Large area assembly of patterned nanoparticles by a polydimethylsiloxane template

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A technique in which a polydimethylsiloxane (PDMS) template is used to assemble silicon oxide nanoparticles is proposed herein. The PDMS substrate was first constructed in a series of casting steps and a copper mask was then made with a laser marking system. Silicon oxide nanoparticles were generated by a modified Stober method. A PDMS substrate covered by the copper mask was then coated with a metal Au layer via sputtering to form the PDMS template. Finally, the silicon oxide nanoparticles were spin-coated on the PDMS template. Because the PDMS template consists of highly hydrophobic PDMS and less hydrophilic Au patterns, the nanoparticles undergo a dual dewetting process on the PDMS template to form an annular distribution around the borders of the Au patterns.

INTRODUCTION

The assembly of ordered patterns of nanoparticles on solid substrates has attracted much attention due to the possible applications of such assemblies in various areas, such as flexible electronics [1,2], biological sensors [3], photonic crystals [4], photoelectrical devices, and data storage [5,6], etc.

Compared with rigid substrates that can utilize traditional techniques, the assembly of nanoparticles on flexible substrates is unusual. Many techniques have been developed for patterning nanoparticles on flexible substrates. Seung *et al.* [7] combined inkjet printing and selective laser sintering to assemble metal nanoparticles on a polymer substrate. Inkyu *et al.* [8] adopted nano-imprinting to directly pattern a metallic nanoparticle solution on a flexible substrate. He *et al.* [9] proposed a simple but rapid approach for synthesis of single-crystalline Co₃O₄ nanorods on silicon substrates, which is compatible with microtechnology and can be used to fabricate metal oxide nanorods at low substrate temperatures with large-scale applicability. Lee *et al.* [10] obtained a smooth SiO_x thin film by atmospheric pressure plasma-enhanced chemical vapor deposition based on the controlled formation of nanopar-

ticles to decrease the surface roughness of the film by optimizing the flow rate of PDMS, oxygen, and helium. Sun *et al.* [11] developed a novel patterning technique to create three-dimensional (3D) patterns of micro- and nanoparticle assemblies by utilizing evaporative self-assembly based on the coffee-ring effect of an evaporating suspension. Researchers in Israel [12] reported a simple method for patterning nanoparticles by combining self-assembly with sintering of silver nanoparticles at room temperature. Yeo *et al.* [13] indicated that direct metal patterning based on laser-induced local melting of metal nanoparticle ink is a promising low-temperature alternative to conventional metal patterning processes. Metal nanoparticles can also be produced by the electrodeposition process. For example, Liu *et al.* [14] prepared platinum (Pt) particles on an indium tin oxide (ITO) substrate by pulsed electrodeposition and investigated the electrocatalytic properties of these species in methanol oxidation. Moreover, hierarchical platinum particles can be synthesized by the electro-deposition technique. Zhong and coworkers [15] prepared hierarchical Pt nanoparticles with various morphologies, including sheet-, flower-, prickly sphere-, and cauliflower-like shapes by controlling the electrodeposition parameters. Du *et al.* [16] proposed a surfactant-free and template-free electrochemical approach for generating well-dispersed Pt nanosheets. By simply changing the anions from SO₄²⁻ to Cl⁻ in the electrodeposition solution, the generated Pt deposits changed from flower-like Pt particles consisting of aggregated Pt nanosheets to well-dispersed Pt nanosheets.

Lee *et al.* [17] assembled Ag nanoparticles into well-ordered line arrays via anisotropic buckling templates with a subsequent transfer process, where a small amount of water rather than glue materials was employed. Chang *et al.* [18] proposed a novel technique for fabricating copper patterns by a patterning-adsorption-plating process, in which ion-adsorption nanoparticles were inkjet printed

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on a polyethylene terephthalate (PET) substrate and the metal patterns were subsequently produced by electroless plating. Cyrille *et al.* [19] devised a reliable technique to obtain nanoparticle supercrystal arrays by confining a gold nanoparticle colloid between a patterned PDMS mold and a flat substrate. Roller *et al.* [20] presented the fabrication of self-assembled ring-shaped plasmonic metamolecules by utilizing DNA origami structures as templates for the synthesis of a wide variety of ring geometries containing nanoparticles.

In this paper, we propose a simple technique for fabricating micro-patterns of silicon oxide (SiO_2) nanoparticles on a flexible substrate. The detailed process includes the fabrication of a PDMS template and a spin-coating step. Firstly, a copper film is patterned by a laser marking system to obtain a copper mask with round hole and square hole arrays. Subsequently, the copper mask is placed on the surface of the PDMS substrate, and the assembly is placed into a sputter to obtain the metal coating. Under the mask of the patterned copper film, the metal patterns (such as the round patterns and the square patterns) emerge on the PDMS substrate. The PDMS template is thus generated for assembly of the SiO_2 nanoparticles. Silicon oxide nanoparticles are generated by the modified Stober Method [21]. Finally, the obtained solution with the SiO_2 nanoparticles is spin-coated on the PDMS template. The SiO_2 nanoparticles wet the metal Au areas and dewet the PDMS areas, leading to their assembly on the PDMS template. The advantages of using the PDMS template to assemble the silicon oxide nanoparticles include the simplicity and low cost of the process and its convenience for large area assembly.

EXPERIMENTAL SECTION

Fabrication of the PDMS template with the patterned Au

After thoroughly mixing PDMS and the curing agent (ES-SIL 291 and ESSIL 293, Axson Corp.) in a ratio of 10:1 by weight, the mixture was degassed and cast on the polished surface of a silicon wafer. The assembly was then cured in an oven at 80°C for 3 h. The PDMS substrate was obtained by peeling the PDMS from the silicon wafer.

A copper film, used as the mask material, was patterned by a laser marking system (Han's Laser Technology Co., Ltd.), where the obtained copper mask contained the round hole and square hole arrays.

The obtained copper mask was placed on the surface of the PDMS substrate and the assembly was placed into an ion sputter (E-1045, Hitachi Japan) to obtain a metal Au coating. The sputtering current was 35 mA and the time

was 70 s. After peeling the copper mask from the PDMS substrate, the PDMS template with the patterned Au was obtained.

Preparation of SiO_2 nanoparticles by the modified Stober Method

Firstly, 4 mL of ammonium hydroxide was added to 50 mL of anhydrous ethanol and stirred for 30 min. Then, 1.1 mL of tetraethylorthosilicate (TEOS) was added to the above solution, forming a SiO_2 nanoparticle suspension after stirring for 4 h. An aliquot of the suspension (11 mL) was withdrawn and ultrasonically dispersed for 10 min, and the SiO_2 nanoparticles were centrifugally separated from the solvent. The supernatant was removed, and the precipitate was dispersed in deionized water. Finally, the SiO_2 nanoparticles were separated from the deionized water by centrifugation and dispersed in 11 mL of anhydrous ethanol.

Assembly of the SiO_2 nanoparticles on the PDMS template

The obtained solution of the SiO_2 nanoparticles was spin-coated on the PDMS template at 1000 rpm for 40 s. Because the PDMS template consists of high surface energy areas (the metal Au areas) and low surface energy areas (the PDMS areas), the SiO_2 nanoparticles wet the metal Au areas but dewet the PDMS areas. The patterned SiO_2 nanoparticles on the PDMS template were thus obtained.

RESULTS AND DISCUSSION

The thickness of the copper film is 30 μm , and the film could be patterned by the laser marking system using a current of 20–24 A. The obtained copper mask with the arrays of round holes and square holes is shown in Fig. 1a. After coating the PDMS substrate (covered by the copper mask) with the metallic Au by ion sputtering, the PDMS template was generated as shown in Fig. 1b.

The PDMS template contains two kinds of Au patterns: the round dot array and the square dot array, as shown in Fig. 2. It is obvious that the fidelity of the patterned round dots or square dots is not very high because the fidelity of the copper mask obtained by the laser marking system is limited. From Figs 2c and d, the width of the square dots and the diameter of the round dots were both determined to be about 170 μm .

In order to determine the thickness of the patterned Au dots on the PDMS template, a polished silicon substrate was coated with Au by sputtering under the aforementioned conditions (current: 35 mA; time: 70 s). After checking the cross-section of the silicon substrate by scanning electron microscopy (SEM), it was deduced that the

Figure 1 Photos of the patterned copper mask (a), the PDMS template (b), and PDMS coated with the patterned SiO₂ nanoparticles (c).

Figure 2 Optical microscopic images of PDMS template with the Au pattern: (a) the round dot array, (b) a single round dot, (c) the square dot array, (d) a single square dot.

thickness of the Au patterns on the PDMS template was approximately 20 nm.

We used the spin-coating process to assemble the SiO₂ nanoparticles on the PDMS substrate. An ethanol solution of the SiO₂ nanoparticles was spin-coated on the PDMS template at 1000 rpm for 40 s. We obtained PDMS coated with the patterned SiO₂ nanoparticles, as shown in Fig. 1c.

The patterned PDMS template was inspected by optical microscopy (Fig. 3). Comparison of the images in Fig. 3 with those in Fig. 2 clearly indicates that the boundaries of the Au dots (round dots and square dots) are covered by the SiO₂ nanoparticles and these species are mainly annular. Moreover, from Fig. 3, it is apparent that the inner sides of these species remains on the borders of the Au dots and the outer borders of these species extended beyond those of the Au dots.

In order to verify whether the adhering species were SiO₂ nanoparticles, the coated PDMS template was subjected to energy dispersive spectroscopy (EDS) and SEM. These results are shown in Figs 4, 5 and 6, respectively.

From Fig. 4, it is obvious that the adhering species are

SiO₂ nanoparticles as anticipated. Figs 5 and 6 show the SEM images of the round dot and the square dot on the coated PDMS template.

From Figs 5 and 6, it is interesting that the distribution of the nanoparticles is uneven. Most of the nanoparticles are spread annularly along the outlines of the round Au dots or the square Au dots, whereas in the extensive central areas of the Au dots, there are only a few or even no nanoparticles. For example, in Figs 5a and e, a few nanoparticles are seen to be distributed at the top area of the circular Au dot. However, as shown in Fig. 6a, the entire area of the square Au dot is bare except for the boundary areas.

To elucidate the reason for the strange distribution of the nanoparticles, we checked the entire bare area of the Au dots and found that the surface of the Au dots consisted of many wrinkles and the width of the wrinkles was approximately 50 nm, as shown in Figs 5f and 6d. In comparison, the same PDMS substrate (without the copper mask) was sputtered with Au metal under the same conditions (sputtering current: 35 mA; time: 70 s). The obtained Au coating on the PDMS substrate was evaluated by SEM (Fig. 7).

Figure 3 Optical microscopic images of PDMS template coated with SiO₂ nanoparticles: (a) the round dot array, (b) a single round dot, (c) the square dot array, (d) a single square dot.

Figure 4 (a) SEM image of the coated PDMS template (the red square denotes the areas inspected by EDS), (b) EDS results for the areas enclosed by red squares.

Figure 5 SEM images of a single round dot (the same dot in Fig. 3b) on the PDMS template coated with SiO_2 nanoparticles: (a) overall image of the round dot, (b) boundary of the round dot, (c and d) magnified image of the boundary, (e) the near-center area covered with the nanoparticles, (f) bare Au area without the nanoparticles.

Figure 6 SEM images of a single square dot (the same dot in Fig. 3d) on the PDMS template coated with SiO₂ nanoparticles: (a) overall image of the square dot, (b) boundary of the square dot, (c) magnified image of the boundary, (d) bare Au area without the nanoparticles.

Fig. 7 shows that the Au coating on the PDMS is not smooth but full of wrinkles. The wrinkles may affect the wettability of the Au coating. Thus, we measured the contact angle of water drops on the Au coating (Fig. 8).

The contact angle of water on the bare PDMS substrate is as high as 112° (Fig. 8a), which verifies the high hydrophobicity of the PDMS surface. Fig. 8b shows that the contact angle of water on the PDMS substrate coated with the Au layer is approximately 55°, indicating that the wrinkled Au layer is hydrophilic. When the wrinkles in the Au layer were removed by deposition of Au metal on a polished silicon substrate, the contact angle was reduced to 37° (Fig. 8c). The data indicate that the smooth Au layer is much more hydrophilic than the wrinkled Au layer. Thus, we propose that the annular distribution of the nanoparticles on the PDMS template can be explained as presented in Fig. 9.

When the ethanol solution containing the nanoparticles is spin-coated on the PDMS template, the solution undergoes volatilization and the nanoparticles will be left on the

Figure 7 SEM image of the Au coating on the PDMS substrate without the copper mask.

template. Because the PDMS template includes the PDMS areas (the hydrophobic areas) and the Au pattern areas (the hydrophilic areas), the nanoparticles will dewet on the PDMS areas and wet on the Au pattern areas. We propose

Figure 8 Contact angles of water drops on the surface of (a) bare PDMS substrate, (b) PDMS substrate coated with Au layer, (c) silicon substrate coated with Au layer.

Figure 9 Schematic representation of the two-step dewetting process for SiO₂ nanoparticles on the PDMS template.

that this step is the first dewetting process of the nanoparticles. However, because the wrinkles in the Au pattern decrease the hydrophilicity of the surface, the nanoparticles will dewet again on the Au pattern areas. We propose that this is the second dewetting process of the nanoparticles. After the second dewetting, the nanoparticles in the central areas of the Au pattern will move to the borders of the Au pattern with consequent emergence of annular structures of the nanoparticles around the Au patterns.

CONCLUSIONS

In conclusion, through a simple spin-coating process, SiO₂ nanoparticles were assembled on a PDMS template comprising Au patterns on the PDMS substrate. The assembled nanoparticles on the PDMS substrate are distributed annularly around the borders of the Au patterns. We propose that the annular distribution of the nanoparticles results from dual dewetting of the nanoparticles on the PDMS template due to the high hydrophobicity of PDMS and the

decreased hydrophilicity of the Au patterns.

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Conflict of interest The authors declare that they have no conflict of interest.

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中文摘要 本文提出了一种利用硅橡胶模板对二氧化硅纳米粒子进行图形化组装的方法. 首先, 采用浇筑法制备了硅橡胶基底并通过激光打标机加工制备了铜掩模板, 然后对覆盖铜掩模板后的硅橡胶基底进行金属金的溅射以得到硅橡胶模板. 二氧化硅纳米粒子采用改进的Stober方法制备, 然后采用离心旋涂方式涂覆到硅橡胶模板表面. 由于硅橡胶模板表面具有图形化的亲水和疏水区域, 而且金表面的皱化也具有不同的亲水性, 纳米粒子将经历两次去湿过程, 最终围绕金图形化区域形成环状分布.