



Full Length Article

Mixed-solvent precipitation: A facile approach for nanoparticle self-assembled monolayers



Shan Wu^{a,1}, Guanbin Gao^{a,1,*}, Shasha Zhang^c, Wenbo Zhu^b, Liang Wang^b, Rui Chen^b,
Wenkang Zhang^a, Juncheng Wang^a, Feifei Yang^b, Jing Li^a, Lei Shen^b, Taolei Sun^{a,b,*}

^a State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, No. 122 Luoshi Road, Wuhan 430070, People's Republic of China

^b School of Chemistry, Chemical Engineering and Life Science, Wuhan University of Technology, No. 122 Luoshi Road, Wuhan 430070, People's Republic of China

^c School of Arts and Media, Wuhan Vocational College of Software and Engineering, No. 117 Guanggu Road, Wuhan 430205, People's Republic of China

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ABSTRACT

Nanoparticle self-assembled monolayers (Nano-SAMs) have drawn great attention for their unique applications in many fields such as plasma, surface-enhanced optics, sensors and catalysts. However, how to fabricate high-coverage and densely-packed Nano-SAMs in a limited time is still a challenge, especially for the ultra-thin Nano-SAMs (< 10 nm). In this paper, high-coverage and densely-packed ultrathin Nano-SAMs were fabricated by using ultra-small nanoparticles (e.g. nanoclusters and quantum dots) to deposit onto substrates in organic/water mixture via the continuous dropping of organic solvent. Compared with the conventional methods such as the electrophoresis deposition and the soaking method, nanoparticles could formed higher coverage and more densely-packed Nano-SAMs with few defects through a shorter period of time by using this mixed-solvent precipitation method. This mixed-solvent precipitation presents a facile approach to design and construct high-coverage densely-packed Nano-SAMs.

1. Introduction

As a promising two-dimensional functional nanostructure materials [1–8], self-assembled monolayers of nanoparticles (Nano-SAMs [6,9–22]) have drawn great attention in recent years. Due to their ability of converting chemical, optical and biological signals [23] into readable electrical signals, Nano-SAMs have many applications [23–30] such as catalysis, nanoelectronics, optoelectronics, energy conversion, molecular recognition bio-electrochemical and many other fields. A large number of Nano-SAMs have been successfully fabricated with nanomaterials containing abundant different organic and inorganic components [31,32]. In the last half century, a series of “bottom-up” [33] methods have emerged to construct the Nano-SAMs on different substrates, including the Langmuir-Blodgett (LB) method [1,3,34–36], the Electrophoresis deposition method [37–39], the template-based method [40], the solvent evaporation method [41], etc. Though these methods have been used to construct many different Nano-SAMs, there are two key issues that have not been solved: (1) stringent ultrathin monolayer, (2) particles compactly arranged on the surface of

substrates. Take Langmuir-Blodgett method for example, the 2D arrays [6] on two-phase boundary usually form islands-like non-close-packed film in the process of transferred onto the substrate [21]. On the other hand, the rising of applications in chemical, optical and biological field in the last two decades have always asked for reform of the fabrication method, which should be progressively improved to get higher coverage and more densely-packed Nano-SAMs. For example, superior imaging performance of magnetic force microscopy called for higher coverage and more densely-packed Nano-SAMs of magnetic nanoparticles to be used as an ideal substrate [28]. Thus how to achieve high-coverage and densely-packed ultrathin Nano-SAMs is still a challenge up to now.

Here we reported a facile method—mixed-solvent precipitation method for constructing high-coverage and densely-packed ultrathin self-assembled monolayer of nanoparticles. Firstly, clean ultra-flat substrates were immersed in the good solvent of ultra-small nanoparticles, then the bad solvent of this nanoparticles were continuously dropped into the mixed-solution, after a few minutes, the ultrathin Nano-SAMs were formed on the surface of the substrates with the

* Corresponding authors at: State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, No. 122 Luoshi Road, Wuhan 430070, People's Republic of China (G. Gao and T. Sun).

E-mail addresses: gbgao@whut.edu.cn (G. Gao), suntl@whut.edu.cn (T. Sun).

¹ These authors contribute equally to this work.

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precipitation of the ultra-small nanoparticles. High resolution images from the transmission electron microscopy (TEM), Atomic force microscopy (AFM) and total internal reflection fluorescence microscopy (TIRFM) showed that the Nano-SAMs fabricated by this mixed-solvent precipitation were high-coverage and densely-packed. This mixed-solvent precipitation method is based on the principle of minimum energy and the solubility differences of ultra-small nanoparticles in diverse solvents. It is widely known that “the energy of system will drop to a minimum value at equilibrium”. Here the arrangement of the nanoparticles in the Nano-SAMs also follows this universal law of nature. It should be noted that the coating of the ligands on the surfaces of nanoparticles created a space barrier which prevented accumulation and agglomeration of the inorganic cores and ended to the stable dispersion in the good solvents. When the bad solvents of the nanoparticles were continuously dropped into the mixed-solution, the normal thermal motion of nanoparticles in the mixed solvents sharply decreased; the nanoparticles would adjust their positions to minimize their energies that corresponding to entropy increase [42], until they form a low-energy, self-organized pattern on the surfaces of the nanomices [43] which generated by the bad solvent aggregating in the good solvent. Then, large numbers of these nanomices integrated with each other to form larger micelles, and finally these micelles coated with nanoparticles deposited on the substrates to attain Nano-SAMs with the lowest energy state. This is consistent with Yan’s [42] previous reports in which they pointed out that the entropy acted as the driving force to tune the spatial organization of NPs to make the particles became as crowded as possible, though it seems to be at odds with the essence of self-assembly: a disordered system forms an organized structure [42]. This work presents a handy method to design and construct ultrathin self-assembled monolayer of nanoparticles.

2. Experimental

2.1. Materials

Chloroauric acid ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 99.9%), $\text{C}_7\text{H}_{13}\text{NO}_3\text{S}$ (97.0%) were purchased from Sigma-Aldrich (NJ, USA). Sodium borohydride ($\text{NaBH}_4 \geq 96.0\%$), HgCl_2 (AR), tetramethyl ammonium hydroxide ($\text{C}_4\text{H}_{13}\text{NO}$ water solution), glacial acetic acid, and $\text{Na}_2\text{S}_9\text{H}_2\text{O}$ were purchased from Sinopharm Chemical Reagent Co., Ltd (Beijing, China). Hydrochloric acid, nitric acid, anhydrous ethanol, anhydrous methanol, sodium hydroxide, glacial acetic acid, sulfuric acid were of analytical grade. Captopril (Cap) was purchased from Adamas. The ultrapure water used was from the Millipore Milli-Q ultrapure water system. All the reaction vessels used were soaked in aqua regia (volume ratio 3:1, HCl/HNO_3) overnight, washed thoroughly with ultrapure water several times and dried in an oven before use. Muscovite Mica (size 25×75 mm) was purchased from Electron Microscopy Sciences (USA). The AuNCs (1.1 ± 0.5 nm) and $\beta\text{-HgS@ZnS}$ QDs (4.0 ± 1.0 nm) were prepared according to our previous works [44–47].

2.2. Mixed-solvent precipitation method to fabricate Nano-SAMs

Clean substrates (freshly cleaved mica sheet, ultra-thin carbon film, ultra-flat quartz film, NH_2 -modified Si substrates, etc.) were immersed in the AuNCs aqueous solution with a pH of 10, (good solvent for AuNCs) with different concentrations of AuNCs (200, 100, 20 and 10 mg/L). Then the organic solvent acetone (bad solvent for AuNCs) were continuously dropped into the solution system. With the precipitation of the AuNCs in the mixed-solvent, the ultrathin AuNCs-SAMs onto different substrates were successfully prepared after 5 min. And then the substrates were removed out and dried naturally in a clean environment for further study.

Similar operations were applied on the $\beta\text{-HgS@ZnS}$ QDs-SAMs. Clean substrates (freshly cleaved mica sheet, ultra-thin carbon film, ultra-flat quartz film) were immersed in the 100 mg/L $\beta\text{-HgS@ZnS}$ QDs

aqueous solution (good solvent for $\beta\text{-HgS@ZnS}$ QDs). Then organic solvent acetone (bad solvent for $\beta\text{-HgS@ZnS}$ QDs) were continuously dropped into the solution system. Remove the substrates to a clean environment and dry naturally after 5 min, the ultrathin $\beta\text{-HgS@ZnS}$ QDs-SAMs were formed on the substrates with the precipitation of the $\beta\text{-HgS@ZnS}$ QDs.

2.3. Electrophoresis deposition method to fabricate nano-SAMs

Due to the existence of $-\text{COOH}$ in the $\text{C}_7\text{H}_{13}\text{NO}_3\text{S}$, the surface of AuNCs modified by this ligand is negatively charged. To fabricate AuNCs-SAMs on mica sheet by this Electrophoresis deposition method, a positive electrode was placed on the back of mica sheet. The negatively charged AuNCs gradually electrophoresed to the positive electrode with the additional voltage on and precipitated on the mica sheet [48]. The power supply adopted the ZDA200-220S series from the Dalian-Electronic Technology Company (input voltage 220 V AC 50/60 Hz; output voltage 5–100 kV). The voltage strength and the concentration of AuNCs aqueous solution with a pH of 10 been used here were 4 kV and 20 mg/L. Control the lasting time of high voltage applied (3 min, 5 min), then remove the mica sheet out of the AuNCs solution. Dry those samples in a clean environment for further study.

2.4. Soaking method to fabricate nano-SAMs

Freshly cleaved mica sheets were immersed into the AuNCs aqueous solution with a pH of 10 with two concentrations of 100 and 20 mg/L, respectively. The substrates were removed out after 12 h and dried naturally in a clean environment for further study.

2.5. TEM measurement

TEM measurements were performed on the JEOL 200CXTEM (JEOL Ltd, Tokyo, Japan) with an accelerating voltage of 100 kV. Observation of samples with randomly selected of the grid areas were essential for the purpose of reduce imaging bias.

2.6. SEM measurement

The surface morphologies of the samples were observed by a Hitachi S-4800 field emission scanning electron microscope (SEM) at an acceleration voltage of 4.0 kV.

2.7. EDS measurement

The element contents of samples were measured by Genesis energy dispersive X-Ray spectroscopy cooperated with SEM at an acceleration voltage of 4.0 kV.

2.8. AFM measurement

AFM (manufactured by Bruker AG, FastScan model) experiments were performed in air mode at room temperature. The scan conditions are as follows: the scanning mode is AAC mode, the scanning speed is 3.95 Hz, the probe model is BRUKER SNL-10-A (f_0 : 50–80 kHz, k : 0.350 N/m), the resonant frequency is 1.3 MHz, the positioning detection noise: $X\text{-}Y \leq 0.15$ nm RMS, $Z = 35$ pm RMS.

2.9. TIRFM measurement

TIRFM measurements were performed on a commercial instrument based on an inverted microscope (Nikon) at room temperature (25 °C). A green He-Ne laser ($\lambda_{\text{exc}} = 532$ nm) was directed to a $100 \times$ objective (Nikon, PlanApo TIRF, NA = 1.45) with a higher angle than the critical angle and a fluorescence image was obtained on CCD.

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