Superhydrophilic Surfaces

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One-Step Assembly of Phytic Acid Metal Complexes for Superhydrophilic Coatings

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Abstract: *While of immense scientific interest, superhydrophilic surfaces are usually difficult to prepare, and preparation methods are typically substrate specific. Herein, a one-step coating method is described that can endow superhydrophilicity to a variety of substrates, both inorganic and organic, using the coordination complexes of natural phytic acid and* Fe^{III} *ions. Coating deposition occurs in minutes, and coatings are ultrathin, colorless, and transparent. Superhydrophilicity is attributed, in part, to the high density of phosphonic acid groups. The ease, rapidness, and mildness of the assembly process, which is also cost-effective and environmental-friendly, points towards potential applications, such as self-cleaning, oil/water separation, antifogging.*

Wettability is a fundamental characteristic of solid surfaces, and at the extremes are superhydrophobic (water contact angle greater than 150°) and superhydrophilic (water contact angle less than 10°) surfaces, which have many practical applications. In general, the wettability of a solid surface is governed by both chemical composition and surface topography.[1] A well-known extreme example is the lotus leaf,[2] which exhibits superhydrophobic and self-cleaning properties arising from its waxy surface and micro/nano-hierarchical structure. Inspired by the lotus leaf, many different approaches have been developed to fabricate functional superhydrophobic surfaces, such as controlled crystallization,[3] phase separation,[4] electrochemical deposition,[5] chemical vapor deposition,[6] and self-assembly.[7] These approaches usually achieve superhydrophobicity via one of the two strategies: chemical modification of a rough surface with a coating of low surface free energy, or creation of hierarchical topography on a hydrophobic substrate. On the opposite extreme of wettability, superhydrophilicity, interest in the past several years has been sparked by potential application of these surfaces for self-cleaning, antifogging, water harvesting, and oil/water separation.[8] Fujishima et al. reported a TiO_2 polycrystalline film that exhibits superhydrophilicity upon exposure to UV radiation in 1997.[8b] Since then, significant efforts have been devoted to the preparation of superhydrophilic surfaces by various methods, including chemical etching, layer-by-layer assembly, hydrothermal treatment.[9] Just as for superhydrophobic surfaces, preparation methods for superhydrophilic surfaces must afford a combination of suitable surface roughness and high-surface-energy chemistry. However, these methods have limitations, for example, multiple preparation steps, complicated fabrication, time-consuming procedures, employment of aggressive chemical reagents, or complex instrumentation, all of which lead to potential environmental harm and high cost. Moreover, these methods are generally applied on a given substrate type, limiting their application to new materials. Therefore, a facile, versatile, and environmentally friendly strategy to make multiple classes of materials superhydrophilic is highly desired.

Recently, many metal-based routes to fabricate functional nature-based coatings have been reported. For instance, inspired by marine mussels, Harrington and co-workers employed dopa-Fe complexes to fabricate hard flexible coatings.[10] Similarly, in pursuit of robust new materials for bio-medicine, Ejima and co-workers reported metal-organic thin films based on natural polyphenol tannic acid and Fe^{III}.[11] Herein, we report a simple, rapid, and solution coating method based on a natural product that makes superhydrophilic—in a single step—a wide variety of substrates, including quartz, silicon, glass, Al, stainless steel, and polycarbonate. The single step invokes the assembly of coordination complexes between phytic acid (PA), a natural, nontoxic, and environmentally friendly compound readily available from plant sources that contains six phosphonic acid groups (see Figure S1 in the Supporting Information),[12] chosen as an organic ligand that binds well to substrates,[13] and ferric ion (Fe^{III}), chosen as an inorganic cross-linker that concatenates phytic acid. Coating deposition occurs just minutes after room temperature mixing of phytic acid and Fe^{III} in water, and complex instrumentation is not necessary. The coating components themselves are readily available and inexpensive. Moreover, the colorless and transparent coatings are suited to a range of potential applications, such as self-cleaning, environmental protection, antifogging, and so on.

Coatings were prepared by the straightforward method described in Supporting Information, with coating thickness a function of substrate immersion time in the coating bath. Atomic force microscopy (AFM) showed that coatings prepared by 1 min immersion were about 8 nm thick and displayed nanoscale roughness (root-mean-square roughness of 11.0 nm), as seen in Figures 1 A,B. Analogous to layer-by-layer assembly, thicknesses of Fe^{III}–phytic acid coatings can be increased by sequentially re-applying the coating procedure, with the AFM data (Figure 1 C) and UV/Vis absorption spectra (Supporting Information Figure S2) demonstrating

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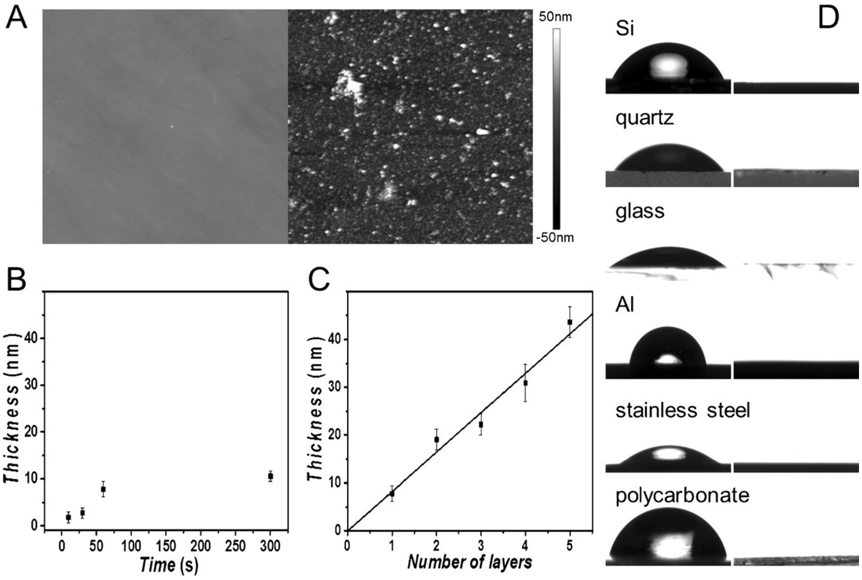

Figure 1. A) AFM topography images (10 μm × 10 μm) of bare Si wafer (left) and Fe^{III}–phytic acid coated Si wafer (right); B) Thickness evolution of Fe^{III}–phytic acid coating on Si wafer as measured by AFM; C) Thickness of Fe^{III}–phytic acid coatings growth with sequential deposition cycles on Si wafer measured by AFM. D) Pictures of water droplets on several unmodified (left) and Fe^{III}–phytic acid coated (right) substrates.

that the thickness increase is linear in the number of immersions.

Surface wettability was evaluated by water contact angle, and as shown in Figure 1D, water wettability was greatly enhanced for substrates as diverse as quartz, glass, Si, Al, stainless steel, and polycarbonate. When a droplet was placed on a coated surface, it quickly spread to a nearly zero water contact angle, reflecting hierarchical surface roughness combined with large density of phosphonic acid groups, which are polar and capable of hydrogen bonding with water molecules.

Recently, inspired by the remarkable oil-repellency of fish scales in aqueous media,[8a] membranes with superhydrophilic and underwater superoleophobic properties were demonstrated as promising materials for oil/water separation.[8d] To illustrate this application for the current coatings, a piece of treated stainless steel mesh was chosen to separate water from oil/water mixtures.

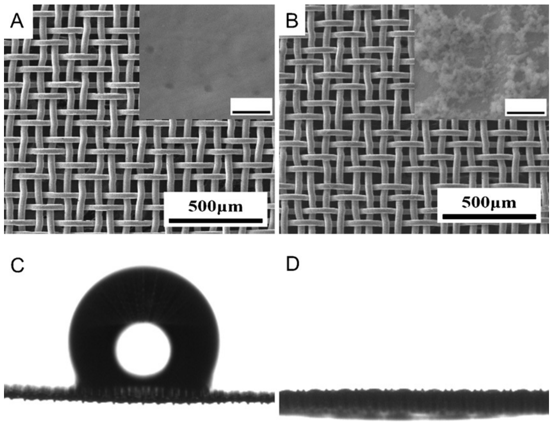

Figure 2. A),B) SEM images of the original stainless steel mesh (A) and Fe^{III}–phytic acid coated mesh (B). Insets show the magnified view of the knitted wire surfaces (scale bars: 500 nm). C) Shape of a water droplet on the original mesh. D) A water droplet spreads on the Fe^{III}–phytic acid coated mesh.

The Fe^{III}–phytic acid coated meshes were prepared through an instantaneously coating process under room temperature. Figure 2A shows scanning electron microscope (SEM) image of the bare stainless steel mesh that exhibits a pore size around 45 μm, and the higher magnification inset to this image establishes that the original wires had smooth surfaces down to the nanoscale. After deposition of Fe^{III}–phytic acid coating, the macroscopic morphology of the mesh, shown in Figure 2B, did not show any significant change, but at the nanoscale, the image's higher magnification reveals a layer of aggregates on the wire surfaces several to several tens of nanometer in size, demonstrating the hierarchical roughness of the Fe^{III}–phytic acid coated mesh. Energy-dispersive X-ray spectroscopy (EDS) reveals phosphorus on the surface (Supporting Information, Figure S3), which comes from phytic acid.

The wetting properties of water and oil on the Fe^{III}–phytic acid coated mesh were characterized comprehensively. In air, the water contact angle of a neat mesh was about 120°, as shown in Figure 2C. Compared to the neat mesh, as illustrated in Figure 2D, the wetting of Fe^{III}–phytic acid coated meshes was greatly enhanced, with a water contact angle lower than 5°. When pre-wetted in water, the Fe^{III}–phytic acid coated mesh becomes highly repulsive for oils such as toluene, hexane, petroleum ether, cyclohexane, hexadecane, and 1,2-dichloroethane. All displayed an oil contact angle above 150°, indicating that the Fe^{III}–phytic acid coated meshes have extraordinary underwater superoleophobicity (Figure S4). Our interpretation is that water adsorb to and is trapped in the nanostructure of the Fe^{III}–phytic acid coatings, resulting in a strong repulsive force between polar (water) and non-polar (oil) molecules. Therefore, the mesh showed underwater superoleophobicity in the oil/water/solid three-phase system.

To test oil/water separation by the Fe^{III}–phytic acid coated meshes, a series of proof-of-concept experiments were performed. The oil/water separation procedure is shown in Figure 3A,B. A 50% v/v mixture of cyclohexane (dyed with Oil Red O) and water was first poured onto the as-prepared mesh, which was fixed with an iron grip between two vertical glass tubes. Water passed quickly through the mesh but cyclohexane was instead repelled and thereby held in the upper glass tube, demonstrating the outstanding underwater superoleophobicity of the Fe^{III}–phytic acid coating. The separation efficiency was high, with nearly no visible oil in the water permeate. A video illustrating the separation process is provided as Supporting Information, Movie S1.

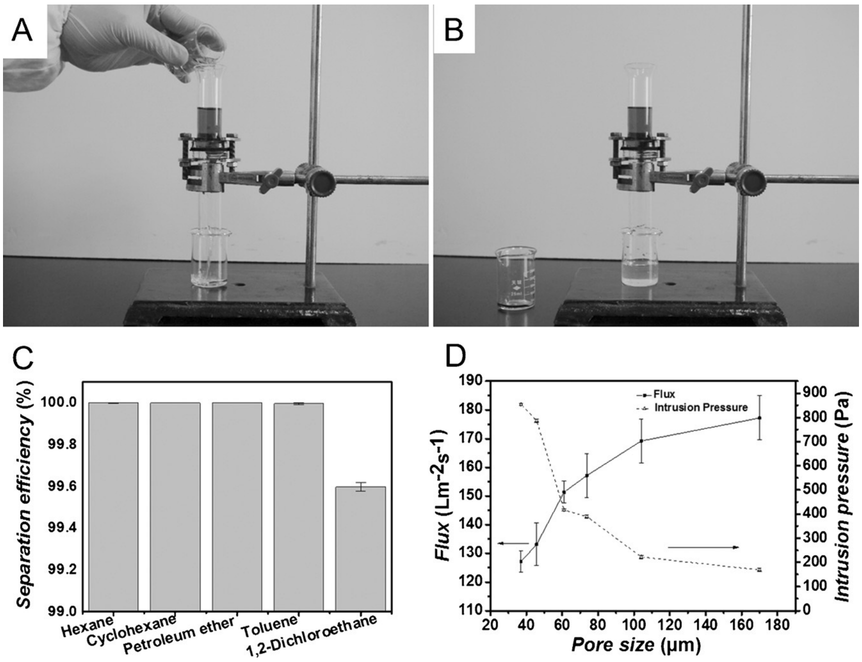

Figure 3. Oil/water separation by the Fe^{III}–phytic acid coated stainless steel mesh. A) Oil/water separation by the Fe^{III}–phytic acid coated mesh. The mesh was pre-wetted by water and fixed between two glass tubes. A mixture of cyclohexane (dyed by Oil Red O, dark) and water (50% v/v) was poured into the upper glass tube, and the water passed through the mesh whereas the cyclohexane remained on top of the mesh in the upper glass tube. (B) Photograph shows collected water and cyclohexane after the separation. No oil was visible in the collected water, indicating a complete separation. C) The separation efficiency of the Fe^{III}–phytic acid coated mesh for various oil/water mixtures. D) Influence of pore size of the Fe^{III}–phytic acid coated mesh on intrusion pressure of cyclohexane and water flux. Solid line: water flux, broken line: intrusion pressure of cyclohexane.

To assess separation efficiency more quantitatively, various oils were mixed with water and the 50:50 v/v mixtures then separated by treated meshes. The purity of the permeated water after one pass through the mesh was measured by gas chromatography, and the separation efficiency was calculated following a literature procedure.[8d] As shown in Figure 3C, the separation efficiency for all oils was above 99.5%. Compared to the other four oils, efficiency for 1,2-dichloroethane was reduced by the solvent's better miscibility (water solubility: 8.7 $g L^{-1}$ at 20°C).

To explore oil/water separation further, both water flux and cyclohexane intrusion pressure were measured as a function of average mesh pore size, and as shown in Figure 3D, the former rose with pore size while the latter fell. The first trend is expected by membrane pore hydrodynamics and the second can be explained in terms of Laplace pressure. The pore size of the mesh is essentially unchanged once coated with Fe^{III}–phytic acid. Selective retention of oil is observed even for a mean pore size as large as 170 μm, where the water flux can reach approximately 175 $L m^{-2} s^{-1}$, or 6.30×10^5 $L m^{-2} h^{-1}$, which is much greater than values reported in the literature.[14]

To evaluate the stability of the Fe^{III}–phytic acid coatings against corrosion, water contact angle and separation efficiency were tested, as described above, after immersing the coated stainless steel meshes into HCl (0.1 M) and NaCl solution (saturated) for 72 h, respectively. The coated meshes still exhibited underwater superoleophobicity, and their corresponding separation efficiency remained above 99.5%, illustrating good stability in harsh conditions. Moreover, the meshes retained their superoleophobicity and oil repellency after 10 separation cycles.

Fog on a transparent surface arises from the condensation of small water droplets that scatter incident light, and the consequence is a loss of transparency. Superhydrophilic surfaces display antifogging activity because the water that condenses spreads to form a thin film rather than beading up into droplets.[8b] With their inherent transparency Fe^{III}–phytic acid coatings are ideally suited for antifogging application in automobile windshields, eyeglasses, swimming goggles, periscopes, lenses in laparoscopes. To study the antifogging performance of Fe^{III}–phytic acid coatings, a quartz slide was subjected to five Fe^{III}–phytic acid depositions, and this slide, along with an uncoated control slide, were placed in a refrigerator (4°C) for several hours. The cold slides were then placed over a beaker of heated water to induce fogging, which was monitored by photographic imaging. The antifogging effect is clearly dis-

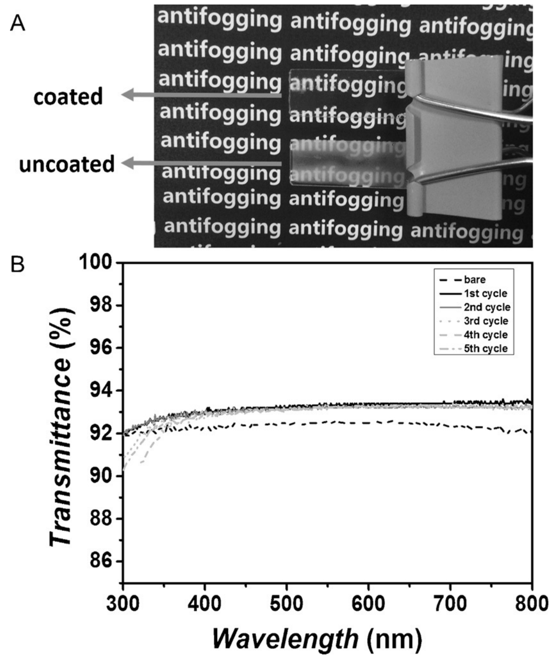

Figure 4. A) Digital image exhibiting antifogging activity of Fe^{III}–phytic acid coating on quartz slide (upper) and bare quartz slide (lower). B) Transmission spectra of bare slide and slides coated with 1 to 5 deposition cycles of Fe^{III}–phytic acid.

played in Figure 4 A for the Fe^{III}–phytic acid coated slide, contrasting sharply with the easily fogged, uncoated slide just below.

Antifogging performance was quantified in terms of light transmission over the 300–800 nm range in experiments performed with a UV/Vis spectrophotometer and coated quartz slides. As shown in Figure 4 B, the Fe^{III}–phytic acid coatings, of one to five Fe^{III}–phytic acid deposition cycles, all exhibited light transmission as high as that of bare quartz (ca. 92 %).

In summary, a facile, environmentally friendly, and cost-effective general method to construct superhydrophilic surfaces in one step is described. This step assembles highly adherent Fe^{III}–phytic acid coordination complexes to substrates of diverse chemistry. A superhydrophilic and underwater superoleophobic Fe^{III}–phytic acid coated stainless steel mesh fabricated via this method selectively separated water from various oil/water mixtures with high separation efficiency and high flux. The same coating, applied to transparent slides, exhibited excellent antifogging performance. It can be expected that Fe^{III}–phytic acid coating will open a new direction for the field of superhydrophilic surfaces.

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Keywords: antifogging · coating · green process · oil/water separation · superhydrophilic

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