ADVANCED COLLOID LITHOGRAPHY FOR SURFACE FUNCTIONALIZATION - EXPANDING THE CURRENT STATE OF THE ART

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https://doi.org/10.37904/nanocon.2019.8623

Abstract

Creation of hydrophobic and hydrophilic surfaces with the spatially selective distribution of grafted organic moieties have great potential in the field of medicine and avionics. The one of more scalable approaches for spatially selective surface modification is based on colloid lithography, which allows large throughput for the subsequent surface grafting and realization of periodic chemical pattern. In this work, we demonstrated the spatially-selective surface grafting by ADT salt with hydrophobic -C_8F_{17} or hydrophilic -COOH groups using following procedure: (i) deposition of PS colloid suspension on substrate; (ii) electrochemical modification of surface with diazonium salt; (iii) removing of PS mask; (iv) second electrochemical modification with diazonium salt. The surface modification through the mask was controlled by PS size, that allowed tuning the area, covered in the first stage of grafting. The modified surface morphology and chemistry was measured by IR spectroscopy and AFM microscopy. Proposed approach allows to effectively decorate surface with different chemical groups in an accurate and precise manner, with additional feature of their mutual “periodic” arrangement.

Keywords: Colloid lithography, 2D arrays of colloidal spheres formation, Polystyrene microspheres, Periodical structures, Double modification

INTRODUCTION

In recent years, the creation of new functional surfaces has become one of the urgent tasks in surface science and engineering [1-3]. Especially attractive are surfaces, having various and spatially-varied properties, for example combination of hydrophilic and hydrophobic grafted chemical moieties. Such surface can found their implementation in medicine (tissue engineering, DNA separation and analysis) and avionics (icephobic phenomena), as well as serves as templates for further deposition of self-assembled materials. [4,5] Modulation of surface chemistry can be performed with utilization of a number of lithographic methods, such as photolithography, electron beam lithography, focused ion beam lithography, and soft lithography [6,7]. One of the cheapest ways to obtain a nanostructured surface is to create a surface using a bottom-up approach with utilization of self-assembled colloid mask. The main advantages of this method is its simplicity and technical scalability [8-10].

In this work, we propose the next step for controlling the surface chemistry using the two-step modification through the PS (polystyrene) microspheres colloid mask. An electrochemical modification of aryl with aryldiazonium tozylates having various properties is used for spatial-selective grafting of hydrophobic and hydrophilic chemical moieties and creation of amphiphilic surface.

1. EXPERIMENTAL

1.1. Materials

Gold targets for metal deposition (purity of metals, 4 N) were purchased from Safina. Deionized water, methanol (reagent grade, ≥99.8%), acetone (97%), and toluene (99%) were purchased from Sigma-Aldrich and used without further purification. Colloid suspension of PS microspheres (PS microspheres size, 500 nm) was supplied by Alfa Aesar. 4-carboxybenzenediazonium tosylate (ADT-COOH) and 4-(heptadecafluorooctyl)benzenediazonium tosylate (ADT-C_8F_{17}) were prepared by the procedure reported in ref [11,12].

1.2. Sample preparation

Thin gold films with thickness ca. 40 nm were deposited onto glass surface (Thermo Scientific) using thermal eva[poration method. PS suspension was dropwise deposited and slowly evaporated on modified Au surface in air under careful control of temperature 40 °C. Then the ADT-COOH (or ADT-C_8F_{17}) salt was grafted electrochemically (4 mM freshly prepared water solutions, −4.0 V applied potential, 2 min) through the PS microspheres mask. After grafting, the PS mask was removed by rinsing with toluene under sonication for 10 min. Then, the metal substrates were sequentially rinsed with deionized water, ethanol, and acetone for 10 min and dried in a desiccator for 3 h. Secondly, the samples were electrochemically grafted with ADT-C_8F_{17} (or ADT-COOH) salt using electrochemical approach (4 mM freshly prepared water solutions, −4.0 V applied potential, 2 min) - see **Figure 1**.

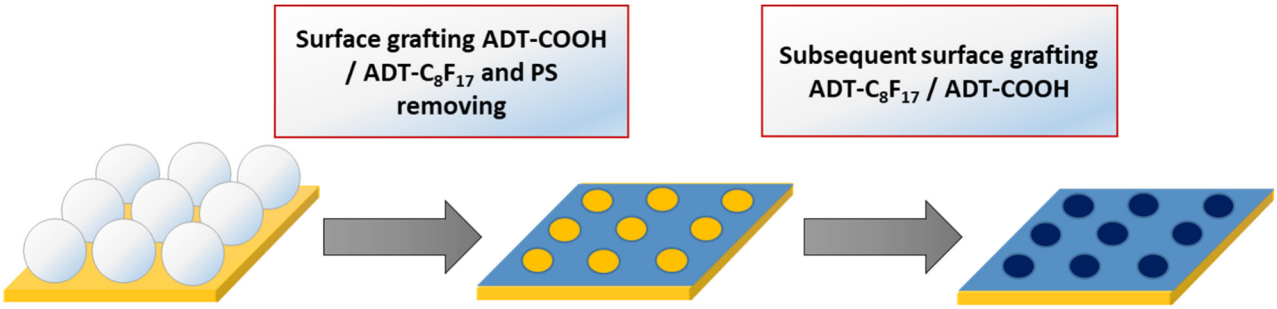

Figure 1 Schematic representation of proposed approach

1.3. Measurement Techniques

For the characterization of the sample surface, the atomic peak force microscopy (AFM) technique was used. Surface mapping was performed with the Icon (Bruker) setup in an area of 3 × 3 μm^2. Surface conductivity characterization was performed in PeakForce Tuna AFM mode, using the Pt/Pd-coated tip with constant voltage (3.0 V).

Fourier transform infrared (FT-IR) spectroscopy was measured on Nicolet iS5 Spectrometer. All measurements were performed in the 600 to 4000 cm^{-1} wavenumber range with 4 cm^{-1} resolution.

2. RESULTS AND DISCUSSION

Figure 2A shows the AFM image of the uniform distribution of PS microspheres on the surface of a gold film. Next, we performed modification of gold film through the PS mask by ADT salts with hydrophobic -C8F17 (**Figure 2B**) or hydrophilic -COOH groups (**Figure 2C**). After electrochemical grafting, the PS microspheres were removed by washing with toluene to reveal the underlying electrodeposited materials. After removal of the PS mask, uniform homogeneous surface structuring was observed. As can be seen from the figure the

size of holes on the surface after the modification with -COOH groups is smaller than the pore size obtained after the modification with -C8F17 groups, which can be attributed to the hydrophilic properties of -COOH groups. At the second stage of the work, further cross-modification of the obtained surfaces was carried out to create a needle-like structure of surfaces with amphiphilic properties (**Figures 2D, 2E**).

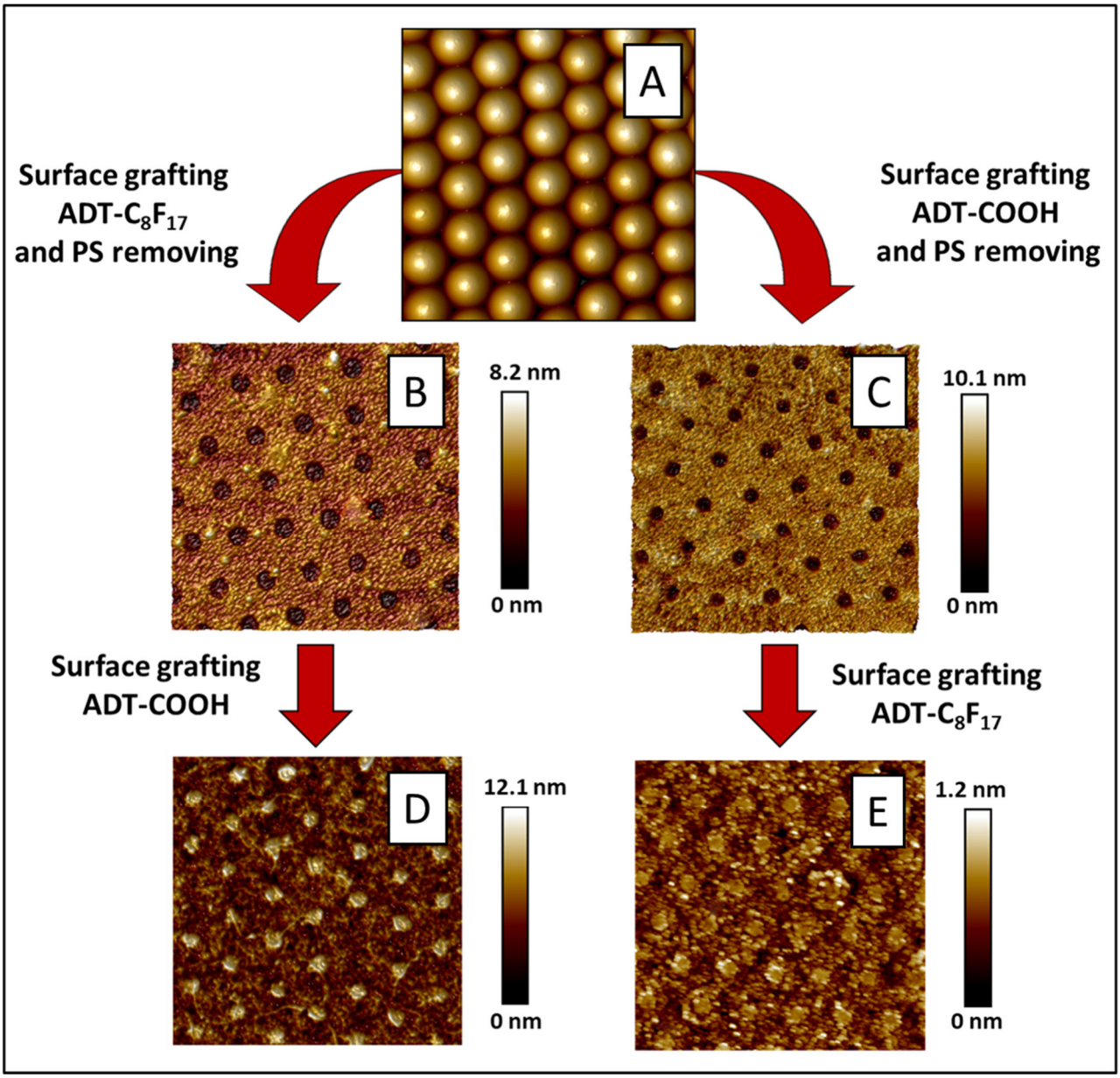

Figure 2 AFM characterization of grafted through the PS microspheres masks gold surface, measured after the removing of PS microspheres: (i) - ADT-COOH / ADT-C_8F_{17} grafting through the pristine PS mask, (ii) - Subsequent surface grafting ADT-C_8F_{17} / ADT-COOH

To prove successful modification, the resulting samples were analyzed by FT-IR spectroscopy technique. As is evident from the **Figure 3**, after the grafting procedure, the Raman bands, typical for ADT-COOH and ADT-C_8F_{17} become apparent. Characteristic bands are designated by arrows. The obtained results confirm a grafting during the both stages of surface modification.

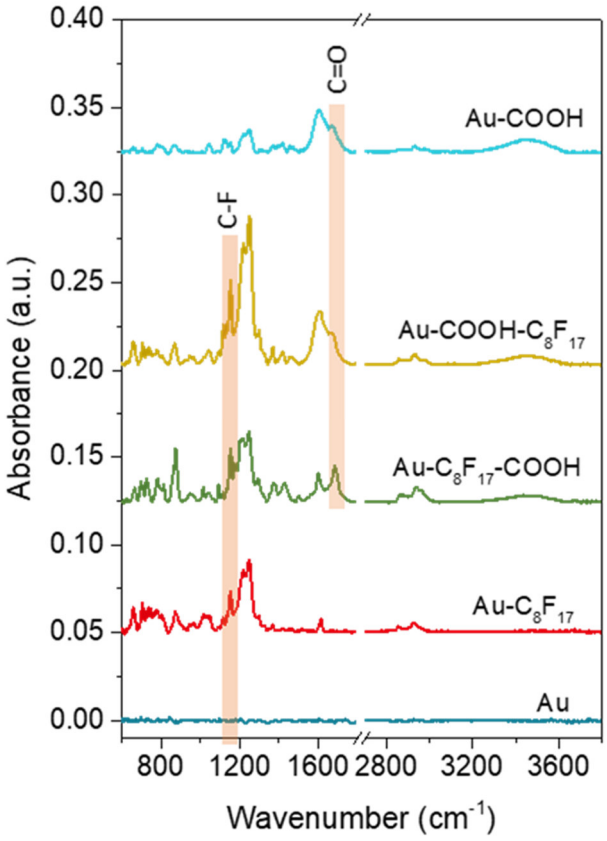

Figure 3 FT-IK spectroscopy measurements performed after the ADT-COOH / ADT-C_8F_{17} grafting through the pristine and vapor-annealed PS colloid mask, and after IK measurements performed the ADT-C_8F_{17} / ADT-COOH

3. CONCLUSION

In this work, we demonstrated the spatially selective surface grafting by ADT salt with hydrophobic -C_8F_{17} or hydrophilic -COOH groups. As a result of PS mask application, the grafting procedure creates an ordered array of micropores or, moreover, a columnar array. Our work illustrates a generalization of the modified colloidal template methodology for the production of monolayer microporous structures with a large surface area. The proposed method was extended to decorate surface with various compounds in a two-step procedure with an adjustable ratio of surface concentrations and thickness and creation of an amphiphilic artificial surface.

ACKNOWLEDGEMENTS

This work was supported by under the project Internal Grant Agency UCT № 126 88 1908.

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