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Combination of Bioinspiration: A General Route to Superhydrophobic Particles

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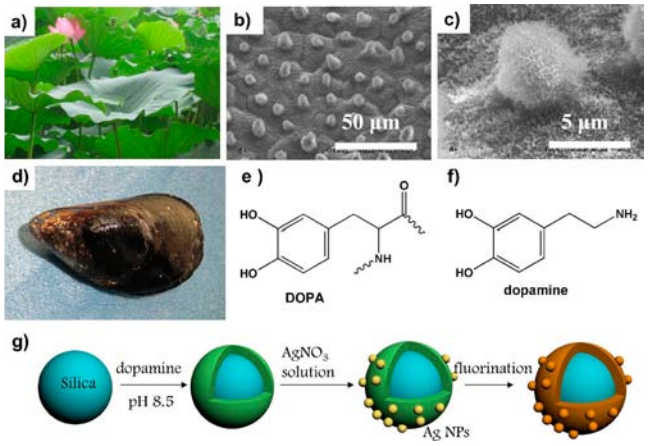
Supporting Information

ABSTRACT: We combine two amazing abilities found in nature: the superhydrophobic property of lotus leaf and the adhesive ability of mussel adhesive protein. The molecular structure mimic of the single units of adhesive proteins, dopamine, was polymerized in an alkaline aqueous solution to encapsulate microparticles. The as-formed thin polydopamine walls worked as reactive templates to generate silver nanoparticles on the capsuled particles. As a result, core/shell/satellite composite particles were generated with a hierarchical structure similar to the micromorphology of lotus leaf. The composite particles exhibited extremely water repellence after fluorination. Because dopamine can deposit and adhere to all kinds of materials, this method can be applied to diverse microparticles, from organic to inorganic. In addition, particles of different sizes and matters can be modified to superhydrophobic particles in one pot. Magnetic particles have also been prepared which could be used as oil-absorbent and magnetic controlled carriers. "Oil marbles" formed underwater were achieved for the first time.

Scheme 1. Nature Origins and the Formation Process of Bio-Inspired Superhydrophobic Particles[a]



[a](a) Photograph of lotus leaf, and SEM photographs of the surface of (b) a lotus leaf and (c) a single papilla. (d) Photograph of a mussel, and chemical structures of (e) DOPA in the mussel adhesive protein and (f) dopamine. (g) Schematic drawing of the synthesis procedure of SiO_2/PD/Ag superhydrophobic particle.

The wettability of microparticles is of great concern because it has a large impact on other related physical and chemical processes, such as adhesion, lubrication, catalysis, and friction. Nature has been a valuable and innovative source of inspiration for scientists due to the amazing properties of biological systems. An important school of biomimicry focuses on mimicking the biostructures with special wettability. One of the most well-known examples is the lotus leaf on which water droplets can ball up and roll off effortless. The extreme water repellent behavior comes from the low surface energy of the botanical wax on the leaf and, more importantly, the unique micronano hierarchical structure constructed by the sparsely populated micropapillae with nanosized wax crystals (Scheme 1a−c).[1] Lotus leaf is the prototype of a superhydrophobic surface, which is defined as a surface with a water contact angle (CA) larger than 150°.[2] Superhydrophobicity promises plenty of valuable usages in practice, such as self-cleaning,[3] drag reduction,[4] energy restoration, and antifouling.[5] Although many efforts have been devoted to preparation of superhydrophobic surfaces,[6] the methods reported were mainly focused on using one or one class of substance. A general method of developing superhydrophobic ability without considering the nature of the targeted materials has seldom been reported.

The bioadhesion of marine organisms, such as mussels, has also drawn strong interest in the last decades (Scheme 1d). Mussels can achieve long-lasting adhesion in wet environment and tether to all kinds of substrates based on the proteins secreted by the byssus.[7] The adhesive proteins have been discovered containing high levels of L-3,4-dihydroxyphenylalanine (DOPA),[8] which is believed to contribute to the cross-linking of the proteins and forming strong covalent and noncovalent interactions with surfaces (Scheme 1e). Messersmith and co-workers[9] identified dopamine (Scheme 1f) as a structural mimic of DOPA and demonstrated dopamine could polymerize and deposit on all kinds of organic and inorganic surfaces, including "nonsticking surfaces" such as poly(tetrafluoroethylene). The resultant polydopamine (PD) is of chemical versatility which can be used as a platform for diverse secondary reactions. Recently, dopamine has found a large area

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of applications in encapsulation, free radical scavenging, biomineralization, carbon precursor, and so on.[10]

Herein, we incorporated the two separate but equally attractive biomimetic subjects together, combining the remarkable adhesive ability of dopamine with a lotus-leaf-like structure to develop a universal route to ultrawater repellent particles. The whole procedure was conducted under a mild environment, and no intricate instruments were needed. Particles of different sizes and chemical compositions, from organic to inorganic, can be modified to superhydrophobic separately or together. And by employing a designated core material, multifunctional microparticles could be achieved. Superhydrophobic magnetic particles were developed as an example, and potential application of these multifunctional particles in oil/water separation was demonstrated.

A typical procedure of preparing the water repellent particles is shown in Scheme 1g. In a basic environment, dopamine spontaneously polymerizes into PD and deposits on the core particles. Then silver nanoparticles (Ag NPs) are formed by reduction and located on the outer surface of PD walls. Both PD and Ag NPs can react with alkanethiol.[9] After modified, the resultant hierarchical particles with 1H,1H,2H,2H-perfluorodecanethiol, superhydrophobic SiO_2/PD/Ag hybrid particles are produced.

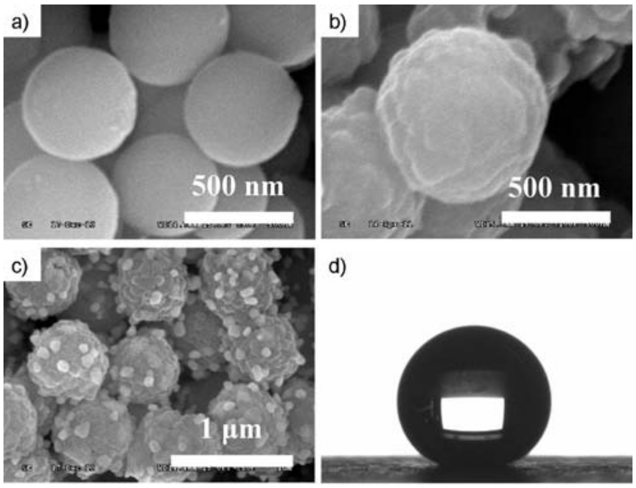

Figure 1. SEM photographs of (a) 500 nm SiO_2, (b) SiO_2 @PD, and (c) SiO_2/PD/Ag NPs particles. (d) Image of a water droplet sitting on the superhydrophobic particles composed surface.

Silica particles of 500 nm in diameter (Figure 1a) were dispersed in dopamine solution at pH of 8.5. After 12 h, the particles showed a rough surface, indicating the capsulation of PD (Figure 1b). The irregularity of the surface resulted from the dopamine particulates from assembly.[11] The polymerization mechanism of dopamine was hypothesized to contain the oxidation of catechol to quinone, intermolecules cross-linking reactions, such as aryl−aryl coupling, Michael addition reaction, and Schiff base substitution.[9,12] The SiO_2@PD microparticles were then reacted with Ag^+ in $AgNO_3$ solution. Due to the reductive capability of PD, no additional reducing agent is needed.[13] Separated Ag NPs with ca. 100 nm in size are formed on the shells after reduction (Figure 1c). The SiO_2@PD particles and Ag NPs served as the first and secondary structure to build a two-tier roughness mimicking the micromorphology of lotus leaf. Each step of the fabrication process is examined by XPS (Supporting Information (SI), Figure S1). After modification with thiol fluoroalkanes, surface composed of the particles shows a water CA of 171.0 ± 2.0° (Figure 1d). The advancing and receding CA of the surface are 171.9 ± 0.9° and 170.0 ± 1.2°, respectively. Water droplets roll off the surface easily. The interplay of dual-scale structure and low surface free energy contributes to this ultrawater repellent state.[14] The SiO_2@PD particles without Ag NPs were also modified by 1H,1H,2H,2H-perfluorodecanethiol, and the CA of the modified particles surface was measured at 138.6 ± 1.5°. This result shows the two-tier structure has great effect on the wettability. During the modification of the microparticles by polydopamine, aggregation of the particles may take place. However, the aggregation only leads to formation of some larger aggregates, which still can be modified to be hierarchically structured superhydrophobic particles without affecting the wettability of the final product.

This strategy is proven to be applicable to various particles with different sizes and chemical compositions. Silica particles with different sizes, polymethylsilsesquioxane (PMSQ) and polystyrene (PS) particles, were coated with PD and Ag NPs, respectively. Surfaces constructed by these particles all have water CAs larger than 150° and little CA hysteresis. (SI, Figure S2 and Table S1). Polycaprolactone (PCL) particles were also modified by this method, and the CA was measured at 141.6 ± 0.1°. Furthermore, different core particles can be modified in one pot (Figure 2). The hierarchical-structured particulates with cores of 2 μm PS, 700 nm PMSQ, and 300 nm SiO_2 particles are formed together in one mixture, demonstrating the versatility of this method regardless of the nature and size of the particles. This result has an incredible benefit for fabricating superhydrophobic surfaces. Hydrophilic defect is a serious problem of superhydrophobic surface in practical usage. Water is inclined to attach to the hydrophilic area, impairing the water proof ability. But in this method, dopamine tends to polymerize and deposit on all of the particles in the raw material, leaving no particles unmodified. Therefore, no hydrophilic particles would remain in the final product harming the superhydrophobic ability. Moreover, one pot fabrication allows integrating multifunctions from different substances to aim at multitasking in a single procedure.

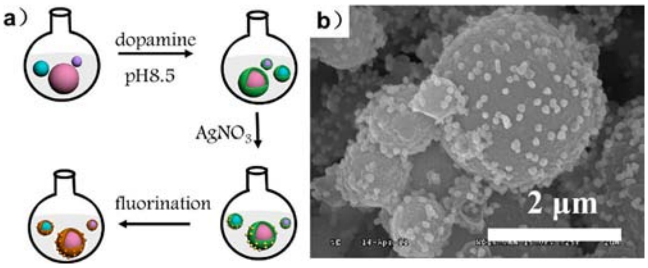

Figure 2. (a) Scheme and (b) SEM photograph of 2 μm PS, 700 nm PMSQ, and 300 nm SiO_2 particles coated with dopamine and Ag NPs in one pot.

To illustrate the versatility of the method of combining other function with superhydrophobicity, magnetic superhydrophobic particles were achieved using carbonyl iron particles as the core material. The particle-composed surface has a water CA as high as 159.6°, whereas CA of oil is nearly 0° (SI, Figure S3). This character can offer application in oil/water separation.[15] As shown in Figure 3a, a drop of oil, which has been dyed red, was dropped on the water surface, and then the magnetic

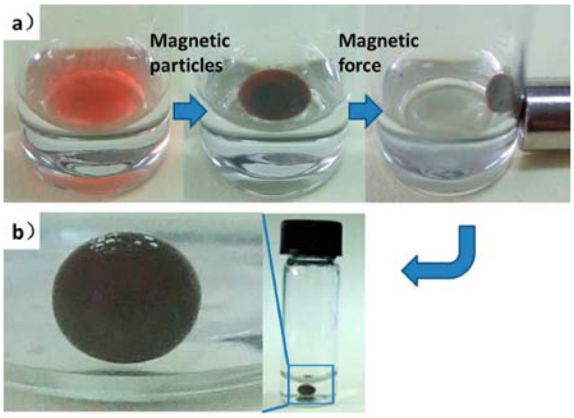

Figure 3. Pictures of (a) water/oil separation and (b) an "oil marble" under water.

superhydrophobic particles were added and dispersed in the oil. When putting a magnet close by, the magnetic particles moved toward the magnet responsively, driving the oil along with them. To remove 0.02 g oil, 0.01 g magnetic particles were needed. This phenomenon suggests magnetic superhydrophobic particles can not only isolate oil spills but also the isolated oil can be facilely transported under external control. These particles can be recycled by wash and filtration with the superhydrophobicity intact.

Another interesting phenomenon is that when the magnetic particles/oil phase was drawn under water and then the magnet was removed, a sphere was formed spontaneously with the solid particles encapsulating the oil droplet (Figure 3b), which was referred as an "oil marble", corresponding to the "liquid marble" of a liquid encapsulated by hydrophobic particles in air.[16] Reported liquid marbles mainly focused on fabricating water marbles which can float on or be immersed in other liquids.[17] Oil marbles in air have been demonstrated using Janus particles.[18] However, this is the first time to find that an oil sphere spontaneously forms under water encapsulated by superhydrophobic magnetic particles under external magnetic field. It is assumed that this liquid–liquid separation took place under the consideration of minimizing the surface free energy. Besides the application in water/oil separation, this new type of macroscopic liquid marble also has huge potential in microreactors and sensing applications.

In conclusion, inspired from the strong adhesion of mussel adhesive protein and the micronano hierarchical structure of lotus leaf, a versatile method has been developed to fabricate highly water repellent microparticles in a mild condition. This method is applicable to diverse types of particles, from hydrophilic to hydrophobic. Due to the nonselective adhesion of dopamine, different particles can be modified together in one pot. Magnetic superhydrophobic particles were fabricated which can be used in oil/water separation and transportation. A phenomenon of oil marbles spontaneously generated under water was found, and the mechanism and adhibition are under further investigation. With a clever choice and combination of core materials, new possibilities and applications could be brought up in optical, medical, and biological fields.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, XPS spectra, and SEM images. 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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