AN EFFECTIVE TOOL TO CONTROL SPATIAL RESOLUTION COLLOID LITHOGRAPHY

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Abstract

Polymer-based colloid lithography represents the very effective approach for creation of a large-scale template for subsequent surface modification. Utilization of this approach, however, is significantly restricted by the ability of used micro/nanospheres to create only limited number of symmetrical structures. In this work, we propose the treatment of polystyrene (PS) microspheres in the solvent vapor, before subsequent surface grafting with diazonium salts as an alternative method for the creation of structures with required geometry and symmetry. Application of vapor treatment allows the effective modification of PS microspheres screened area and. As a result, the subsequent grafting procedure leads to the creation of ordered micropores array with tunable size and height. Combination of different solvents with slight heating was studied and found to be suitable for further creation of different surface grafting pattern. The success of surface grafting through the treated PS microsphere mask was verified using Raman spectroscopy and AFM microscopy techniques.

Keywords: Colloid lithography; polystyrene microspheres; vapor annealing; periodical structures

1. INTRODUCTION

The physicochemical methods of surface modification changing surface morphology or chemistry provide a unique way of creation of new materials with functional surfaces [1-4]. As examples, the introduction of superhydrophilicity/phobicity, water or oil adhesion and repellence, specific chemical recognition events, externally triggered or self-related smart surface response, as well as many other useful surface singularities can be mentioned [5-10]. Among the common techniques for the introduction of specific surface properties different masks-based approaches, where the material is area-selective chemically modified are of considerable importance [11-13]. In this field even, the colloid lithography can be considered as one of the more common approach due to its simplicity and reliability [13-16]. In particular, deposited by spin- or deep-coating polymer latex microspheres tends to spontaneously form the ordered array on the samples surface, effectively creating the mask for further surface pattering [17,18] Thus, this simple lithographic approach has been commonly applied for the preparation of ordered microporous structures via the surface modification through the polymer microspheres mask and subsequent surface modification or electrodeposition of metals [19-23].

In this paper, we propose an alternative approach, enhancing the range of surface patterns accessible by the common polystyrene (PS) colloid lithography. Vapor annealing of closed packed polymer microspheres array deposited on the gold substrate is used. Deformation and conglutination of microspheres depending on the applied solvent and partial pressure is expected, leading to the effective modification of uncovered by PS microspheres gold surface, available for further grafting by a diazonium salt.

2. EXPERIMENTAL

2.1. Materials

Gold targets for metals deposition (purity of metals 4 N) were purchased from Safina. Deionized water, methanol (reagent grade, ≥ 99.8 %), acetone (97 %), 4-nitrobenzenediazonium tosylate, toluene (99 %) were

purchased from Sigma-Aldrich and used without further purification. Colloid suspension of polystyrene (PS) microspheres (PS microspheres size - 500 nm) was supplied by Alfa Aesar.

2.2. Samples preparation

Thin gold films (thickness 20 nm) were deposited onto glass surface (Thermo Scientific), covered by adhesive titanium layer (thickness ca 10 nm), using thermal evaporation method. PS suspension was drop deposited and slowly evaporated on Au surface, under the careful control of temperature (40°C). After deposition of PS colloid mask, samples were annealed in (i) toluene (≈0.01 and ≈0.03 bar partial pressure) or (ii) ethanol vapors (≈0.02 and ≈0.05 bar partial pressure) during 10 min. The 4-nitrobenzenediazonium tosylate (ADT-NO_2) salt was grafted electrochemically (4 mM freshly prepared water solutions, -1.0 V, 7 min) through the annealed PS microspheres mask. After grafting, the PS mask was removed by rinsing in the toluene under sonication for 10 min. Then the metal substrates were sequentially rinsed under sonication with deionized water, ethanol, and acetone for 10 min and dried in a desiccator for 3 h.

2.3. Measurement techniques

For the characterization of the sample surface, the atomic peak force microscopy (AFM) technique was used. Surface mapping was performed with Icon (Bruker) set-up on the areas of 3×3 μm^2 Surface conductivity characterization was performed in Peak Tuna AFM mode, using the Pt/Pd coated tip with constant voltage (3.0 V). Raman spectra were measured on ProRaman-L (Laser power 30 mW) Raman spectrometer with 785 nm excitation wavelengths. Spectra were measured 30 times, each of them with 3 s accumulation time.

3. RESULTS AND DISCUSSION

The array of PS latex microspheres was deposited on the Au surface and a closely spaced periodical structure with hexagonal symmetry was formed, according the previous experiments. The samples were then annealed in the vapors of organic solvents (ethanol or toluene) with the aim to initiate PS microspheres swelling and partial conglutination. After the probing of several organic solvents, we chose for further experiments the toluene and ethanol, which conserve the PS microspheres periodicity and do not create periodical structure irregularities. It was previously expected that vapor-initiated conglutination of PS microspheres could lead to changes in the tuning of PS microspheres screened surface area. In the next step, the electrochemical surface grafting by ADT-NO_2, through the pristine or vapor annealed PS masks, followed by sequential removing of microspheres was applied.

First, the grafting of organic moities to tjhe gold surface was verified using the Raman spectroscopy. Results are presented in the **Figure 1** and it is evident that after the grafting procedure, the Raman bands, typical for C_6H_4-NO_2 becomes apparent. In particular, the Raman spectra show the presence of following characteristic peaks: 482 cm^{-1} (C-N bending); 637 cm^{-1} (NO_2 def vib, in-plane Ar_{C-C}); 795 cm^{-1} (Ar_{C-H} out of plane def); 830 cm^{-1} (NO_2 scissors bending); 868 cm^{-1} (Ar_{C-H} out of plane def); 1046 cm^{-1}, 1075 cm^{-1} (Ar_{C-H} in plane bends); 1334 cm^{-1}, 1352 cm^{-1} (NO_2 symmetric stretch); 1520 cm^{-1}, 1554 cm^{-1} (Ar_{C-C} ring deformation). Additionally, it is evident that Raman bands intensities are a strong function of previous vapor treatment of PS microspheres. The greatest intensities were observed in the case of nontreated PS microspheres mask, which indicate the attachment of largest amount of organic moieties. In turn, grafting through the PS mask annealed in the ethanol vapor leads to a peak intensity decrease, which is proportional to partial solvent pressure. Even more pronounced decrease of Raman bands intensity is also observed for the grafting through PS microspheres array annealed in toluene. It is evident that at higher toluene partial pressure the Raman bands become barely noticeable. So, we can conclude that the highest amount of organic moieties was grafted in the case of nontreated PS microsphere, while the annealing in the ethanol leads to a slight decrease in the amount of grafted organic moieties, and the annealing with toluene significantly screens the Au surface against grafting.

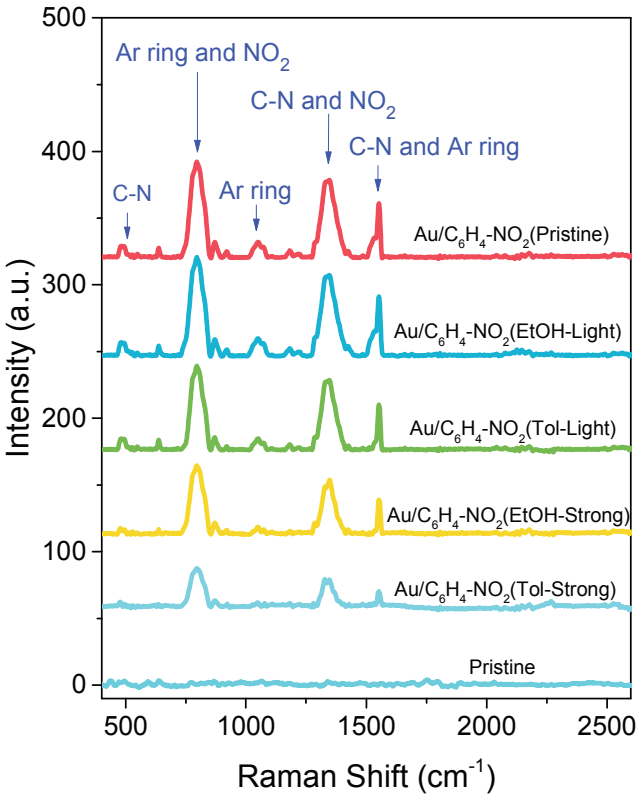

Figure 1 Raman spectroscopy measurements performed after the ADT-NO2 grafting through the pristine and vapor annealed PS colloid mask

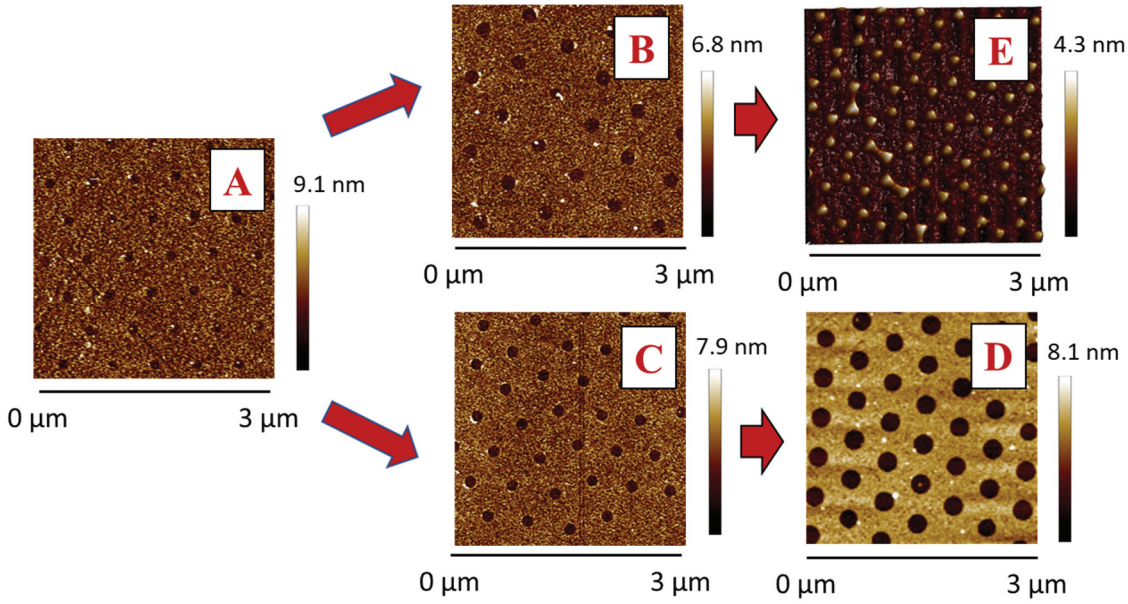

Figure 2 AFM characterization of grafted through the PS microspheres masks gold surface, measured after the removing of PS microspheres: A - ADT-NO_2 grafting through the pristine PS mask, B - ADT-NO_2 grafting through the annealed (ethanol, partial pressure ≈0.02 bar) PS mask, C - ADT-NO_2 grafting through the annealed (ethanol, partial pressure ≈0.05 bar) PS mask, D - ADT-NO_2 grafting through the annealed (toluol, partial pressure ≈0.01 bar) PS mask, E - ADT-NO_2 grafting through the annealed (toluol, ≈0.03 bar) PS mask.

The different residual surface patterns, determined by the surface regions “available” for ADT-NO2 grafting, were created after the PS microspheres removal, according the AFM results (**Figure 2**), in dependence on the applied vapor annealing procedure. In particular, the strong vapor annealing conditions (i.e. utilization of high solvent pressure and/or solvent with high affinity to PS microspheres) lad to almost full surface blocking and the grafting through such “strongly-annealed” structure produced the columnar-like pattern (as is evident in thre **Figure 2E**). Oppositely, the softer annealing conditions resulted in the slight increase of the area screened by PS microspheres and the pores, remained on the surface have larger size compared to the case of nontreated PS (**Figures 2B, 2C**).

Generalizing the AFM investigations, it can be concluded that the formation of bi-dimensional well-ordered pores with a regular round shape and size determined by the previous vapor annealing procedure was observed. In the case of nonannealed PS microspheres, the diameter of the pores was found to be 0.10 μm, and it increases with increasing ethanol vapor pressure (**Figure 2D**). The high surface blocking in the case of toluene vapors utilization leads to the grafting of organic layers in a columnar form. The thickness of the grafted organic layer was also estimated from z-axis scale bars on the presented AFM scans and as can be expected the thickness decreases with increasing impact of organic vapor.

4. CONCLUSION

In this work, we propose the vapor annealing of ordered PS microspheres array, followed by the diazonium surface modification as an alternative possibility to effective tune the PS microspheres screened surface area and altering of the size of created surface chemical and morphological pattern. The grafting through the polymer colloid mask procedure results in the creation of ordered micropores array with tunable size or, moreover, columnar array. Combination of ethanol and toluene solvents with slight heating (40^{o} C) was founded to be the more suitable for PS microspheres blocked surface area.

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REFERENCES

[1] BELANGER, Daniel, PINSON, Jean. Electrografting: a powerful method for surface modification. Chem. Soc. Rev. 2011. 40, pp. 3995-4048.

[2] PINSON, Jean, PODVORICA, Fetah. Attachment of organic layers to conductive or semiconductive surfaces by reduction of diazonium salts. Chem. Soc. Rev. 2005. 34, pp. 429-439.

[3] LYUTAKOV, Oleksiy, HUTTEL, Ivan, SIEGEL, Jakub, ŠVORČÍK, Vaclav. Regular surface grating on doped polymer induced by laser scanning. Appl. Phys. Lett. 2009. 95, 173103.

[4] GUSELNIKOVA, Olga, POSTNIKOV, Pavel, KALACHYOVA, Yevgeniya, KOLSKA, Zdenka, LIBANSKY, Milan, ZIMA, Jiri, ŠVORČÍK, Vaclav, LYUTAKOV, Oleksiy. Large-Scale, Ultrasensitive, Highly Reproducible and Reusable Smart SERS Platform Based on PNIPAm-Grafted Gold Grating. CHEMNANOMAT 2017. 3, 2, pp. 135-144.

[5] UEDA, Erica, LEVKIN, Pavel A. Emerging Applications of Superhydrophilic-Superhydrophobic Micropatterns. Adv. Mater. 2013. 25, pp. 1234-1247.

[6] ZHANG, Xi, SHI, Feng, NIU, Jia, JIANG, Yugui, WANG, Zhigiang. Superhydrophobic surfaces: from structural control to functional application. J. Mater. Chem. 2008. 18, pp. 621-633.

[7] ZHANG, Junji, MA, Wenjing, HE, Xiao-Peng, TIAN, He. Taking Orders from Light: Photo-Switchable Working/Inactive Smart Surfaces for Protein and Cell Adhesion. ACS Appl. Mater. Interfaces. 2017. 9, pp. 8498-8507.

[8] GUSELNIKOVA, Olga, POSTNIKOV, Pavel, SAJDL, Petr, ELASHNIKOV, Roman, ŠVORČÍK, Vaclav, LYUTAKOV, Oleksiy. Functional and Switchable Amphiphilic PMMA Surface Prepared by 3D Selective Modification. Adv. Mater. Interfaces. 2018. 5, 1701182

[9] ELASHNIKOV, Roman, TRELIN, Andrej, OTTA, J., FITL, P., MARES, D., JERABEK, V., ŠVORČÍK, Vaclav, LYUTAKOV, Oleksiy. Laser patterning of transparent polymers assisted by plasmon excitation. SOFT MATTER 2018. 14, 23, pp. 4860-4865.

[10] Slepicka, Petr, Siegel, Jakub, Lyutakov, Oleksiy, Kasalkova, Nikola, Kolska, Zdenka, Bacakova, Lucie, Svorcik, Vaclav. Polymer nanostructures for bioapplications induced by laser treatment. Biotechnology Adv. 2018. 36, 3, pp. 839-855.

[11] LEDERHOSE, Paul, ABT, Doris, WELLE, Alexander, MÜLLER, Rouven, BARNER-KOWOLLIK, Christopher, BLINCO, James P. Exploiting λ-Orthogonal Photoligation for Layered Surface Patterning. Chem. Eur. J. 2018. 24, pp. 576-580.

[12] FORNER-CUENCA, A.; MANZI-OREZZOLI, V.; KRISTIANSEN, P. M.; GUBLER, L.; SCHMIDT, T. J.; BOILLAT, P. Mask-assisted electron radiation grafting for localized through-volume modification of porous substrates: influence of electron energy on spatial resolution. Radiat. Phys. Chem. 2017. 135, pp. 133-141.

[13] WANG, Yuli, LAI, Hsuan-Hong, BACHMAN, Mark, SIMS, Christopher E.; LI, G. P.; ALLBRITTON, Nancy L. Covalent micropatterning of poly (dimethylsiloxane) by photografting through a mask. Anal. Chem. 2005. 77, pp. 7539-7546.

[14] YANG, Seung-Man, JANG, Se Gyu, CHOI, Dae-Geun, KIM, Sarah, YU, Hyung Kyun. Nanomachining by colloidal lithography. Small 2006. 2, pp. 458-475.

[15] HOOGENBOOM, J. P.; VOSSEN, D. L. J.; FAIVRE-MOSKALENKO, C.; DOGTEROM, M.; BLAADEREN, A. V. Patterning surfaces with colloidal particles using optical tweezers. Appl. Phys. Lett. 2002. 80, 4828-4830.

[16] LIN, Meng-Hsien; CHEN, Chi-Fan, SHIU, Hung-Wei, CHEN, Chia-Hao, GWO, Shangjr. Multilength-scale chemical patterning of self-assembled monolayers by spatially controlled plasma exposure: nanometer to centimeter range. J. Amer. Chem. Soc. 2009. 131, pp. 10984-10991.

[17] GOSECKA, Monika, GRIFFETE, Nebewia, MANGENEY, Claire, CHEHIMI, Mohamed M, SLOMKOWSKI, Stanislaw, BASINSKA, Teresa. Preparation and optical properties of novel bioactive photonic crystals obtained from core-shell poly (styrene/α-tert-butoxy-ω-vinylbenzyl-polyglycidol) microspheres. Colloid Polym. Sci. 2011. 289, 1511-1518.

[18] NGUYEN, Van-Quynh, SCHAMING, Delphine, TRAN, Dai Lam, LACROIX, Jean-Christophere. Ordered Nanoporous Thin Films by Nanosphere Lithography and Diazonium Electroreduction: Simple Elaboration of Ultra-Micro-Electrode Arrays. ChemElectroChem. 2016. 3, pp. 2264-2269.

[19] ZHANG, Junhu, LI, Yunfeng, ZHANG, Xuemin, YANG, Bai. Colloidal self-assembly meets nanofabrication: From two-dimensional colloidal crystals to nanostructure arrays. Adv. Mater. 2010. 22, pp. 4249-4269.

[20] BARTLETT, Philip N.; BIRKIN, Peter R.; GHANEM, Mohamed A. Electrochemical deposition of macroporous platinum, palladium and cobalt films using polystyrene latex sphere templates. Chem. Commun. 2000. pp. 1671-1672.

[21] BARTLETT, P. N.; BAUMBERG, J. J.; BIRKIN, P. R.; GHANEM, M. A.; NETTI, M. C. Highly Ordered Macroporous Gold and Platinum Films Formed by Electrochemical Deposition through Templates Assembled from Submicron Diameter Monodisperse Polystyrene Spheres. Chem. Mater. 2002. 14, pp. 2199-2208.

[22] HU, Jin, ABDELSALAM, Mamdouh, BARTLETT, Philip, COLE, Robin, SUGAWARA, Yoshihiro, BAUMBERG, Jeremy, MAHAJAN, Sumeet, DENUAULT, Guy. Electrodeposition of highly ordered macroporous iridium oxide through self-assembled colloidal templates. J. Mater. Chem. 2009. 19, pp. 3855-3858.

[23] CAO, Bingqiang, CAI, Weiping, SUN, Fengqiang, LI, Yue, LEI, Yong, ZHANG, Lide. Fabrication of large-scale zinc oxide ordered pore arrays with controllable morphology. Chem. Commun. 2004, pp. 1604-1605.