

Fabrications of Bifunctional Janus and Triblock Saturn Colloids

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ABSTRACT

A synthetic approach for the fabrications of Janus and Saturn colloids was demonstrated by the sequential embedment and surface modification of silica colloids. Electrospinning of poly(methyl methacrylate) (PMMA) and poly(4-vinyl pyridine) (P4VP) blends produced polymer fibers with high specific surfaces for the colloid adsorption and embedment. Colloid adsorption on fiber surfaces was established by the interaction between silanol and pyridine groups located on silica and P4VP, respectively. The thermally-induced colloid embedding was precisely manipulated by the heat treatment, which allowed the uniform and controllable colloid embedding. The exposed colloid surfaces were selectively modified by the chemical vapor deposition of silanes with desired functional groups, followed by labeling with magnetite or gold nanoparticles. Synthesis of bifunctional Janus and triblock Saturn colloids were demonstrated and discussed.

Keywords: Janus Colloids, Saturn Colloids, Electrospinning, Colloid Embedding, Asymmetric Nanomaterials

1 INTRODUCTION

Particles with two hemispheres in different chemical, physical or geometric properties are often referred as Janus particles [1]. These particles carry not only two different functionalities, but also the spatial distribution on particle surfaces. These kinds of colloids attracted significant attention because of their potential applications in dual-functional devices, building materials for supra-structures [2][3], electronic papers [4], surfactants for pickling emulsions [5], biomaterials [6], photovoltaics, and nano-probes [7][8].

Efficient productions of Janus particles with desired two-hemispheric features are the crucial issues as reported elsewhere [1][9][10]. An instinctive method is to confine monodispersed colloids at the interface between two phases [11], followed by the functionalization of hemispheric surfaces individually. To achieve the mass production, a large amount of surface area as the working substrates is needed. Thus, a polymer-based electrospinning [11] technique was employed for the fabrication of polymer fibers, containing high surface-to-volume ratios. The electrospinning process involves the utilizing an electrostatic attraction between a charged polymer medium and a ground electrode where a high voltage is applied in between (see the apparatus in Figure 1). Electrospinning

occurs when the surface tension and viscoelastic forces of a polymer medium is defeated by the electrical charge. A highly charged polymer jet is then ejected and forms solidified nanofibers as the solvents evaporate.

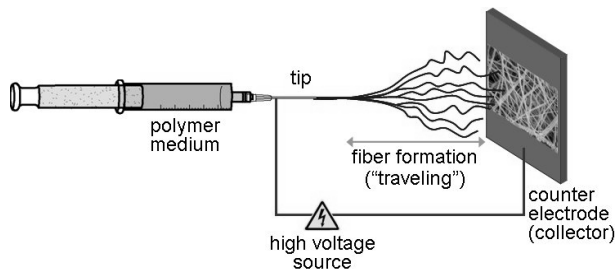


Figure 1: Electrospinning apparatus and process for the polymer fiber fabrications.

In recent years, the electrospinning technique was utilized for the applications involving both colloids and polymeric fibers [12][13]. Thermally-induced embedding of colloids on the surfaces of polymer fibers was conducted to attach and stabilize colloids at air/polymer interfaces. In the embedding process, controlling parameters included the embedding temperatures, the glass transition temperatures (T_g) of polymers, the adhesion between colloid/polymer interfaces, the attraction forces, and the thermodynamic factors [14].

The temperature-sensitive embedding process between colloids and electrospun polymer fiber mats was carefully investigated. It was important to control the polymer softening from the thermodynamic point of view, as well as to maintain the fiber morphologies without melting. Once the colloid embedding process was completed, the exposed surfaces of embedded colloids were modified via the chemical vapor deposition of desired functional groups, so that a thin layer of nanoparticles could attach onto the modified surfaces. Finally, colloids with symmetric or asymmetric functionality were retrieved by dissolving the polymer fiber mats in organic solvents.

In this research work, two immiscible polymers, poly(methyl methacrylate) (PMMA) and poly(4-vinyl pyridine) (P4VP), with opposite hydrophobic/hydrophilic properties were blended and dissolved in co-solvents of DMF/MEK. Composite electrospun fiber mats provided stable scaffolds and a large amount of surface area to confine colloids. Following colloid embedding was carefully manipulated by isothermal treatments at desired temperatures. Colloid embedding at certain degrees can be achieved. The exposed surfaces of embedded colloids were selectively modified by the chemical vapor deposition of 3-aminopropyltrimethoxysilane (3-APTMS). Uniform

functionalization of symmetric and asymmetric Janus colloids were further confirmed by the attachment of gold nanoparticles onto the amino-enriched surfaces. Eventually, polymeric fiber mats were dissolved in organic solvents, and Janus or Saturn-like colloids with symmetric or asymmetric functionality were recovered.

2 EXPERIMENTAL SECTION

Two different polymers were used for preparation of electrospun fibers, poly(methyl methacrylate) (PMMA, Mw = 120,000, Aldrich) and poly(4-vinylpyridine) (P4VP, Mw = 60,000, Aldrich). Methyl Ethyl Ketone (MEK, J.T. Baker), N,N-dimethylformamide (DMF, Fluka), 3-aminopropyltrimethoxysilane (3-APTMS, Fluka), Chloroauric acid \cdot 3H₂O (HAuCl₄ \cdot 3H₂O, Alfa Aesar), and Sodium citrate \cdot 2H₂O (J.T. Baker) were used as received. SiO₂ colloids with diameter of 500 nm were obtained from Alfa Aesar.

With ultrasonic treatment, silica colloids were cleaned in the mixture of 5 wt% aqueous NaOH and ethanol (1:1 by volume), followed by deionized water (DI water) washing and centrifuge eight times. Cleaned SiO₂ colloids were dispersed in DI water to form 1 wt% silica/DI water solution.

A general method was applied to produce uniform gold nanoparticles around 10 nm [15]. A 114 mL HAuCl₄ aqueous solution (1 mM) was vigorously stirred and heated to 80°C. A rapid addition of 11.4 mL sodium citrate aqueous solution (38.8 mM) to the HAuCl₄ solution resulted in the color change from yellow to burgundy. After 15 min heating, the solution was cooled down to room temperature. The resulting gold nanoparticle solution was stored in a refrigerator for future uses.

Three polymer solutions were formulated for the polymer electrospinning. PMMA was dissolved in DMF:MEK (1:1 by volume) to form 20.6 wt% of PMMA solution. P4VP was dissolved in the same co-solvent with concentration of 31.5 wt%. PMMA/P4VP (1:1 by weight) blend in the co-solvent resulted in 26.5 wt% of solution.

Three polymer solutions described above were electrospun under the high voltage of 10 kV. The ejection flow rate during the electrospinning process was controlled in the range of 15 ~ 35 μ l/min by using a syringe pump. The inside diameter of steel needle was 0.9 mm, and the distance from needle to ground was about 15 cm. The metallic target as the grounded counter electrode was the copper foil which was covered by aluminum foil. The average diameter of these electrospun fibers was about 3 μ m, according to the SEM examinations.

Three fiber mats were then dipped into the 1 wt% of silica colloid solution for 10 min, following by the DI water rinsing for several times. The removal of moisture contain was ensured by the vacuum at room temperature and the sample storage in a desiccator for 24 hours. Thermally-induced colloid embedding was conducted by the 4-hour

isothermal treatment at 120°C and 135°C to achieve 1/3 and 1/2 colloid embeddings.

Chemical vapor deposition of amino-silane (3-APTMS) was utilized for the silanization on the exposed silica surfaces. An aqueous solution containing gold nanoparticles was then introduced to label the amino-enriched silica surfaces. After that, electrospun polymer fiber mats were dissolved in acetone/ethanol solution to recover the modified silica particles. Additional solvent washing to the Janus particles was applied for several times.

3 RESULTS AND DISCUSSIONS

Silica surfaces after the base solution and DI water cleaning process were enriched with silanol groups [16]. The silanol as a weak acid group provided the ionic interaction with the pyridine groups located on P4VP molecular chains [17]. P4VP itself is a hydrophilic polymer which is unstable while being dipped into the silica-dispersed aqueous solution. As shown in Figure 2, the pure P4VP fiber surfaces effectively captured the silica colloids from their suspension aqueous solution. However, the poor moisture resistance of P4VP has failed to maintain the original fiber scaffolds.

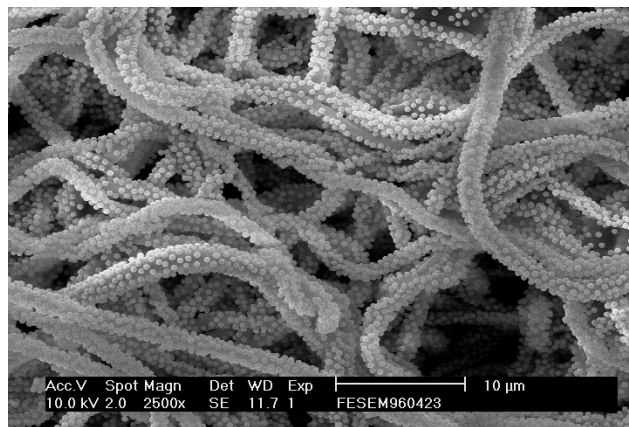


Figure 2: The adsorption of silica colloids on P4VP fiber mats via a solution dipping process.

The addition of hydrophobic PMMA component in the P4VP polymer fibers became essential in terms of the fiber reinforcement to the dipping process in an aqueous solution, while the P4VP domains still served as the active surface for the colloid adsorption. Dipping process in an aqueous silica suspension and the following thermal treatments at 120°C or 135°C revealed no significant damage to the polymer scaffolds. Presumably, the P4VP domain was responsible for the silica colloid adsorption. And, the PMMA component improved the resistance to the aqueous solutions. As shown in Figure 3, PMMA/P4VP (1:1) fiber mats demonstrated the evenly distributed colloid adsorption on fiber surfaces. And, the dipping process in the aqueous solution showed no effect to the polymer fiber scaffolds.

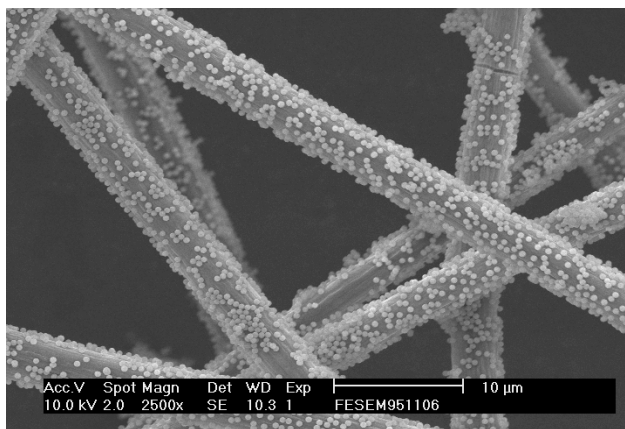


Figure 3: The adsorption of silica colloids on PMMA/P4VP fiber mats via a solution dipping process.

According to the previous report [12], electrospun fibers consisted of PMMA and P4VP blends also had the advantage of broadening the colloid embedding degree as a function of heating temperatures. Uniform colloid embeddings from 1/3 to 2/3 were achieved at the heating temperatures from 120°C to 150°C. The phase separation in electrospun PMMA/P4VP fibers [18] was also carefully investigated. The polymer domains in PMMA/P4VP fibers were found to be about 60 nm, which was much smaller than the diameter of silica colloids. Therefore, the silica colloid adsorption on fiber surfaces showed no preference to the P4VP domains. Presumably, the P4VP domains were responsible for the adsorption of silica colloids, and PMMA phase prevented the fiber softening from the solvent swelling. Well-dispersed silica colloids in the aqueous suspensions prevented the formation of silica clusters. Therefore, extra silica colloids which did not directly attach to polymer fiber surfaces were easily removed by the solution washing process. Interesting enough, the attached silica colloids tended to line-up along with the direction of electrospun polymer fibers.

Silica colloid embedding on the surface of PMMA/P4VP fibers was manipulated by the isothermal temperatures. As shown in Figure 4, the isothermal treatments at 120°C, 135°C, and 150°C resulted in the 1/3, 1/2 and 2/3 colloid embedding, respectively. At 120°C, PMMA/P4VP polymer fibers had reached the glass transition temperature of PMMA at about 115°C, which provided the initiation of polymer softening. Continuous colloid embedding was further encouraged as the increase of heating temperature. The half colloid embedding was achieved at the isothermal temperature at 135°C, which was between the two glass transition temperatures of PMMA and P4VP. Above the glass transition temperature of P4VP domain at about 145°C, the significant polymer softening gave the 2/3 colloid embedding.

After the colloid embedding process, the CVD surface modification by using the amino-silane was conducted to complete the hemispheric surface coating. Electrospun fiber mats were excellent 3-dimensional scaffolds allowing the gas phase agents to pass through. CVD process,

therefore, ensured the uniform surface modification with desired silane thicknesses. Similar advantage was also available in the solution washing process.

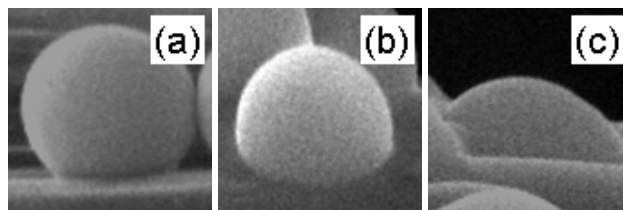


Figure 4: Colloid embedding as a function of heating temperature. (120°C, 135°C, and 150°C, respectively)

Additional labeling with gold nanoparticles to the amino-enriched silica surfaces was carried out for the easy identification of surface functionalities on silica surfaces. Gold nanoparticles in an aqueous suspension were introduced to the hemispheric embedded silica colloids. Gold nanoparticles then were caught by the amino groups, which in fact illustrated the recognizable multiple surfaces in TEM images.

Resulting colloids were recovered by dissolving the polymer fibers in the acetone/ethanol co-solvent, followed by the centrifuge separation. Additional washing with the same co-solvent was conducted for five more times to ensure the removal of polymer residuals and other contaminations on colloid surfaces. Figure 5 illustrated the TEM images of symmetric and asymmetric Janus colloids with gold nanoparticle attachment on 2/3 and 1/2 colloid surfaces.

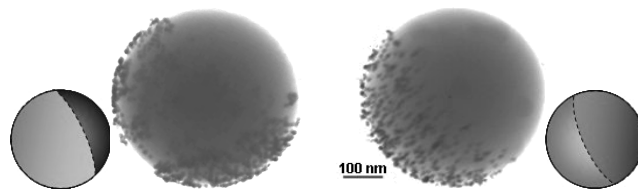


Figure 5: An asymmetric Janus colloid (left, 2/3 surface-functionalized) and a symmetric Janus colloid (right, 1/2 surface-functionalized).

Statistics for the colloid submerging was estimated by analyzing the diameters of exposed hemispheres in the SEM images. For the 1/2 embedded colloids, the diameters of silica hemispheres with observable submerged margins were outlined and measured. Even though the margins of colloids with less than 50 % submerging were theoretically not observable in SEM images, this analytical approach provided practical statistic accuracy. Based on the evaluation of more than 200 submerged colloids, it was found that 90 % of exposed hemispheres contained the diameters in the range of 500 ± 25 nm, i.e. within 5 % tolerance. Meanwhile, due to the large fiber surface area and the uniform colloid adsorption on fiber surfaces, it was then calculated that more than 10^9 silica colloids could be embedded from 1 mg of electrospun polymer fibers in this high productive fabrication approach.

Using this novel colloid embedding and surface modification process, tri-block Saturn colloids can be also

fabricated. Careful temperature controls in the heating process manipulated and achieved the uniform particle embedment. With these advantages, Figure 6 illustrated the procedure of making tri-block Saturn colloids. Sequential colloid embedding and surface modification allow the precise surface functionalities with desired hemispherical ratios or multiple sections.

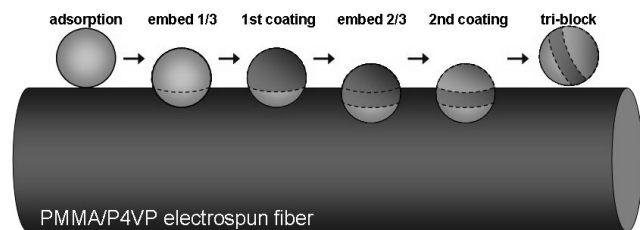


Figure 6: Fabrication of tri-block Saturn particles from the surface of electrospun polymer fibers.

4 CONCLUSIONS

In this research work, symmetric and asymmetric Janus colloids were successfully demonstrated. Using the PMMA and P4VP polymer blends, the electrospun fiber mats with desired surface properties were utilized for the silica colloid adsorption and embedding. Following surface modifications via the amino-silane CVD process completed the hemispheric surface functionalities. Gold nanoparticles were introduced to label the amino-enriched silica surfaces. Isothermal treatment at the desired temperatures manipulated the colloid submerging degrees. The symmetric and asymmetric Janus colloids and the tri-block Saturn colloids became possible.

5 ACKNOWLEDGEMENT

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