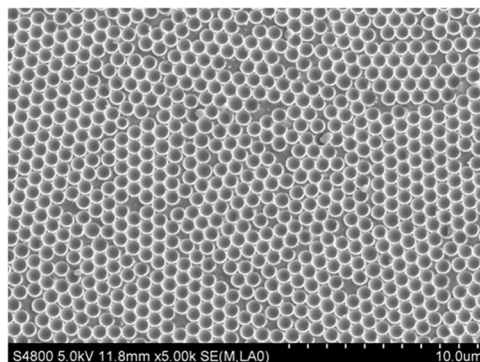


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Nanobowl Array Fabrication via Conglutination Process Based on Thiol–Ene Polymer

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Abstract: The technique to fabricate nanostructures with high resolution is of crucial importance to nanosciences and nanotechnology. This paper presented a nonconventional method to fabricate metallic nanobowl arrays via the conglutination process, which relied on the high adhesive material to “stick” nanostructures. The ultraviolet (UV)-curable thiol–ene had low viscosity and was cured under UV light to form a cross-linked polymer with high Young's modulus and high surface energy via “click chemistry,” which was used as the adhesive material to firmly stick nanostructures from the mold. By using the method, a self-assembly polystyrene (PS) sphere template with a metallic layer was stuck by the cross-linked thiol–ene polymer from the substrate. After removing the PS spheres, the metallic nanobowl structure with the thiol–ene substrate was achieved. In this paper, we fabricated gold nanobowl arrays composed of nanoholes with the average diameter of ca. 60 nm between nanobowls, which verified the feasibility of the fabrication method.

Index Terms: Metallic nanobowl array, conglutination process, cross-linked polymer, thiol–ene, self-assembly.

1. Introduction

Nanostructures have been paid increasingly more attention due to exhibiting great potential applications in the areas of photo-catalysis [1], biosensors [2], magnetic [3]–[8], and super-hydrophobic materials [9]. Advanced lithographic techniques currently being used to fabricate nanostructures include photolithography, electron beam direct writing, focused ion beam technology, and proximal-probe lithography [10]–[15]. These techniques are capable of fabricating high-resolution features, but low cost and high volume for practical commerce still leads to great challenges.

The conglutination process is used widely in mechanical conglutination to stick one element to another element using adhesive material in industry [16]. Hence, adhesive material is the crucial component for conglutination process. Some research groups reported nanostructures could be fabricated via conglutination process based on different adhesive material. Truong *et al.* [17] described composite patterning elements that use a-PFPE as the features layer

on the poly(dimethylsiloxane) (PDMS) or polyethylene terephthalate (PET) support. The PDMS or PET film was used as the adhesion material to stick the a-PEPF nanostructures peeling off from the substrate. Chen *et al.* [18] reported a 2-D metallic nanobowl array on a thermoplastic substrate was fabricated using a piece of thermoplastic polycarbonate (PC) as adhesive material to be welded to the CNT film with metallic nanobowl array by microwave heating. Xu *et al.* [19] demonstrated the fabrication of nanobowl arrays composed of silver nanoparticle with an average diameter of ca. 10 nm via sphere lithography. As the adhesive material, a tape was stuck on the top of polystyrene (PS) spheres coated with silver film and then peeled off from the substrate. Therefore, the conglutination fabrication method was very simple, large-area, and low-cost, which provided a good idea for fabricating nanostructures in an economic and high-fidelity fashion. However, the common adhesive materials suffered some disadvantages, such as low adhesion, soft, and non-high-temperature resistance, to lead to the deformation or even damage of nanostructures and its distributions, which included glue, tape, and thermosetting materials such as PDMS, PET, and PC.

In 2001, Sharpless *et al.* [20] described a new concept for conducting organic reactions called “click reactions” to highly selectively form carbon heteroatom-linked molecular systems (C-X-C) with high efficiency under a variety of undemanding conditions. Hoyle and Bowman [21] reviewed the radical-mediated thiol–ene reaction as one click reaction. Because of the excellent mechanical and physical properties, thiol–ene polymer has been used widely as the nanoimprint resist in nanoimprint lithography (NIL) to fabricate high resolution nanostructures [22]–[24].

Herein, we proposed a simple and low-cost method to fabricate metallic nanobowl array via conglutination process based on the UV-curable thiol–ene. The low viscous thiol–ene prepolymer was firstly coated on the self-assembly PS spheres template with metallic layer by confecting the thiol–ene monomers. When exposed under UV light, the prepolymer formed a cross-linked polymer network with high Young's modulus and surface energy to stick firmly to the metallic layer and peel off the PS sphere template from the substrate. The metallic nanobowl structure was obtained after dissolving the PS spheres into corrosive solution. Based on the new method, a gold nanobowl array with nanoheaves with the average width of ca. 60 nm between nanobowls was fabricated. The experimental results demonstrated that the fabrication method was feasible.

2. Experimental Details

The experimental approach is schematically presented in Fig. 1. A monolayer of nanospheres was firstly self-assembled on a glass substrate in Fig. 1(a). A metallic layer was then deposited on the nanospheres template in Fig. 1(b). A UV-curing prepolymer with high adhesion and Young's modulus was spin-coating onto the metallic layer to form a thick film in Fig. 1(c). When exposed under UV radiation in benign ambient, the prepolymer formed a cross-linked polymer network and stuck firmly to the metallic layer because of the high adhesion in Fig. 1(d). The cross-linked polymer was then peeling off from the glass substrate with the metallic layer and PS spheres template in Fig. 1(e). The PS spheres could be removed in the corrosion resolution and the metallic nanobowl structures on the polymer substrate were achieved in Fig. 1(f). Because the cross-linked polymer was very rigid, the nanobowl structure was keeping the original arrangement of PS spheres.

2.1. Materials and Instruments

Monodispersed 10 wt% polystyrene (PS) spheres with a diameter of 520 nm and 1-dodecanethiol were obtained from Duke. Tetrahydrofuran (THF) solution was purchased from commercial sources. Deionized water ($18.25 \text{ M}\Omega \cdot \text{cm}$) was used directly from Aquapro Company. Thiol–ene monomer materials such as poly(mercaptopropyl)methyl siloxane (PMMS), 2,2-Dimethoxy-2-phenylacetophenone (DMPA), and ethylene glycol dimethacrylate (EGDMA) were purchased from MERYER. The chemical structures of the thiol–ene monomers are shown in Fig. 2. The

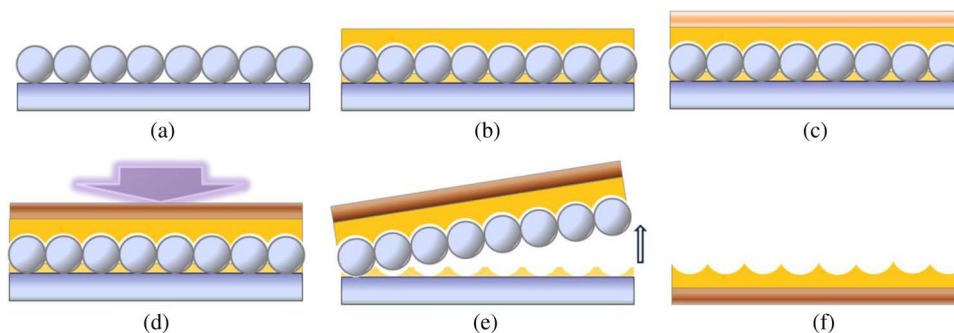


Fig. 1. Fabrication process of the metallic nanobowl array. (a) Self-assembly layer of nanospheres on glass wafer. (b) Depositing a metallic layer onto the nanospheres template. (c) Spin-coating UV-curing prepolymer film onto the metallic layer. (d) Curing by exposing under UV irradiation and form the cross-linked polymer network. (e) Peeling off the nanospheres template adhering to the metallic layer and polymer film. (f) Removing the nanospheres and achieve the metallic nanobowl array on the polymer substrate.

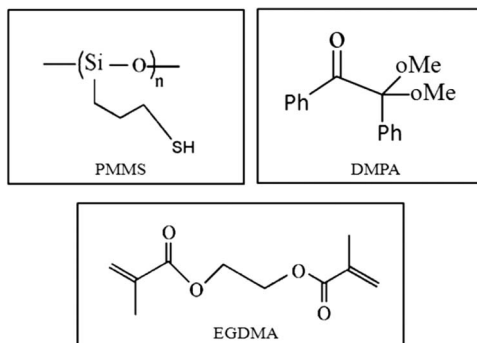


Fig. 2. Chemical structures of PMMS, DMPA, and EGDMA.

thiol-ene polymer was curing under UV irradiation and used to be adhesive material because of modulated physical and mechanical properties.

The glass wafers of $\Phi 30$ mm were firstly hydrophilic-treated in H_2SO_4 (98%) : H_2O_2 (85%) = 3 : 1 mixture solution at 80 °C in a water bath for about one hour and cleaned by the deionized water. The glass wafers was then rinsed in HNO_3 (95%) : H_2O_2 (85%) : H_2O = 1 : 1 : 5 solution for about one hour. Finally, they were cleaned with deionized water and dried with nitrogen. The cupping machine and dynamic contact angle instrument were used to measure the Young's modulus and surface energy, respectively.

2.2. Self-Assembly of PS Spheres

The PS spheres monolayer was prepared on the cleaned glass substrate via a self-assembling process [25]. The 10 wt% PS spheres solution was first diluted with an equal volume of deionized water and ultrasonicated for 10 s to improve the mixing. A 10- μL PS spheres mixed suspension was then assembled on the glass substrate by spin-coating at 2000 rpm for 25 s. The highly ordered template of the PS spheres was fabricated with the glass substrate after being dried at room temperature.

2.3. Deposition of Gold Film

A 100 nm thick gold film was deposited on the PS spheres template using a thermal evaporation system at a pressure of 5×10^{-4} Pa. The spheres were embedded firmly into the gold film.

2.4. Fabrication of UV-Curing Polymer Substrate

The UV-curing thiol-ene prepolymer was coated onto the self-assembled nanospheres template, which was the compositions of PMMS (41.5 wt%), EGDMA (58.1 wt%), and DMPA (0.4 wt%) as the photoinitiator. Because of the low viscosity, the thiol-ene was dripped onto the nanospheres template to form a uniform film with thickness of 1 nm. Upon curing completely under a UV-LED lamp with the wavelength of 365 nm at 40 mW/cm² for 1 min, the thiol-ene prepolymer formed a cross-linked polymer network with the properties of high Young's modulus and high adhesion to the metal film [26], [27]. The Young's modulus of the cross-linked polymer was 5.5 GPa through measured by the cupping machine. The measured water contact angle of the cross-linked thiol-ene was 40° using dynamic contact angle instrument, showing that the surface energy was high to adhere firmly to the gold layer. The cross-linked thiol-ene polymer filled into the spaces among nanospheres and stuck firmly to the gold film. Because the adhesion between cross-linked polymer film and gold film was stronger than that between nanospheres template and glass substrate, the PS nanospheres template was better peeling off from the glass substrate with gold film and polymer substrate.

2.5. Removing of PS Spheres

To achieve the metal nanobowl structure, the PS spheres were removed with THF resolution. The PS spheres embedded into the gold film with polymer substrate was firstly immersed in a 5 mL THF solution for 2 min and then thoroughly rinsed into the ultrapure water. The PS spheres were dissolved in the THF solution and the gold nanobowl array with polymer substrate was obtained.

2.6. Characterization

Scanning electron microscopy (SEM) images were measured using a Hitachi S-4800 field-emission SEM at the primary electron energy of 3 kV. In order to observation to improve conductivity, the samples were sputtered with a thin gold layer (ca. 10 nm).

3. Results and Discussions

The SEM images show the experimental results of each step described above in Fig. 3. As shown in Fig. 3(a), the monolayer of self-assembled PS spheres was coated with the gold film in a hexagonal close-packing structure, which was compact and uniform. The space between the spheres was partially filled as a result of the gold evaporation. Subsequently, the PS spheres coated with gold were peeled off from the glass substrate by applying a cross-linked thiol-ene polymer onto the top of the gold film. A top view of the transferred 520 nm diameter PS spheres with gold film and polymer substrate is shown in Fig. 3(b). A large-area gold nanobowl array was created after removing the PS spheres in Fig. 3(c). The nanoscale gaps among the nanospheres were filled with the gold to become the nanoheaves among the nanobowls. Thus, the nanobowl array was composed of gold nanoheaves with an average size of ca. 60 nm, as depicted in Fig. 3(d). Due to the high rigid cross-linked polymer network, the nanobowl positions were unchanged and the coupling nanoheaves were uniformly distributed. The fabrication results indicated that the nanobowl array was high-precision and high-resolution, which demonstrated the feasibility of the novel fabrication method.

Some triangle spaces between the neighboring three nanobowls were not filled with metal to lead to some nanobowls distributed separately, because the PS nanospheres were not completely distributed compactly during the self-assembly process. Due to the thin metal film, some large gaps weren't filled with metal to lead to the separate nanobowls, which could be improved through optimizing the PS spheres self-assembly process.

The sizes of the nanobowl and nanoheaves between nanobowls can be modulated independently by selecting PS sphere with different diameters or by decreasing the PS sphere size with oxygen plasma etching after the self-assembly process. Therefore, the procedure of nanobowl

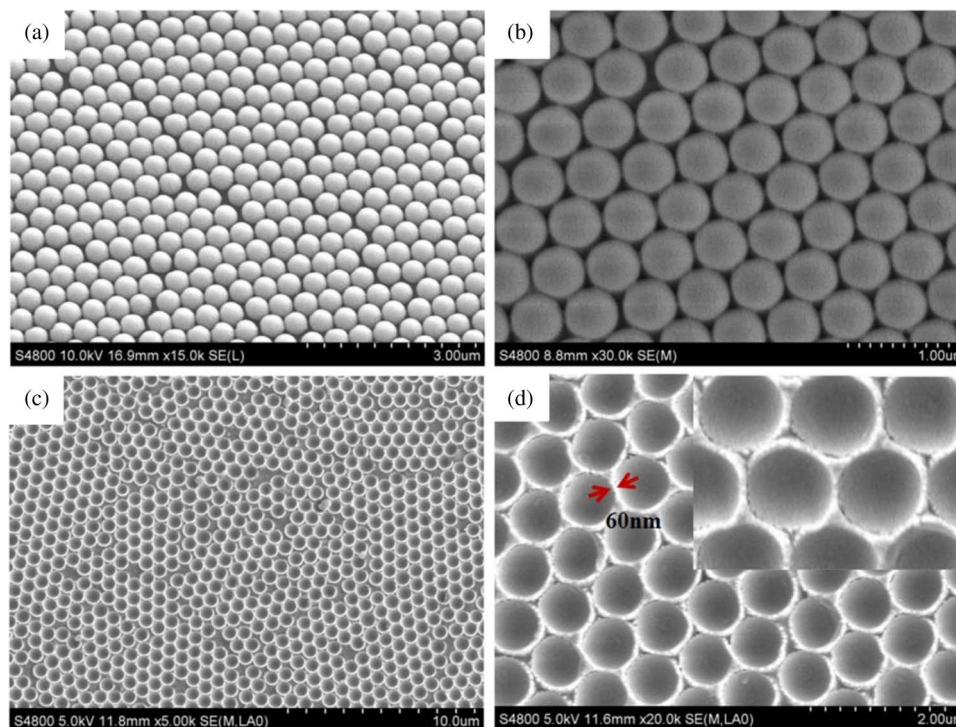


Fig. 3. SEM images of experimental results. (a) The monolayer of PS spheres coated with a gold film, (b) the transferred PS spheres with gold film and polymer substrate, (c) the generated gold nanobowl array on the cross-linked polymer substrate, and (d) an enlarged SEM image of the gold nanobowl array.

fabrication could be extended to a wide range of applications with different self-assembled structures, sizes, and coating materials.

4. Conclusion

In summary, we developed a nonconventional method to fabricate metallic nanobowl array based on thiol-ene polymer via conglutination process, which relied on the high adhesive material to “stick” nanostructures. The low viscous thiol-ene prepolymer was coated on the self-assembly PS spheres template with metallic film. When exposed under UV light, the prepolymer formed a cross-linked polymer network with high Young's modulus and surface energy to stick highly to the metallic film. After peeling off from the glass substrate and dissolving the PS spheres in the corrosive solution, the metallic nanobowl array was fabricated. Using the novel method, a gold nanobowl array with ca. 60 nm nanoheaves was fabricated, which has great potential in applications of photonics, photo-catalysis, and magnetics.

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