Three-Dimensional Colloidal Crystal-Assisted Lithography for Two-Dimensional Patterned Arrays

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In this paper, we report our recent work on preparing two-dimensional patterned microstructure arrays using three-dimensional colloidal crystals as templates, namely, colloidal crystal-assisted lithography. Two alternative processes are described and involved in colloidal crystal-assisted lithography. One is based upon imprinting the polymer films with three-dimensional silica colloidal crystals, and the other is based upon chemically depositing Ag microstructures on Au substrates covered by polymer colloidal crystals. By varying the experimental conditions in the colloidal crystal-assisted lithography process, we can intentionally control the morphologies of the resulting microstructures. The resultant Ag-coated Au substrates can be used as surface-enhanced Raman scattering substrates, and they would provide an ideal system for the mechanism study of surface-enhanced Raman scattering. We expect that colloidal crystal-assisted lithography will be a versatile approach which can be applied to patterning other materials such as functional molecules, polymers, oxides, and metals.

1. Introduction

Large areas of patterned arrays formed on various surfaces may be more and more attractive for a broad range of applications in engineering microelectronic and optoelectronic devices,1–4 fabricating biological and chemical sensors,5,6 and controlling crystallization.7,8 Many approaches for patterning surfaces in the micrometer and sub-micrometer ranges have been developed and successfully applied in microelectronics and plastic electronics, including photolithography, electron beam lithography, X-ray lithography, scanning probe lithography, imprint lithography, soft lithography, and so forth.9–20 However, each of these technologies has advantages and disadvantages regarding resolution, structural ordering, and cost involved in structuring large surface areas. Photolithography, a milestone and mainstay in semiconductor industries, is expected to be limited to ~100 nm in resolution.20 On the other hand, using newly developed nanolithographic techniques,10,21 such as electron beam lithography, X-ray lithography, and scanning probe lithography, structures of perfect shape and order can be made down to several nanometers, whereas the cost to produce microstructures in a large area is very high due to the equipment needed.

Self-assembled colloidal crystals composed of monodispersed nanospheres have been widely used as structural templates for the facile and cheap fabrication of periodic nanostructures over large areas. Commonly, three-dimensional (3D) colloidal crystals are used to prepare 3D photonic band gap and multiporous materials;22–23 and two-dimensional (2D) colloidal crystals are used as masks for 2D patterned microstructures.24–28 However, 3D colloidal crystals have seldom been intentionally utilized to produce 2D ordered structures. Using a double-layer of nanospheres as a mask in nanosphere lithography, Van Duyne and co-workers have created size-tunable noble metal nanoparticle arrays,26,29 Recently, Jiang used 3D colloidal crystals for 2D surface gratings.30 In our previous reports on “colloidal crystal-assisted imprint” (CCAIP)31 and “colloidal crystal-assisted capillary nanofabrication” (CCACN),32 we have intentionally developed colloidal crystal-assisted lithography (CCAL), utilizing 3D colloidal crystals to produce surfaces with 2D patterned arrays.

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Compared with other methods, the CCAL method has at least three advantages in preparing 2D patterned arrays: (1) as 3D colloidal crystals are accessible in a large area, CCAL is an efficient and facile way of preparing patterned arrays in a large area; (2) both the periodicity and morphology of the patterns can be intentionally adjusted by varying the template nanosphere size and other parameters; and (3) a mass of functional materials from molecules to polymers, oxides, and metals can be applied in CCAL.

Herein, we present our recent work on CCAL. There are two processes of CCAL described here. One is based upon imprinting the polymer films with 3D silica colloidal crystals. By varying the polymer film thickness and other experimental conditions in the imprinting process, we can intentionally control the morphology of the resulting polymer microstructures. The other process depends on chemically depositing Ag microstructures on Au substrates covered by 3D polymer colloidal crystals. The morphologies of the Ag structures formed on Au substrates can be controlled by adjusting the chemical deposition time and template nanosphere size. The resultant Ag-coated Au substrates thus prepared can be used as surface-enhanced Raman scattering (SERS) substrates and can provide ideal models for researching the mechanism of the SERS effect.

2. Experimental Section

Materials. All polystyrene (PS) nanospheres used in this work were prepared using surfactant-free emulsion polymerization as mentioned in our previous report. All silica nanospheres were prepared in ethanol according to the Störber method at ambient temperature. Silicon and gold substrates were cut into pieces of ~10 × 10 mm². Silicon wafers were then soaked in a 7:3 volumetric mixture of 98% H₂SO₄ and 30% H₂O₂ for 20 min under boiling (caution: strong oxide), and gold substrates were soaked in the same solvent at ambient temperature for 12 h. Subsequently, all substrates were rinsed with deionized water several times. Silver enhancer solutions A and B composed of AgNO₃ and hydroquinone, respectively, were obtained from Sigma. They were used as a 1:1 volumetric mixture. Solvents such as alcohol and toluene were used as received. Deionized water was applied for all experiment processes.

Preparation of Substrates Coated with Polymer Films. PS films of different thicknesses were prepared by spin-coating a solution of PS (MW = 1.39 × 10⁶) in toluene on dried silicon wafers. The concentration of the solutions ranged from 0.5 to 20 mg/mL. The rotation speed we chose in spin-coating ranged from 2000 to 9000 rpm. And the film thickness can be changed from 2 to 180 nm by varying the PS concentration and spin speed. (as listed in the Supporting Information, Table S1).

Preparation of Surfaces with 2D Microstructured Arrays by CCAL Imprint Processes. CCAL imprint processes were carried out as follows. First, 3D silica colloidal crystals (see the Supporting Information, Figure S1a) were prepared in between two substrates coated with polymer films by means of two-substrate vertical imprinting (step A, Scheme 1). Second, the sandwichlike chips, which were made of two substrates and a confined colloidal crystal chip in between them, were heated to a temperature above the glass transition temperature (Tg) of the polymer films for a period of time under a pressure of 1 × 10³ Pa (step B, Scheme 1). In this way, the polymer films were conformal to the 3D colloidal crystals. Finally, the colloidal crystals were removed by etching with hydrofluoric acid (HF) aqueous solution (40%) (step C, Scheme 1) after the chips were cooled down, leaving 2D patterned polymer arrays on the substrates. By varying the thickness of the polymer films and size of the template nanospheres, we could pattern surfaces with different structures, including 2D polymer ringlike arrays and polymer films with craterlike and crocklike porous arrays, as illustrated in Scheme 1a–c. Except for the studies on the temperature and time dependence, all CCAL imprint processes were carried out at 130 °C for 3 h. For temperature dependence, CCAL imprint processes were carried out at different temperatures for 3 h. The processes for investigating the time dependence were carried out at 130 °C for different times.

Preparation of Patterned Ag Arrays on Au Substrates. To fabricate 2D Ag patterned arrays on Au substrates, we first prepared 3D PS colloidal crystal chips with two Au wafers (see the SEM image in the Supporting Information, Figure S1b) according to a CCAL procedure (see the Supporting Information, Scheme S1). We then put these colloidal crystal chips with gold substrates into the solution of silver enhancer (A/B = 1:1). The solution was sucked into the interstices of the colloidal crystals. After reacting in the dark for a certain period of time at room temperature, the colloidal crystals were picked out and then dipped into toluene for 3 h to remove the polymer templates. The gold substrates were finally rinsed with deionized water and alcohol three times each and dried under a stream of nitrogen in sequence.

Characterization. Atomic force microscopy (AFM) images were recorded in the tapping mode with a Nanoscope IIIa scanning probe microscope from Digital Instruments under ambient conditions. Scanning electron microscopy (SEM) micrographs were taken with a JEOL FESEM 6700F electron microscope with a primary electron energy of 3 kV. Before imaging, the samples with polymer structures were sputter-coated with ~5 nm of Pt. All samples of the Ag patterns on Au substrates were not sputtered. UV–vis spectra were taken by using a Shimadzu UV-3600 spectrophotometer. For SERS measurements, Rhodamine 6G (R6G) was selected as the model compound. The procedures to modify the substrates were as follows. Substrates were immersed in a 1.0 × 10⁻⁶ M solution of R6G in absolute methanol for 30 min and rinsed with pure water, and then the Raman spectra were taken immediately after drying under a stream of nitrogen. Raman spectra were measured in ambient air with a Renishaw 1000 model confocal microscopy Raman spectrometer with a charged-coupled device detector and a holographic notch filter. The SERS excitation was provided by the 514.5 nm line of Ar⁺ laser with the same laser power of ~2 mW. The image integration time was 10 s.

3. Results and Discussion

3.1. CCAL Imprinting for 2D Patterned Polymer Arrays. Figure 1 presents typical AFM images of the 2D patterned arrays fabricated by the CCAL imprint approach. To achieve these results, we spin-coated PS films of different thicknesses onto silicon wafers and carried out the experiment process shown in
Scheme 1 with colloidal crystals constructed from nanospheres of different sizes. Figure 1a shows the ringlike patterned arrays fabricated by using silica nanospheres of 278 nm as templates. The average height of the ringlike structure is 32 nm. (All height, depth, and periodicity figures of the microstructures, as well as the film thickness, given in this paper were obtained by section analysis of AFM images.) Figure 1b shows the craterlike arrays derived from nanospheres of 283 nm, and the average depth of the craterlike holes is 143 nm. Figure 1c presents the crocklike porous arrays fabricated by imprinting with colloidal crystals of 245 nm silica nanospheres; the average depth of the pores is 160 nm.

In these cases, we can achieve patterned arrays with controllable morphologies by varying the experimental conditions. We found that many factors, especially the template nanosphere size, polymer film thickness, heating temperature, and imprinting time, have great influence on the morphology of the resulting structures.

3.1.1. Template Size Dependency of the Patterned Array Periodicity. The template size dependency of the periodicity presents that the periodicity of patterns is basically in accordance with the diameters of the template nanospheres used in the CCAL imprint process (Supporting Information, Figure S2). As the periodicity of the patterned polymer arrays prepared by this method depends on the template nanospheres greatly, we can control the patterned array periodicity by varying the template nanosphere size. The AFM image (Supporting Information, Figure S3a) of the patterned surface with ringlike nanoarrays implies the flexibility of CCAL imprinting. In this case, we used nanospheres of 60 nm in diameter, and a PS film of 21 nm thick. The inset presents a magnified 3D AFM image of this sample, from which we can see that the periodicity of this pattern is also 60 nm, and the size of every ringlike structure is of the nanoscale. Figure S3b shows an AFM image of the crocklike nanoarrays fabricated by CCAL imprinting with the same nanospheres. The PS film thickness was 21 nm. The inset shows a magnified 3D AFM image of the ruptured area. From this image, we can see the inside morphology of the crocklike

Figure 1. Typical AFM images of 2D patterned arrays fabricated by CCAL imprinting: (a) sub-micrometer scale ringlike arrays and (b and c) polymer films with patterned craterlike and crocklike porous arrays, respectively. The insets show 3D AFM images of the patterned structures.

Figure 2. 3D AFM images of patterned arrays fabricated by CCAL imprinting with substrates coated by PS films of different thicknesses: (a) \( T_f = 21 \) nm, (b) \( T_f = 44 \) nm, and (c) \( T_f = 165 \) nm. The insets illustrate the formation of the patterns. (\( R = 180 \) nm.)
nanopatterns. Thus, it can be seen that, due to the template size dependency of the structure periodicity, the CCAL approach is suitable not only for preparing sub-micrometer scale patterned arrays but also for nanoscale structures.

3.1.2. Film Thickness Dependency of the Patterned Array Morphology. By varying the concentration of the polymer solution and the rotation speed in the spin-coating process, we prepared silicon substrates coated with PS films of different thicknesses. We then imprinted these substrates with colloidal crystals of 360 nm nanospheres. Figure 2 shows 3D AFM images of patterned surfaces fabricated by imprinting substrates coated with PS films of 21, 44, and 165 nm. As the polymer films become more soft and mobile at the temperature above their Tg, they behave like a liquid and flow toward the nanospheres due to capillary force. When the films are relatively thin, this movement will lead to dewetting and rupture of the polymer film and will finally result in the ringlike structures shown in Figure 2a. As the film thickness increases, the dewetting process does not continue, which leads to the craterlike patterns shown in Figure 2b. With a further increase in the thickness, the polymer will flow over from the interstices between the nanospheres, and crocklike porous arrays (Figure 2c) would be achieved.

From the images shown in Figure 2, we can see that as the film thickness increases, the patterned structures change regularly. By analyzing the formation process of the microstructures, we put up empirical equations that can be used to guide the experiments of CCAL imprinting. The insets in Figure 2 are cross-sectional sketches simulating the formation of every single microstructure in each figure. As shown in these sketches, R is the radius of the template nanosphere, r is the radius of the microstructure hatch, h is the height of the microstructure, and Tt is the thickness of the spin-coated polymer film. Because the colloidal crystals are typically of a face-centered cubic (fcc) lattice with the (111) facet parallel to the substrates, every nanosphere should possess a polymer of a hexagonal prism. The height of the prism is Tt, and the radius of its inscribed circle is R. Thus, we can calculate the volume of the polymer before CCAL imprinting (Vpolymer) by

\[ V_{\text{polymer}} = 2 \sqrt{3} R^2 T_t \]  

(1)

When \( 0 < T_t \leq \pi / (6 \sqrt{3}) R \), we extremely assume that complete dewetting of the polymer film will occur (as illustrated by the insets in Figure 2a and b). We then obtain the polymer volume after CCAL imprinting (Vpolymer) as

\[ V_{\text{polymer}} = \pi R h^2 - 2 \sqrt{3} \pi h^3 \]  

(2)

As the total polymer mass before and after the CCAL imprint process should be equal according to the conservation of matter, we could assume that the total volume of the polymer does not change before and after the imprinting, namely

\[ V_{\text{polymer}} = V_{\text{polymer}} \]  

(3)

and

\[ \frac{2}{3} \pi h^3 - \pi R h^2 + 2 \sqrt{3} R^2 T_t = 0 \]  

(4)

When \( \pi / (6 \sqrt{3}) R < T_t \leq 0.531 R \), we assume the formation of polymer films with patterned pores processed by template nanospheres and ignore the wetting effect on the surfaces of the nanospheres (illustrated by the inset in Figure 2c). By using a similar geometry calculation process, we can obtain another function:

\[ \frac{\pi}{3} h^3 - \pi R h^2 + 2 \sqrt{3} R h - 2 \sqrt{3} R^2 T_t = 0 \]  

(5)

When \( T_t > 0.531 R \), the polymer will get to the second layer of the colloidal crystals during CCAL imprinting. The situation will become very complex, and we will not discuss it here.

As R and Tt can be adjusted and measured directly, we can calculate h by solving functions 4 and 5. Table 1 lists the calculated and observed h values of microstructures fabricated by CCAL imprinting with different R and Tt values. Due to the assumptions we took in setting up the model functions and the system warps in measuring the h, R, and Tt values, the calculated values show departures compared with the observed values. However, these functions are still useful in directing the CCAL imprinting experiments, and we can intentionally design the microstructures assisted by them.

3.1.3. Heating Temperature Dependency of the Ringlike Structure Height. As the ringlike arrays can be characterized more easily and accurately than other structures, we have studied the temperature and time dependency of the microstructures based on a series of experiments for preparing ringlike patterns. The heating temperature of CCAL imprinting is an important factor that influences the morphology of the resultant microstructures.

Figure 3a−d shows AFM images of ringlike patterns fabricated by CCAL imprinting at 85, 90, 100, and 110 °C, respectively, for 3 h. These patterns were prepared by imprinting substrates coated with PS films of 8.8 nm. And the silica nanospheres we used to prepare the colloidal crystal templates were 278 nm in diameter. As the Z range of these images is the same (100 nm), we can see the height change of the ringlike structures clearly.

Table 1. Calculated and Observed h Values Derived from Different R and Tt Values

<table>
<thead>
<tr>
<th>R (nm)</th>
<th>Tt (nm)</th>
<th>Tcalcd</th>
<th>Tobs</th>
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<tr>
<td>180</td>
<td>21</td>
<td>79</td>
<td>67.5</td>
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<tr>
<td>180</td>
<td>44</td>
<td>129</td>
<td>138</td>
</tr>
<tr>
<td>141.5</td>
<td>8.8</td>
<td>41</td>
<td>35</td>
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<tr>
<td>141.5</td>
<td>41</td>
<td>124</td>
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<tr>
<td>139</td>
<td>8.8</td>
<td>40</td>
<td>32</td>
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<tr>
<td>122.5</td>
<td>50</td>
<td>138</td>
<td>160</td>
</tr>
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Figure 3e presents the plot data of the microstructure height against the heating temperature of CCAL imprinting. The curve shows that the height of the microstructures increases as the temperature changes from 80 to 130 °C, and then the curve tends to flatten. This temperature dependency can be explained by the classical rheology of polymers. There are two factors that influence the mobility of a melting polymer. One factor is the energy, and the other is the free volume of the melting polymer. When the temperature is low, both the energy and free volume of the melting polymer are low. As the viscosity of the polymer is high, it is difficult for the polymer chains to move and the fluidity of the melting polymer is low. That is why the fabricated ringlike structures are relatively short in Figure 3a. When the temperature rises up, the energy of the melting polymer increases accordingly. The viscosity of the polymer gets lower, and the free volume and fluidity of the melting polymer get higher, which leads to growth of the resulting ringlike structures. However, the microstructures would not grow unlimitedly; there would be an equilibrium state between the capillary force and strain force. When it gets to the equilibrium state, the microstructures would not grow anymore, though the temperature continues to increase.

That is why the microstructure height does not vary very much after the temperature reaches 130 °C.
3.1.4. Imprinting Time Dependency of the Ringlike Structure Morphology. Imprinting time is another important factor that influences the morphology of microstructures fabricated by CCAL imprinting. Imprinting substrates coated with PS films (8.8 nm in thickness) by template silica nanospheres of 360 nm for different times, we have studied the imprinting time dependency of the ringlike structure morphology. Figure S4 (see the Supporting Information) shows SEM images of the ringlike structures fabricated by CCAL imprinting for different times. We can see that when the time is short (Figure S4a), the ringlike structures are not round. As the time increases, the morphology gets better and better. And round ringlike structures would be achieved by imprinting over 3 h. From these SEM images, we can see that the ringlike structures are not real rings. They are structures more like plates. And even at relatively high temperature, the dewetting process would not be complete. There would still be polymer chains at the areas between the ringlike structures (Figure S4c and d).

Figure S4e (see the Supporting Information) shows the time dependency of the height of the ringlike structures fabricated by CCAL imprinting. The curve shows that the height of the microstructures increases steadily at the stage from 0 to 90 min. After that, the structure height would change enormously. This also can be explained by the rheology of polymers. As the melting polymer under a certain temperature and pressure would show a certain flow rate, it takes some time for the polymer chains to move and get to the equilibrium state as mentioned above. That is why the ringlike structures keep on growing at the early stage of CCAL imprinting. When it comes to the equilibrium state, the polymer chains do not move acutely anymore, and the microstructures stop growing. As the growing stage is of high Gibbs free energy, it is not stable, which leads to the rough morphology the microstructures (Figure S4a−c). While at the equilibrium state, the ringlike structures become smooth due to the creepage of the polymer chains. When the time is long enough, round patterned arrays will be achieved, as it is the state of the lowest Gibbs free energy.

3.2. Patterned Ag Films Fabricated by CCAL for SERS Substrates. CCACN is another alternative method of CCAL. It is effective in fabricating a surface possessing 2D patterned arrays and self-assembled monolayers. Recently, we developed an alternative CCAL approach for preparing patterned Ag films on gold wafers by combining CCACN with chemical deposition. The morphology of the Ag patterns can be controlled by the chemical deposition time. As the microstructures of the Ag patterns with periodicities of the sub-micrometer scale are composed of Ag nanoparticles, the resulting substrates are very suitable as SERS substrates. Moreover, because the periodicity and morphology of the patterns can be tuned easily, these substrates may provide ideal models for the mechanism study of the SERS effect.

Figure S5 (see the Supporting Information) shows SEM images of the patterned Ag films formed on Au substrates by using colloidal crystals of 660 nm PS nanospheres as templates. Figure S5a−c was obtained by chemical deposition times of 5, 30, and 120 min, respectively. When the reacting time is relatively short, the template effect of the colloidal crystals is not obvious. There are only black dots at the points possessed by the PS nanospheres (Figure S5a). As the reacting time increases, the template effect gets strong, and compact films form according to the templates (Figure S5b and c). Figure S5d shows the section image of Figure S5c, with the inset showing a magnified view. From this image, we can see that the Ag film was formed by using two layers of nanospheres as the template. These results show that the microstructures of the Ag patterns can be tuned by controlling the chemical deposition time. Moreover, the periodicity and shape of the patterns can be easily tuned by changing the building blocks of the colloidal crystals. Thus, it can be seen that our method is an efficient way for preparing patterned Ag films of various microstructures.

The Ag-coated Au substrates prepared by CCAL are very suitable as SERS substrates, since they possess three important characteristics for SERS signal enhancement. First, compared with flat substrates, the rough patterned structures increase the accessible surface area for probe molecules. Second, periodic structures formed from colloidal crystal templates are useful for enhancement of surface plasmon resonance (SPR). Third, as shown by the SEM images of Figure S5, the microstructures of

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the Ag patterns were formed by Ag particles with diameters ranging from the nanometer scale to sub-micrometer scale, and this is also desirable for enhancement of Raman scattering. We evaluated the performance of the as-prepared Ag-coated Au substrates as SERS substrates using R6G as a probe molecule. R6G was chosen as an analyte because it has been well characterized by SERS and resonance Raman spectroscopy. The SERS spectra of single R6G molecules have been obtained, and most of the prominent Raman bands have been assigned.

As the wavelength of 514.5 nm corresponds to a resonant excitation of R6G, a surface-enhanced resonance Raman spectrum (SERRS) is acquired in the present study. Figure 4c shows the Raman spectra obtained on different Au substrates with the same laser power of ~2 mW. Sample I is the Au substrate coated with Ag patterns shown in Figure 4a. It was prepared by CCAL with colloidal crystals of 200 nm PS nanospheres for 30 min. Sample II is Ag-coated Au substrates prepared by dipping the Au substrate directly into the silver enhancer solvent for 30 min, and Figure 4b shows the SEM image of this sample. Sample III is the Au substrate without modification, which shows no obvious SERS effect. The intense band at 773 cm$^{-1}$ is assigned to an out-of-plane bending motion of the C–H of the xanthene skeleton. And the peak at 611 cm$^{-1}$ corresponds to the C–C–C ring in-plane vibration. It shows that as-prepared patterned silver patterns present high efficiency of Raman enhancement (EF $\geq 10^{10}$, the estimation of SERS enhancement has been included in the Supporting Information, Figure S6). The SERS enhancement of Ag patterns can be attributed to the localized surface plasmon resonance (LSPR) of the nanostructured surface.

In summary, by using 3D colloidal crystals as templates, CCAL is a simple and effective procedure for the fabrication of surfaces with large area 2D patterned arrays. By carefully studying the experimental condition dependency of the patterned arrays fabricated by CCAL imprinting, we can control the morphology of the resulting microstructures by intentionally varying the template nanosphere size, the polymer film thickness, the heating temperature, and the time of the imprinting process. By combining CCACN with chemical deposition, we reported an alternative CCAL approach for preparing patterned Ag films on Au substrates. The morphology of the Ag films can also be tuned simply. These Ag-coated Au substrates show intriguing applications as SERS substrates, and they would further provide an ideal system for the mechanism study of SERS effects.

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Supporting Information Available: SEM images of 3D colloidal crystals of silica and PS nanospheres; plot of the template size dependency of the patterned array periodicity; AFM images of ringlike

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Figure 4. SEM images of (a) a patterned Ag film fabricated by using colloidal crystals of 200 nm PS nanospheres as the template and (b) Ag structures formed on Au substrates by chemical deposition. (c) SERRS spectra of R6G on different substrates: (I) Au substrates coated with Ag patterns shown in (a); (II) Au substrates coated with Ag structures shown in (b); and (III) Au substrates without modification.
and crocklike patterns; SEM images of ringlike arrays fabricated by CCAL imprinting at different times; plot of the time dependency of the ringlike structure height; SEM images of patterned Ag films on Au substrates fabricated by CCAL imprinting at different times; Raman absorbance spectra of R6G; UV–vis spectra of Ag patterns on Au substrates; schematic representation of the procedure used to prepare patterned Ag films on Au substrates; and data showing the influence of PS concentration and spin coating rotation speed on the final film thickness. This material is available free of charge via the Internet at http://pubs.acs.org.

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