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Wet Etching-Assisted Colloidal Lithography: A General Strategy toward Nanodisk and Nanohole Arrays on Arbitrary Substrates

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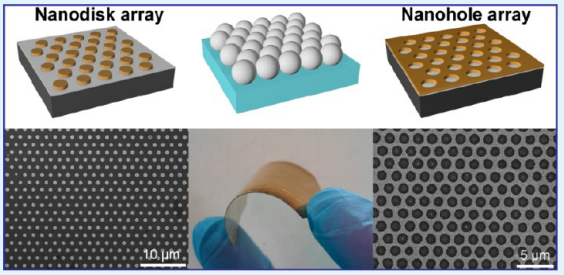
Supporting Information

ABSTRACT: A simple and facile strategy is presented to fabricate the metal nanodisk and nanohole arrays based on a wet etching-assisted polystyrene colloidal lithography. Gold is chosen to demonstrate the validity of such a strategy. The hexagonally arranged Au nanodisk and nanohole arrays are thus fabricated with large area and good uniformity. The structural parameters of the arrays, such as thicknesses, diameters, and spacings of the nanodisks or nanoholes, are facilely tunable and controllable by predeposition conditions, etching conditions and colloidal monolayer structure. More importantly, these arrays can be produced on any supporting substrates, such as conductive or nonconductive and even flexible substrates with flat, rough, or even curved surfaces. In general, the presented strategy is low in cost, simple in operation and arbitrary in substrate, and the as-prepared arrays could find potential devices' applications with nice compatibility in the fields of optics, surface-enhanced Raman spectroscopy, biosensing, and so forth.



KEYWORDS: *colloidal lithography, wet etching, nanodisk, nanohole, array*

1. INTRODUCTION

Ordered nanostructured arrays, consisting of regularly arranged nano-objects, have attracted much attention in the past decade because of their potential devices' applications in such as surface-enhanced Raman scattering (SERS) substrates,[1−3] data storage media,[4] and biosensors.[5−7] The most widely used manufacture techniques are photolithography, electron beam lithography, and focused ion beam lithography, etc.[1,8] However, these methods are limited by high cost, low throughput, and difficulty in accessing the facilities.[9] In addition to these conventional techniques, utilizing monolayer colloidal crystals as templates or masks, or the colloidal lithography,[10−13] various patterned nanostructured arrays including nanoparticle arrays, nanopore arrays, nanoring arrays, and nanorod/nanotube arrays, were also fabricated by some assisted chemical and physical processes, such as solution/sol dipping strategy,[14−16] electrochemical deposition,[17−21] thermal evaporation deposition,[22−24] e-beam evaporation deposition,[25] pulsed laser deposition,[26−29] etc. It has been proven that the colloidal lithography is a facile, flexible strategy to prepare ordered nanostructured arrays and is advantageous in terms of cost, reproducibility, size of the produced arrays and time required to prepare. However, the performance of the colloidal lithography is closely related to the assisted techniques. For example, the solution dipping method based on the colloidal lithography was commonly used to prepare metal oxide (e.g., ZnO) arrays, and powerless for metal arrays.[30]

Recently, nanodisk and nanohole arrays have stimulated much attention because of their unique optical properties and promising applications in extraordinary optical transmission, SERS devices, nanoscale waveguides, biosensors, nanopatterning, and molecular plasmonics, etc.[31−36] It is well-known that controlled fabrication of such arrays with tunable structural parameters (size and spacing of the nanodisk or nanohole) and high structural uniformity, especially on any substrates (with flat, rough, curved and even flexible surfaces), in a simple way is very important for their device applications. Nowadays, it is mainly on the basis of the nonclose-packed colloidal monolayer array, which is obtained by reactive ion etching (RIE) on self-assembled monolayer, and then deposition of metal to prepare nanodisk arrays, or using nanoposts secondary template to obtain nanohole arrays.[9,37−39] As is known, the RIE technique need a special instrument to prepare ordered arrays on flat substrate. Until now, attaining high-throughput and large-area fabrication of nanodisk or nanohole arrays on any substrate continues to be a major challenge in a simple and direct way in any lab.

In this article, a simple and facile strategy is presented to fabricate the metal nanodisk and nanohole arrays based on a wet etching-assisted colloidal lithography. Gold is chosen as an example to demonstrate the effectiveness of the strategy. The hexagonally arranged nanodisk and nanohole arrays with controlled thickness and structural parameters have been fabricated. Importantly, these arrays can be produced on any supporting substrates, such as conductive or nonconductive and even flexible substrates with flat, rough, or curved surfaces. The

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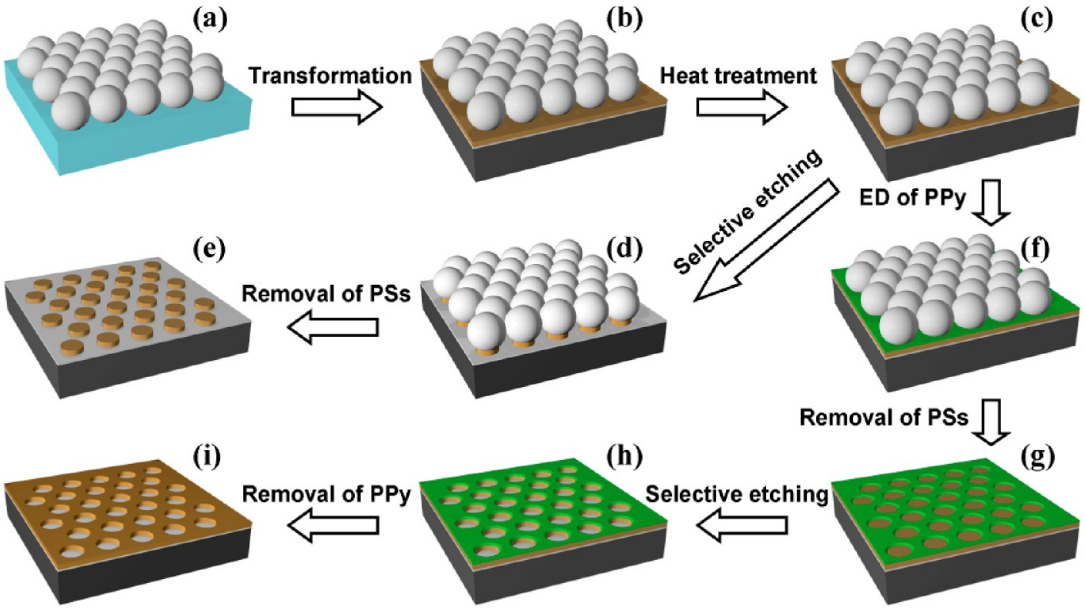

Figure 1. Schematic illustration of the fabrication of Au nanodisk array (a → b → c → d → e) and nanohole array (a → b→ c → f→ g → h→ i). (a) Large-area PS colloidal monolayer on a glass slide by an interface self-assembly method. (b) PS colloidal monolayer on an Au-coated substrate (i.e., Au/Ti/supporting substrate) by transferring from the glass slide. (c) PS monolayer becomes firm (area) contact with the Au-coated substrate by heating at 110 °C. (d, e) Au nanodisk array is formed and obtained after selective wet-etching and removal of PS spheres. (f) PPy thin layer is electrodeposited on the heated PS/Au-substrate. (g) Ordered PPy pore array on the Au-substrate after removal of the PS monolayer. (h, i) Au nanohole array is produced and obtained after selective wet-etching and removal of the PPy.

presented strategy is low in cost, simple in operation, and arbitrary in substrate, providing an effective and simple way. The obtained arrays can find potential devices' applications in the fields of optics, surface-enhanced Raman spectroscopy, biosensing, and so forth.

2. EXPERIMENTAL SECTION

2.1. Materials. The PS (0.5, 1, and 2 μm in diameter) suspensions (2.5 wt % in water) were purchased from Alfa Aesar Corporation. Thiourea and iron nitrate nonahydrate (Sinopharm Chemical Reagent Co., Ltd.), pyrrole (Shanghai Kefeng Industry Co., Ltd.), sodium dodecyl benzenesulfonate (Aladdin Chemistry Co., Ltd.), and solvents including acetone and ethanol were used without further purification. Deionized water (18.2 MΩ·cm) was obtained from an ultrafiltration system (Milli-Q, Millipore, Marlborough, MA).

2.2. Preparation of PS/Au Substrate. Some substrates including silicon wafers, ITO conductive glasses, and quartz plates were washed sequentially by ultrasonic cleaning for 15 min each in acetone, ethanol, and deionized water. Screen protectors (i.e., polyethylene terephthalate (PET) flexible substrates) were washed sequentially by ultrasonic cleaning for 15 min each in ethanol and deionized water. Then, an Au-substrate (i.e., Au/Ti/supporting substrate) was prepared by an ion-sputtering deposition method of ∼60 nm of gold onto the supporting substrate that had been primed with ∼10 nm of titanium to promote adhesion between the gold layer and the supporting substrate. In all experiments, the thicknesses of the gold and titanium film were fixed and estimated according to the sputtering deposition rate curve provided by the instruction manual of the sputter coater (Emitech K550X). The ∼60 nm gold film was obtained at 25 mA for 8 min, and the ∼10 nm titanium layer was obtained at 20 mA for 90 s. Next, a large-area (centimeter square) uniform PS monolayer colloidal crystal was prepared on the well-cleaned glass slide by a gas−liquid interface self-assembly method, as previously described in detail.[40,41] The as-prepared PS monolayer was integrally transferred onto the Au-substrate by a floating method.[42] After drying at room temperature, the Au-coated substrate covered with the PS monolayer (i.e., PS/Au-substrate) was heated in an oven at 110 °C for a certain time (about 5−10 min) so that the PS monolayer had a firm (or an area) contact with the Au substrate. For the formation of different periodic arrays, three differently sized PS spheres including 0.5, 1, and 2 μm in diameter were chosen.

2.3. Synthesis of Au Nanodisk Arrays. The fabrication procedure is schematically illustrated in Figure 1a-e. First of all, the PS/Au-substrate was prepared and heated, as described above. Then, the heated PS/Au substrate was etched in an aqueous solution of $Fe(NO_3)_3$ (20 mM) and thiourea (30 mM) at room temperature (∼20 °C) with gentle stirring.[43,44] After that, the sample was taken out and rinsed with deionized water and dried naturally, and then immersed into methylene chloride (CH_2Cl_2) solution to dissolve the PS spheres and rinsed with ethanol several times. The Au nanodisk arrays were thus obtained. The etching solution was freshly prepared in each experiment.

2.4. Synthesis of Au Nanohole Arrays. Figure 1a−c, f−i schematically shows the fabrication of an Au nanohole array. The as-heated PS/Au-substrate was first electrodeposited to form a layer of polypyrrole (PPy) on it, in a solution composed of 0.1 M pyrrole and 0.1 M sodium dodecyl benzenesulfonate, at a deposition current density of 0.5 mA/cm^2 for 15 s.[45,46] After subsequent removal of PS spheres in the CH_2Cl_2 solution and rinsing with deionized water several times, the sample was etched in the aqueous solution the same as that used in the fabrication of the Au nanodisk array. The nanoholes were thus formed where the gold film was not covered by the PPy. Finally, the Au nanohole array was obtained after removal of PPy by heating at 250 °C for 24 h.[46]

2.5. Characterization. The morphologies of the as-prepared arrays were observed on a field-emission scanning electronic microscope (FE-SEM, Sirion 200) operated at an acceleration voltage of 10 kV.

3. RESULTS AND DISCUSSION

Figure 1 gives a schematic illustration of the wet etching-assisted colloidal lithography strategy. The detailed description is seen in the Experimental Section. On the basis of such a strategy, the structural parameters of the arrays, such as the sizes and spacings of the nanodisks or nanoholes, can be tunable and controllable by the PS colloidal monolayer and

etching conditions. The thicknesses can be adjusted by the sputtering deposition current and deposition time. Also, because of the transferability of the PS colloidal monolayer,[41,47] such arrays could be fabricated on any supporting substrates with flat, rough, or curved and even flexible surfaces.

3.1. Au Nanodisk Arrays. For the fabrication of an Au nanodisk array, according to the strategy in Figure 1, a large-area polystyrene (PS) colloidal monolayer was prepared and transferred onto the Au-coated Si substrate (i.e., Au-substrate). Here, a silicon wafer was used as supporting substrate. The PS monolayer covered Au substrate (i.e., PS/Au-substrate) was then heated for 10 min to get a firm (or an area) contact between the PS monolayer and the Au-substrate. After that, the heated PS/Au-substrate is directly etched in the etching solution composed of $Fe(NO_3)_3$ and thiourea with gentle stirring for 6 min. After removal of PS spheres, a gold array on the silicon substrate was thus obtained, as shown in Figure 2. It

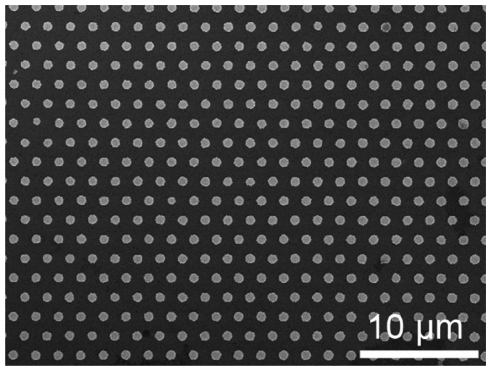

Figure 2. Typical FESEM images of an Au nanodisk array, with a period 2 μm, on a silicon substrate by wet-etching for 6 min.

has been shown that the as-prepared array consists of the hexagonally arranged and nearly circular nanodisks with ~740 nm in diameter, ~60 nm in thickness and uniformly distributed on the silicon substrate. The circular disks are of nanoscaled-rough profile due to the wet-etching, and the surface morphology of the nanodisk reserves that of the Au film precoated on the silicon substrate by an ion-sputtering method before transferring PS monolayer and wet-etching, as clearly seen in Figure 3b. Such well-ordered hexagonal array with a proximate disks' central distance of 2 μm, which depends on the diameter of the as-chosen PS spheres.

Further, the structural parameters of the array could be tuned and controlled only by changing the etching time but keeping the other conditions unchanged. Figure 3a–c demonstrate the arrays with different disks' diameters from ~280 to ~1030 nm after etching for different times (4–12 min). The corresponding disks' diameter distributions are shown in the Supporting Information (Figure S1a–c). Obviously, most of the Au nanodisks formed by the wet etching-assisted colloidal lithography strategy are uniform in size and approximately circular in shape. Similarly, the Au arrays with the period of 1 μm and the disks' diameters ranging from ~110 to ~400 nm were also produced by the 1 μm PS spheres and different etching times (5–8 min), as shown in Figure 3d–f. The disks' diameter distributions are relatively narrow, as illustrated in the Supporting Information (Figure S1d–f). These results imply that the structural parameters of the array could be tuned just by the etching time and PS template. It should be mentioned it

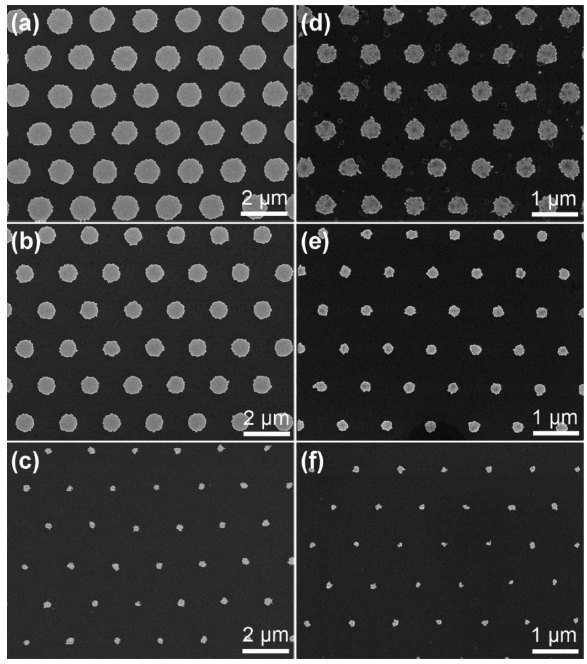

Figure 3. FESEM images of differently sized Au nanodisk arrays, with periods of (a–c) 2 μm and (d–f) 1 μm on the silicon substrates, after etching for different times (4–12 min).

is difficult to obtain small period arrays (such as less than 200 nm) because of weak controllability.

3.2. Au Nanohole Arrays. According to the strategy in Figure 1, a PPy layer with orderly arranged pore array will be formed after electrodeposition of PPy on the heated PS/Au substrate and subsequent removal of the PS spheres by dissolution (Figure 1f, g). Then, an Au nanohole array with the hexagonal pattern should be obtained after wet-etching the PPy pore array and subsequently removal of it (Figure 1h, i), which is in good agreement with our experiments. Figure 4a illustrates

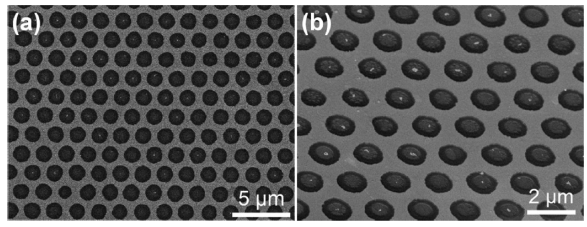

Figure 4. Typical FESEM images of an Au nanohole array, with a period 2 μm, on a silicon substrate by wet-etching for 3 min: (a) front view; (b) tilted view.

the typical results for the Au nanohole array prepared by static etching for 3 min, with 2 μm in period and ~1.35 μm in hole diameter, on a silicon substrate. The holes in the array are approximately cylindrical, and hexagonally arranged because of the template geometry, and the surface of the array is smooth.

Here, the thickness of the Au-coated layer was ~60 nm, corresponding to the depth of the holes in the array. The diameter of nanoholes in the array can be tuned by the etching time. Figure 5a–d shows the nanohole arrays with different hole's diameters (from ~950 to ~1750 nm) after etching for different times (2–6 min). The distributions of the holes' diameters are uniform, as shown in the Supporting Information (Figure S2a–d). Similarly, using other sized PS monolayer as

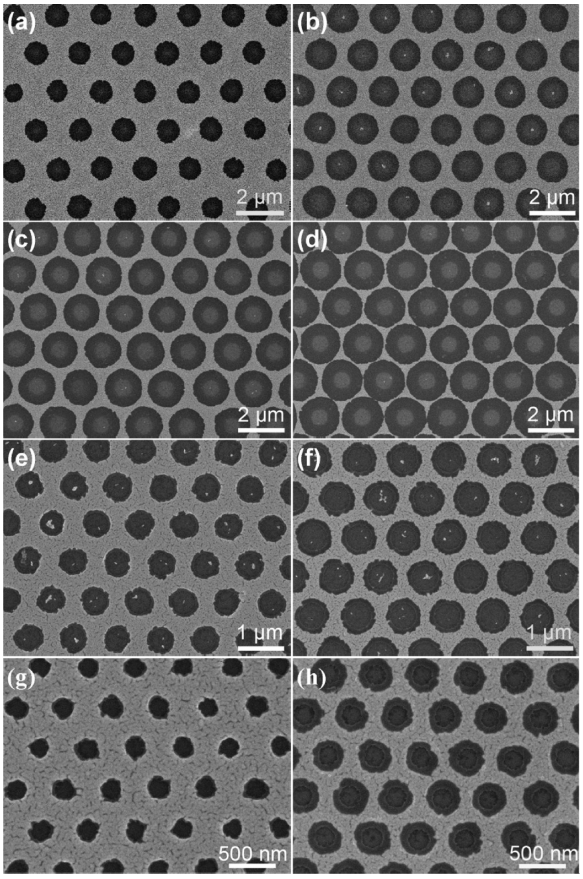

Figure 5. FESEM images of differently sized Au nanohole arrays with a period of 2 μm (a-d), 1 μm (e and f) and 500 nm (g and h) on the silicon substrates after etching for different times (1−6 min).

the template, various periodic Au nanohole arrays were also fabricated on the silicon substrates. Figure 5e, f and g, h show the Au nanohole arrays with 1 μm and 500 nm in periods, respectively. The corresponding hole's diameter distributions are seen in the Supporting Information (Figure S2e−h), showing nearly monodispersed diameter.

3.3. Arbitrary Substrates. In the previous experiments, the as-used supporting substrate was silicon wafer. In fact, on the basis of the strategy shown in Figure 1, the supporting substrate is arbitrary. We can produce the arrays on any substrates, such as conductive or nonconductive, rough or smooth, flat or curved ones, because of the transferability of the PS monolayers. Figure 6 demonstrates some typical arrays on different substrates, including rough ITO conductive substrate, smooth nonconductive substrate (quartz plate), after etching for different times, exhibiting the patterns similar to those shown in Figures 3 and 5. In addition, more interestingly, the array could also be formed on a flexible substrate using our strategy, as typically illustrated in Figure 7, corresponding to a nanohole array on the flexible PET supporting substrate. The most nanodisks or nanoholes could be hexagonally arranged uniformly if choosing the appropriate experimental parameters. Furthermore, the as-prepared arrays did not influence the substrate flexibility and can still be freely bent without damage of the pattern structure. Such substrate arbitrariness of the Au nanodisk and nanohole arrays is important to the device fabrication and integration, and can promise applicability ranging from biotechnology to optoelectronics.

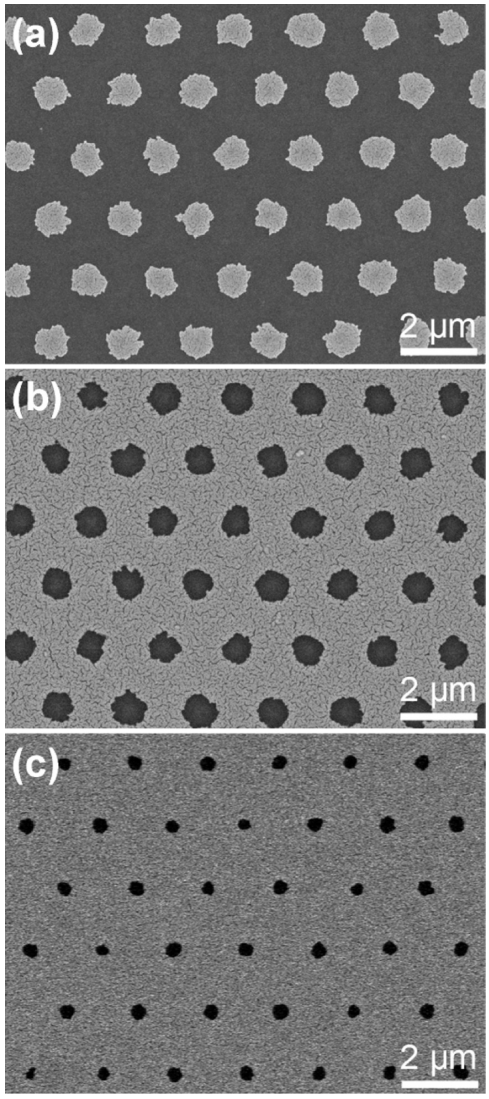

Figure 6. FESEM images of the Au nanodisk and nanohole arrays, with the same period of 2 μm, on different substrates: (a, b) ITO conductive glass; (c) nonconductive quartz plate.

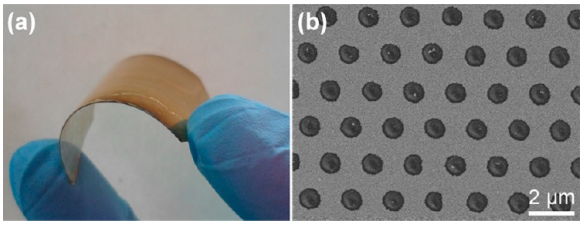

Figure 7. Au nanohole array on the flexible screen protector. (a) Photo of the whole array. (b) FESEM image of the array.

As mentioned above, the structural parameter-controlled hexagonally arranged Au nanodisk and nanohole arrays can be readily fabricated on any supporting substrates. In the fabrication process, the heat treatment for a certain time is very necessary to attain an area contact between PS spheres and Au-substrate, as shown in Figure S3 in the Supporting Information. Because of such contact geometry between the PS spheres and Au-substrate, the Au film that was not contacted with PS spheres was first to be etched, that is the PS sphere can be used as etching mask and not be etched in the

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etching process, an Au nanodisk array with hexagonal pattern can thus be obtained. While in the fabrication process of Au nanohole array, the PS monolayer was first used as electrodeposition template, in order to obtain ordered PPy hole array after removal of PS spheres. Such electro-polymerized PPy layer can not be etched in the solution of $Fe(NO_3)_3$ and thiourea. Thus, the PPy hole array can be used as etching mask, and the spaces where not protected by the PPy layer was first etched, and with increasing the etching time, the hole size increased gradually, so the Au nanohole array can be prepared in this way. Whether for Au nanodisks or nanoholes array, the pattern or symmetry of the ordered array is restricted by the colloidal template.

Finally, it should be mentioned that the heating time at above glass-transition temperature of PS, etchant and its concentration, stirring rate in the etching solution during the etching process are important to produce the nanodisk and nanohole arrays with high quality (uniform structure). The heating time for the PS-covered substrates should be proper so that an appropriate contact area between PS spheres and substrate is formed. Overheating may lead to that the channels between the spheres almost disappear,[48] which will prevent the etching solution passing through the channels to etch the gold layer for fabricating the nanodisk array. In addition, without these channels, PPy ordered array cannot be electrodeposited and obtained as the secondary template for next fabrication of nanohole array. In a word, different heating time may have important influence on the final diameters of nanodisks and nanoholes, but they are also depended on the etching time. The etchant and concentration should be selected so that only the Au film could be etched at an appropriate rate. The other etching solution, such as mixtures of nitric acid and hydrochloric acid, potassium iodide solution, or cyanides, because of too fast etching rate, can lead to a bad controllability, and thus failure of the fabrication. Furthermore, fabrication of Au nanodisk array, the stirring rate in the solution should be fast enough to ensure good homogeneity of the whole etching solution so that uniform etching takes place on the whole substrate.

The strategies in our case are very important technical progresses. General colloidal lithography methods are usually based on colloidal monolayer template, combined with vacuum evaporation deposition technique, and easy to obtain triangular nanoparticles. The particles' sizes are mainly depended on the size of colloidal sphere. Or using RIE technique to prepare non-close-packed colloidal monolayer, then using such array as deposition or etching mask. In this method, RIE technique needs a special instrument that is not easy to realize in any lab. In our case, the metal film was first deposited on the supporting substrate, making the as-prepared surfaces of arrays flat. And the size can be adjustable in a wide range, not only by the sphere size but also the etching time. All of these can be easily realized on any supporting substrates in any lab.

Through choosing appropriate periodicity (i.e., PS sphere's size) and etching time, disks' sizes can be adjustable from 100−1100 nm and holes' sizes adjustable from 200−1800 nm. Such a large adjustable range is very useful for possible applications. Figure 8 is the optical transmission spectra of Au film and Au nanohole array with ∼750 nm diameter. Comparing these two curves, we can find after etching, a new peak in infrared region appeared, which shows the as-prepared arrays may be used in enhanced infrared transmittance field. In addition, the peak at ∼526 nm shifted to ∼500 nm and the corresponding intensity

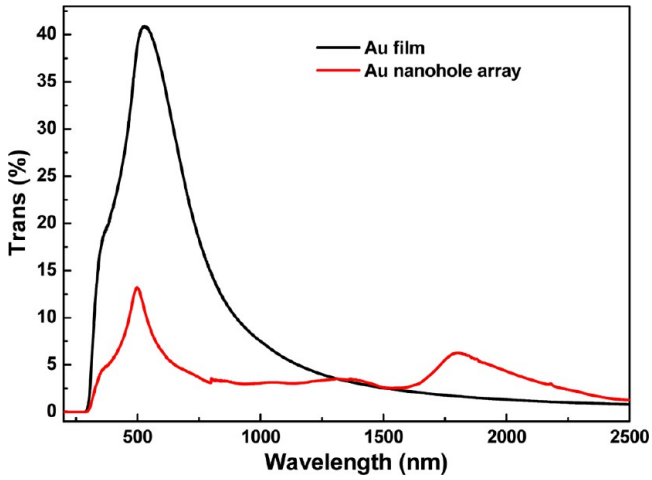

Figure 8. Transmission spectra of Au film and Au nanohole array with ∼750 nm diameter.

decreased significantly. The reduced visible transmittance means enhanced absorbance and scattering. All the optical properties may find potential applications in optical devices and solar cells. Deeper research is in process.

4. CONCLUSION

In summary, a wet etching-assisted colloidal lithography strategy has been presented and the hexagonally arranged Au nanodisk and nanohole arrays are thus fabricated with large area and good uniformity because of the geometry of the PS colloidal template and selective etching. By etching conditions and PS monolayer structure, we can easily achieve a good tunability and controllability of the structural parameters of the arrays in a quite large range. The obtained arrays could find potential applications in the fields of optics, surface enhanced Raman spectroscopy, biosensing, and so forth. More importantly, owing to the easy transferability of the PS colloidal monolayer, the arrays can be fabricated, with high quality, on any supporting substrates, such as conductive or nonconductive or even flexible ones with flat or rough, or even curved surfaces. The strategy presented in this study is low in cost, simple in operation, and arbitrary in substrate, and should be suitable for the other metal arrays as long as an appropriate etchant and etching conditions are chosen. This work provides a simple and flexible route for fabrication of some nanodisk or nanohole array-based devices on any substrates.

■ ASSOCIATED CONTENT

Supporting Information

Diameter distributions of the nanodisk and nanohole arrays with different structural parameters. This material is available free of charge via the Internet at http://pubs.acs.org/.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Yue, W.; Wang, Z.; Yang, Y.; Chen, L.; Syed, A.; Wong, K.; Wang, X. Electron-Beam Lithography of Gold Nanostructures for Surface-Enhanced Raman Scattering. *J. Micromech. Microeng.* **2012**, *22*, 125007.
(2) Abdelsalam, M. E.; Mahajan, S.; Bartlett, P. N.; Baumberg, J. J.; Russell, A. E. SERS at Structured Palladium and Platinum Surfaces. *J. Am. Chem. Soc.* **2007**, *129*, 7399−7406.
(3) Choi, D.; Choi, Y.; Hong, S.; Kang, T.; Lee, L. P. Self-Organized Hexagonal-Nanopore SERS Array. *Small* **2010**, *6*, 1741−1744.
(4) Cheng, J. Y.; Ross, C. A.; Chan, V. Z.; Thomas, E. L.; Lammertink, R. G.; Vancso, G. J. Formation of a Cobalt Magnetic Dot Array Via Block Copolymer Lithography. *Adv. Mater.* **2001**, *13*, 1174−1178.
(5) Haes, A. J.; Van Duyne, R. P. A Nanoscale Optical Biosensor: Sensitivity and Selectivity of an Approach Based on the Localized Surface Plasmon Resonance Spectroscopy of Triangular Silver Nanoparticles. *J. Am. Chem. Soc.* **2002**, *124*, 10596−10604.
(6) Menezes, J. W.; Ferreira, J.; Santos, M.; Cescato, L.; Brolo, A. G. Large-Area Fabrication of Periodic Arrays of Nanoholes in Metal Films and Their Application in Biosensing and Plasmonic-Enhanced Photovoltaics. *Adv. Funct. Mater.* **2010**, *20*, 3918−3924.
(7) Holgado, M.; Barrios, C. A.; Ortega, F. J.; Sanza, F. J.; Casquel, R.; Laguna, M. F.; Banuls, M. J.; Lopez-Romero, D.; Puchades, R.; Maquieira, A. Label-Free Biosensing by Means of Periodic Lattices of High Aspect Ratio Su-8 Nano-Pillars. *Biosens. Bioelectron.* **2010**, *25*, 2553−2558.
(8) Wallraff, G. M.; Hinsberg, W. D. Lithographic Imaging Techniques for the Formation of Nanoscopic Features. *Chem. Rev.* **1999**, *99*, 1801−1821.
(9) Zheng, Y.; Shi, J.; Juluri, B. K.; Huang, T. J. Ordered Au Nanodisk and Nanohole Arrays: Fabrications and Applications. *J. Nanotechnol. Eng. Med.* **2010**, *1*, 031011.
(10) Deckman, H. W.; Dunsmuir, J. H. Natural Lithography. *Appl. Phys. Lett.* **1982**, *41*, 377−379.
(11) Winzer, M.; Kleiber, M.; Dix, N.; Wiesendanger, R. Rapid Communication Fabrication of Nano-Dot-and Nano-Ring-Arrays by Nanosphere Lithography. *Appl. Phys. A: Mater. Sci. Process.* **1996**, *63*, 617−619.
(12) Jensen, T. R.; Duval, M. L.; Kelly, K. L.; Lazarides, A. A.; Schatz, G. C.; Van Duyne, R. P. Nanosphere Lithography: Effect of the External Dielectric Medium on the Surface Plasmon Resonance Spectrum of a Periodic Array of Silver Nanoparticles. *J. Phys. Chem. B* **1999**, *103*, 9846−9853.
(13) Li, L.; Zhai, T. Y.; Zeng, H. B.; Fang, X. S.; Bando, Y.; Golberg, D. Polystyrene Sphere-Assisted One-Dimensional Nanostructure Arrays: Synthesis and Applications. *J. Mater. Chem.* **2011**, *21*, 40−56.
(14) Li, Z.; Liu, P.; Liu, Y.; Chen, W.; Wang, G. Fabrication of Size-Controllable Fe_2O_3 Nanoring Array via Colloidal Lithography. *Nanoscale* **2011**, *3*, 2743−2747.
(15) Jia, L.; Cai, W.; Wang, H.; Sun, F.; Li, Y. Hetero-Apertured Micro/Nanostructured Ordered Porous Array: Layer-by-Layered Construction and Structure-Induced Sensing Parameter Controllability. *ACS Nano* **2009**, *3*, 2697−2705.
(16) Jia, L.; Cai, W. Micro/Nanostructured Ordered Porous Films and Their Structurally Induced Control of the Gas Sensing Performances. *Adv. Funct. Mater.* **2010**, *20*, 3765−3773.
(17) Cao, B.; Cai, W.; Sun, F.; Li, Y.; Lei, Y.; Zhang, L. Fabrication of Large-Scale Zinc Oxide Ordered Pore Arrays with Controllable Morphology. *Chem. Commun.* **2004**, 1604−1605.
(18) Bartlett, P. N.; Birkin, P. R.; Ghanem, M. A. Electrochemical Deposition of Macroporous Platinum, Palladium and Cobalt Films Using Polystyrene Latex Sphere Templates. *Chem. Commun.* **2000**, 1671−1672.
(19) Abdelsalam, M. E.; Bartlett, P. N.; Baumberg, J. J.; Coyle, S. Preparation of Arrays of Isolated Spherical Cavities by Self-Assembly of Polystyrene Spheres on Self-Assembled Pre-Patterned Macroporous Films. *Adv. Mater.* **2004**, *16*, 90−93.
(20) Duan, G.; Cai, W.; Li, Y.; Li, Z.; Cao, B.; Luo, Y. Transferable Ordered Ni Hollow Sphere Arrays Induced by Electrodeposition on Colloidal Monolayer. *J. Phys. Chem. B* **2006**, *110*, 7184−7188.
(21) Duan, G.; Cai, W.; Luo, Y.; Sun, F. A Hierarchically Structured $Ni(OH)_2$ Monolayer Hollow-Sphere Array and its Tunable Optical Properties over a Large Region. *Adv. Funct. Mater.* **2007**, *17*, 644−650.
(22) Zhang, G.; Wang, D. Fabrication of Heterogeneous Binary Arrays of Nanoparticles via Colloidal Lithography. *J. Am. Chem. Soc.* **2008**, *130*, 5616−5617.
(23) Haynes, C. L.; Van Duyne, R. P. Dichroic Optical Properties of Extended Nanostructures Fabricated Using Angle-Resolved Nanosphere Lithography. *Nano Lett.* **2003**, *3*, 939−943.
(24) Gwinner, M. C.; Koroknay, E.; Fu, L.; Patoka, P.; Kandulski, W.; Giersig, M.; Giessen, H. Periodic Large-Area Metallic Split-Ring Resonator Metamaterial Fabrication Based on Shadow Nanosphere Lithography. *Small* **2009**, *5*, 400−406.
(25) Kosiorek, A.; Kandulski, W.; Glaczynska, H.; Giersig, M. Fabrication of Nanoscale Rings, Dots, and Rods by Combining Shadow Nanosphere Lithography and Annealed Polystyrene Nanosphere Masks. *Small* **2005**, *1*, 439−444.
(26) Li, Y.; Fang, X.; Koshizaki, N.; Sasaki, T.; Li, L.; Gao, S.; Shimizu, Y.; Bando, Y.; Golberg, D. Periodic TiO_2 Nanorod Arrays with Hexagonal Nonclose-Packed Arrangements: Excellent Field Emitters by Parameter Optimization. *Adv. Funct. Mater.* **2009**, *19*, 2467−2473.
(27) Li, Y.; Sasaki, T.; Shimizu, Y.; Koshizaki, N. A Hierarchically Ordered TiO_2 Hemispherical Particle Array with Hexagonal-Non-Close-Packed Tops: Synthesis and Stable Superhydrophilicity without UV Irradiation. *Small* **2008**, *4*, 2286−2291.
(28) Li, Y.; Sasaki, T.; Shimizu, Y.; Koshizaki, N. Hexagonal-Close-Packed, Hierarchical Amorphous TiO_2 Nanocolumn Arrays: Transferability, Enhanced Photocatalytic Activity, and Superamphiphilicity without UV Irradiation. *J. Am. Chem. Soc.* **2008**, *130*, 14755−14762.
(29) Li, L.; Li, Y.; Gao, S.; Koshizaki, N. Ordered Co_3O_4 Hierarchical Nanorod Arrays: Tunable Superhydrophilicity without UV Irradiation and Transition to Superhydrophobicity. *J. Mater. Chem.* **2009**, *19*, 8366−8371.
(30) Li, Y.; Cai, W.; Duan, G.; Cao, B.; Sun, F.; Lu, F. Superhydrophobicity of 2D ZnO Ordered Pore Arrays Formed by Solution-Dipping Template Method. *J. Colloid Interface Sci.* **2005**, *287*, 634−639.
(31) Yu, Q. M.; Guan, P.; Qin, D.; Golden, G.; Wallace, P. M. Inverted Size-Dependence of Surface-Enhanced Raman Scattering on Gold Nanohole and Nanodisk Arrays. *Nano Lett.* **2008**, *8*, 1923−1928.
(32) Brolo, A. G.; Arctander, E.; Gordon, R.; Leathem, B.; Kavanagh, K. L. Nanohole-Enhanced Raman Scattering. *Nano Lett.* **2004**, *4*, 2015−2018.
(33) Masson, J. F.; Murray-Methot, M. P.; Live, L. S. Nanohole Arrays in Chemical Analysis: Manufacturing Methods and Applications. *Analyst* **2010**, *135*, 1483−1489.
(34) Park, T. H.; Mirin, N.; Lassiter, J. B.; Nehl, C. L.; Halas, N. J.; Nordlander, P. Optical Properties of a Nanosized Hole in a Thin Metallic Film. *ACS Nano* **2008**, *2*, 25−32.
(35) Hutter, E.; Fendler, J. H. Exploitation of Localized Surface Plasmon Resonance. *Adv. Mater.* **2004**, *16*, 1685−1706.
(36) Zheng, Y. B.; Jensen, L.; Yan, W.; Walker, T. R.; Juluri, B. K.; Jensen, L.; Huang, T. J. Chemically Tuning the Localized Surface Plasmon Resonances of Gold Nanostructure Arrays. *J. Phys. Chem. C* **2009**, *113*, 7019−7024.
(37) Sun, C.-H.; Min, W.; Jiang, P. Templated Fabrication of Sub-100 nm Periodic Nanostructures. *Chem. Commun.* **2008**, 3163−3165.
(38) Coïsson, M.; Boarino, L.; Celegato, F.; De Leo, N.; Tiberto, P.; Vinai, F. Exchange Bias in Nanopatterned Co Antidots Prepared by

Self-Assembling Polystyrene Nanospheres. *J. Nanopart. Res.* **2011**, *13*, 5641−5651.
(39) Tiberto, P.; Boarino, L.; Celegato, F.; Coisson, M.; Enrico, E.; De Leo, N.; Vinai, F.; Allia, P. Synthesis of Ni80Fe20 and Co Nanodot Arrays by Self-Assembling of Polystyrene Nanospheres: Magnetic and Microstructural Properties. *J. Nanopart. Res.* **2011**, *13*, 4211−4218.
(40) Wang, J.; Duan, G.; Liu, G.; Li, Y.; Dai, Z.; Zhang, H.; Cai, W. Gold Quasi Rod-Shaped Nanoparticle-Built Hierarchically Micro/Nanostructured Pore Array via Clean Electrodeposition on a Colloidal Monolayer and its Structurally Enhanced SERS Performance. *J. Mater. Chem.* **2011**, *21*, 8816−8821.
(41) Dai, Z.; Li, Y.; Duan, G.; Jia, L.; Cai, W. Phase Diagram, Design of Monolayer Binary Colloidal Crystals, and Their Fabrication Based on Ethanol-Assisted Self-Assembly at the Air/Water Interface. *ACS Nano* **2012**, *6*, 6706−6716.
(42) Sun, F.; Cai, W.; Li, Y.; Cao, B.; Lu, F.; Duan, G.; Zhang, L. Morphology Control and Transferability of Ordered through-Pore Arrays Based on Electrodeposition and Colloidal Monolayers. *Adv. Mater.* **2004**, *16*, 1116−1121.
(43) McLellan, J. M.; Geissler, M.; Xia, Y. Edge Spreading Lithography and its Application to the Fabrication of Mesoscopic Gold and Silver Rings. *J. Am. Chem. Soc.* **2004**, *126*, 10830−10831.
(44) Geissler, M.; Wolf, H.; Stutz, R.; Delamarche, E.; Grummt, U. W.; Michel, B.; Bietsch, A. Fabrication of Metal Nanowires Using Microcontact Printing. *Langmuir* **2003**, *19*, 6301−6311.
(45) Duan, G.; Lv, F.; Cai, W.; Luo, Y.; Li, Y.; Liu, G. General Synthesis of 2D Ordered Hollow Sphere Arrays Based on Nonshadow Deposition Dominated Colloidal Lithography. *Langmuir* **2010**, *26*, 6295−6302.
(46) Ghanem, M. A.; Bartlett, P. N.; Groot, P.; Zhukov, A. A Double Templated Electrodeposition Method for the Fabrication of Arrays of Metal Nanodots. *Electrochem. Commun.* **2004**, *6*, 447−453.
(47) Sun, F.; Cai, W.; Li, Y.; Cao, B.; Lei, Y.; Zhang, L. Morphology-Controlled Growth of Large-Area Two-Dimensional Ordered Pore Arrays. *Adv. Funct. Mater.* **2004**, *14*, 283−288.
(48) Li, Y.; Cai, W. P.; Cao, B. Q.; Duan, G. T.; Sun, F. Q. Fabrication of the Periodic Nanopillar Arrays by Heat-Induced Deformation of 2D Polymer Colloidal Monolayer. *Polymer* **2005**, *46*, 12033−12036.