

Methodology for Robust Superhydrophobic Fabrics and Sponges from In Situ Growth of Transition Metal/Metal Oxide Nanocrystals with Thiol Modification and Their Applications in Oil/Water Separation

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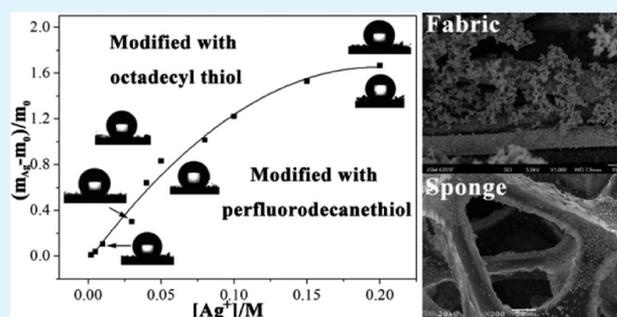
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S Supporting Information

ABSTRACT: Solid surfaces possessing both superhydrophobic and superoleophilic properties have attracted significant interest in fundamental investigations and potential applications in the fields of self-cleaning surfaces, oil/water separation, and microfluidic channels. In this paper, a general methodology for robust superhydrophobic fabrics and sponges was proposed via the in situ growth of both transition-metal oxides and metallic nanocrystals, including the simple neutralization reaction and oxidation–reduction reaction. The porous surfaces coated with Group VIII and IB nanocrystals (such as Fe, Co, Ni, Cu, and Ag) can not only present multiscale surface roughness, but also readily coordinate with thiols, leading to special wettability. In our previous work, it has been confirmed that the interaction between the nanocrystals and thiols plays a significant role in the introduction of hydrophobic ingredients. In this work, it has been demonstrated that the efficient control of the nucleation and growth of Group VIII and IB nanocrystals on the porous surfaces becomes the key factor in the formation of multiscale surface roughness, resulting in the achievement of controllable special wettability. In addition, these as-prepared superhydrophobic and superoleophilic fabrics and sponges were successfully used for application in oil/water separation.

KEYWORDS: superhydrophobic, fabric, sponge, in situ growth, thiol, oil/water separation



1. INTRODUCTION

With the ever-increasing industrial oily wastewater and the frequent oil spill accidents, the treatment of oily wastewater has become a worldwide problem. Combining superhydrophobicity (water contact angles of $>150^\circ$) with superoleophilicity (oil contact angles of $<5^\circ$), surfaces with special wettability are introduced to separate oil from water, or water from oil. Recently, solid surfaces with both superhydrophobic and superoleophilic properties have received broad attention for both fundamental research and potential application in the fields of self-cleaning surfaces,^{1–4} low-friction films,^{5–7} oil/water separation systems,^{8–10} and functional microfluidic devices.^{11,12} As reported,^{3,13} the wettability of a solid surface is governed by both the chemical composition and the surface topography. Therefore, hydrophobic and oleophilic properties are generally applied to modify the porous surfaces that provide sufficient surface roughness.

Inexpensive and ubiquitous porous materials such as fabrics and sponges possess excellent air permeability, softness, and flexibility, which makes them the good candidates for oil/water

separation substrates, because of the fact that its sufficient specific surface area can strongly bond with transition-metal oxides by absorbing the polar groups inside and outside. Various chemical and physical strategies have been proposed to achieve superhydrophobic properties; special consideration was given to the enhancement of the surface roughness on the microscale fabric fiber and sponge skeleton. To date, nanoparticles—especially inorganic nanoparticles such as TiO_2 ,¹⁴ ZnO ,¹⁵ carbon nanotubes (CNTs),^{16,17} graphene,¹⁸ and silica^{19,20}—were successfully coated on fabrics/sponges, showing the improvement in surface roughness. Xue et al.¹⁴ had the cotton fabric immersed in a TiO_2 sol–gel and then used stearic acid as the modifier to prepare a superhydrophobic fabric. Cai et al.¹⁵ fabricated a superhydrophobic ZnO nanorod array film on a cotton substrate via a wet chemical route and subsequent modification with a layer of *n*-dodecyltrimethoxysilane. Liu et al.¹⁶ prepared

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water-repellent and functional common cotton fabrics coated with CNTs, using a simple dipping coating method. Tai et al.¹⁸ reported a strategy to fabricate superhydrophobic graphene-based sponges via a facile dip coating method. Lin et al.¹⁹ proposed stable superhydrophobic surfaces by simply coating a particulate silica sol solution from cohydrolyzed tetraethylorthosilicate and fluorinated alkyl silane with $\text{NH}_3 \cdot \text{H}_2\text{O}$ on fabrics. Among them, the dip coating method is still the main method of preparing superhydrophobic fabrics/sponges; the in situ growth method is seldom reported.^{21,22} The biggest defect for the dip coating method is that the physical adsorption is quite mild, so that the coating of nanocrystals is limited and uncontrollable. In this respect, the in situ growth method exhibits its specific advantages. Superhydrophobic fabrics that are loaded with inorganic materials using an in situ growth method possess more stable and robust mechanical properties, controllability of the coated nanocrystals, time-saving properties, simplicity, and resource-saving properties. Therein, transition-metal/metal oxides have attracted greater interest, because they possess many unique properties that can be conducive to realizing the multifunctional properties. For example, Fe, Co, and Ni nanoparticles are the magnetic materials that have been widely applied for recyclable materials; CuO is a semiconductor that endows the materials with more functions; Ag nanocrystals provide an antibacterial effect. Although constructing the rough surface via the in situ growth of transition-metal/metal oxides is important, modification of the rough surface also is very crucial to achieving high superhydrophobicity. Thus, in order to effectively coat or fix hydrophobic ingredient on the hydrophilic surface and reverse the water wettability in the premise of maintaining superoleophilicity, the use of thiols as a surface modification agent is currently becoming a primary strategy.

Transition-metal/metal oxides in Groups VIII and IB can strongly interact with the polar groups, which can not only improve the interaction between the nanocoatings and the surfaces, but also are easily modified with thiols. In our previous paper,²³ we successfully achieved superhydrophobicity and superoleophilicity on a fabric from absorbing the as-prepared nanocrystals, followed by thiol modification. In the present work, we continue to investigate the superhydrophobicity and superoleophilicity of a fabric, which is caused by the mutual interaction between the transition metal elements and thiols. Discriminating from the former one, in this paper, Group VIII and IB metals and oxide nanoparticles (e.g., Fe, Co, Ni, Cu, and Ag) were prepared in situ on the fabrics, as well as the other porous materials, instead of a two-step dip coating method, which prepared the stable nanoparticle suspensions before the fabric was immersed into it. Moreover, as-prepared fabrics and sponges from in situ growth method realized filtration and absorption of oils from water selectively and effectively, and could be applied repeatedly many times.

2. MATERIALS AND METHODS

2.1. Materials. The fabrics (containing 65% polyester and 35% cotton) and sponges used for different metal nanocrystals are uniform, which were purchased from a local store. The original fabrics and sponges were sequentially cleaned using distilled water, anhydrous ethanol, and distilled water in an ultrasonic cleaner, to remove possible impurities. *n*-Octadecyl thiol (96%) was obtained from Acros Organics, and 1H,1H,2H,2H-perfluorodecane thiol (97%) was purchased from

Aldrich. All other chemicals were analytical-grade reagents and used as received.

2.2. Iron Oxides. The original hydrophilic fabric was immersed into a 3 M ammonia solution (5 mL) at room temperature for 1–3 min. Then, 1 M $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution (20 mL) was added into the aqueous solution dropwise, under ultrasonic cleaning. Next, the fabric with iron oxides grown on it was removed and washed with distilled water and ethanol. After that, the as-prepared product was immediately modified by a modifier without being dried in the drying oven.

2.3. Cobalt Oxide. The original hydrophilic fabric was immersed into 1 M $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (10 mL) solution at room temperature for 1–3 min. In this process, the aqueous solution of $\text{Co}(\text{NO}_3)_2$ was absorbed into the fabric adequately and penetrated into the fabric fibers because of its hydrophilicity. The Co(II) solution with the fabric inside was heated to 80 °C. Then, 3 M ammonia solution (40 mL) was added dropwise into the aqueous solution at 80 °C under magnetic stirring (a homemade porous polyethylene baffle was used to separate the fabric from the magneton, for the purpose of preventing the nonuniform growth of nanoparticles aroused by the magnetic stirring). After that, the fabric coated with cobalt oxides nanocrystals was removed and washed with distilled water and anhydrous ethanol three times. The fabric then was dried in a drying oven.

2.4. Nickel Oxide. A 0.5 M $\text{Ni}(\text{NO}_3)_2$ solution was prepared as the nickel resource. The cleansed fabric was immersed in the aqueous solution (40 mL) and heated to the constant temperature at 80 °C under magnetic stirring. Superfluous 3 M sodium hydroxide solution was then added dropwise into the $\text{Ni}(\text{NO}_3)_2$ solution until no more precipitation formed (Ni was precipitated completely). The fabric with nickel oxide grown on it was washed with distilled water and ethanol, and then was dried in a drying oven.

2.5. Copper Oxide. The CuO nanoparticle suspensions were prepared according to the literature method.²⁴ In the synthesis, the fabric was immersed in an ethanol solution of 10 mM $\text{Cu}(\text{CH}_3\text{CO}_2)_2$ (100 mL) for 1–3 min. The ethanol solution was heated to 78 °C under magnetic stirring. Then, 4 mM NaOH ethanol solution (20 mL with a tiny bit of distilled water to dissolve the granular NaOH) was added dropwise into the $\text{Cu}(\text{CH}_3\text{CO}_2)_2$ ethanol solution under magnetic stirring at 78 °C. After that, the fabric with copper oxide grown on it was removed and washed with anhydrous ethanol. It was dried in a drying oven.

2.6. Silver. The original fabric was immersed into 0.04 M AgNO_3 aqueous solution (50 mL) at room temperature for 2 min. Next, an aqueous solution of ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$, 0.05 M, 50 mL) was added dropwise into the AgNO_3 solution at room temperature under magnetic stirring. Half an hour later, the fabric coated with Ag nanocrystals was drawn from the solution and wash by distilled water and anhydrous ethanol three times. After that, the fabric was dried in a drying oven.

2.7. Iron, Cobalt, Nickel, and Copper. In situ growth of the simple substance of iron, cobalt, nickel, and copper nanoparticles on fabric were realized using exactly the same procedures. Both the concentrations and volumes of the precursors were rigidly equal. The original fabric was immersed into a 0.04 M precursor (50 mL), i.e., FeSO_4 , $\text{Co}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$, and CuSO_4 that provided the transition-metal sources, at room temperature under normal atmospheric conditions for 1–3 min. Then, 0.04 M sodium borohydride solution (50 mL) was added dropwise into the aqueous solution at room temperature under constant magnetic stirring. After that, the fabric with

metal nanoparticles grown on it was drawn and sequentially washed with distilled water and ethanol at least three times to eliminate the residual solution. The fabric then was dried in a drying oven.

2.8. In Situ Growth of Nanocrystals on Sponges. The as-cleaned sponges were pretreated by immersing them into an etching solution that contained CrO_3 (100 g L^{-1}) and H_2SO_4 (98 wt %) (100 g L^{-1}) for 90 s. After being washed five times with distilled water, the sponges were immersed in 50 mL of 0.04 M aqueous solutions of all types of precursors (FeSO_4 , $\text{Co}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$, CuSO_4 , and AgNO_3). Other experimental procedures were the same as the preparation of the corresponding metal nanocrystals on fabric.

2.9. Surface Modification. The as-dried fabrics/sponges coated with nanocrystals were immersed in 50 mL of 4 mM *n*-octadecyl thiol or 10 mM 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol anhydrous ethanol for 24 h at room temperature. The fabrics/sponges then were thoroughly cleaned with anhydrous ethanol to remove any residual thiol and dried in a drying oven.

2.10. Weight Measurement and Color Changes of Fabrics Coated with Metal Nanocrystals. The weights of the fabrics from the in situ growth of the five metal nanocrystals were measured twice, before and after being coated with the metal nanoparticles under clean and dry conditions. All of the weight differences are obtained to identify the growth of the metal nanoparticles. The color changes were recorded during the entire process of fabricating superhydrophobic fabrics. They directly showed the reaction between the transition metal/metal oxides and thiol.

2.11. Characterization. The water contact angle was measured with a 5- μL droplet of distilled water at ambient temperature with a DSA100 contact angle (CA) meter (Kruss Company, Germany). The average CA value was obtained by measuring the sample at five different positions, and the images were captured with a traditional digital camera. Scanning electron microscopy (SEM) images were obtained on JEOL JSM-7500, JSM-6510LV, and JSM-5600LV SEM microscopes with Au-sputtered specimens. Field-emission scanning electron microscopy (FESEM) images were obtained on a JEOL JSM-6701F FESEM system with Au-sputtered specimens. The chemical composition of the as-prepared surfaces were investigated using X-ray photoelectron spectroscopy (XPS), which was conducted on a PHI-5702 electron spectrometer (Physical Electronics, USA) using the Al $K\alpha$ line as the excitation source. The C 1s binding energy (284.6 eV) was used as the reference.

3. RESULTS AND DISCUSSION

3.1. Processing of the Original Fabric/Sponge. Fabrics, as well as sponges, are well-known for their excellent air permeability, softness, and flexibility, so they are commonly used in daily life. In the field of superhydrophobic surfaces, they are good candidates for use as oil/water separation substrates, because of their porosity and large specific surface area. Because of the presence of different oxygen groups on the fabric/sponge surfaces, the original fabrics/sponges are quite hydrophilic (see Figures S1a and S1b in the Supporting Information) and can easily absorb and fix the various transition metals and oxide nanocrystals from various polar solvent (such as water and ethanol), forming nanosized structures in a microscale rough surface.²³ The fabric/sponges with as-prepared metal nanoparticles grown on them are intrinsically superhydrophilic, because of the high surface free energy that the metals possess. The surface modification then was carried out using the

hydrophobic/oleophilic *n*-octadecyl thiol. As we know, the wettability of a surface is closely related to its chemical composition and its surface topography. The as-prepared transition-metal nanocrystals retain the morphology of the porous template and form spherical or filmlike nanostructures with a high specific surface area. The multiscale rough surface plays a more significant role, compared to the original fabric and sponge surface, since the metal/metal-oxide nanocrystals coated on them further increase the surface roughness and therefore amplify the wettability to their extreme. The transition metal/metal oxide nanoparticles efficiently interact with *n*-octadecyl thiol via the coordinate bonds. After surface modification, the hydrophobicity and oleophilicity were respectively magnified to superhydrophobicity and superoleophilicity by the multiscale rough surface. The modified RS-M on the fabric/sponge provided not only the hydrophobic/oleophilic alkyl chain but also the strong interaction with the polar ligands on the fabric/sponge. The unique surface roughness constructed by both the metal/metal oxide nanocrystals and the porous fabric/sponge itself is indispensable for realizing a superhydrophobic surface, whereas the *n*-octadecyl thiol that covered it provided the chemical composition with low free energy.

As shown in Figure 1, we used the commercial fabrics and sponges as the substrates and have the transition metal/metal

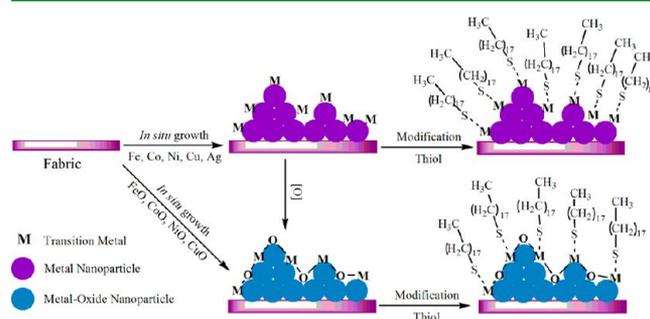


Figure 1. Schematic illustration of the preparation procedure of the superhydrophobic and superoleophilic fabric from the in situ growth of transition-metal/metal oxide nanocrystals with thiol modification.

oxide nanocrystals grown in situ on them. Compare to the two-step dip coating method, the in situ growth of metal/metal oxide nanocrystals has more advantages. First and foremost, superhydrophobic fabrics obtained by using an in situ growth method possess more-stable and more-robust mechanical properties. Zhu et al.²² fabricated superhydrophobic fabric via the in situ growth method, and the excellent mechanical stability was investigated experimentally in detail. Second, the as-selected metal/metal oxides in Groups VIII and IB, which can strongly interact with the polar ligands on the fabric surface, can not only rely on the physical adsorption, but also directly nucleate on the fabric surface. In our previous work,²³ it has been demonstrated that the fabrics from using a dip coating method show good superhydrophobic stability by applying various external forces, such as ultrasonic treatment and heat treatment; therefore, the fabrics/sponges from the in situ growth method also would possess excellent stability, since the physical absorption is taking place secretly as the in situ growth method progresses. In addition, the in situ growth method shortens the fabrication cycle and saves more time for preparing fabric with a nanocoating. Third, it is unnecessary for the in situ growth method to add any surfactants (such as cetyltrimethylammonium bromide and

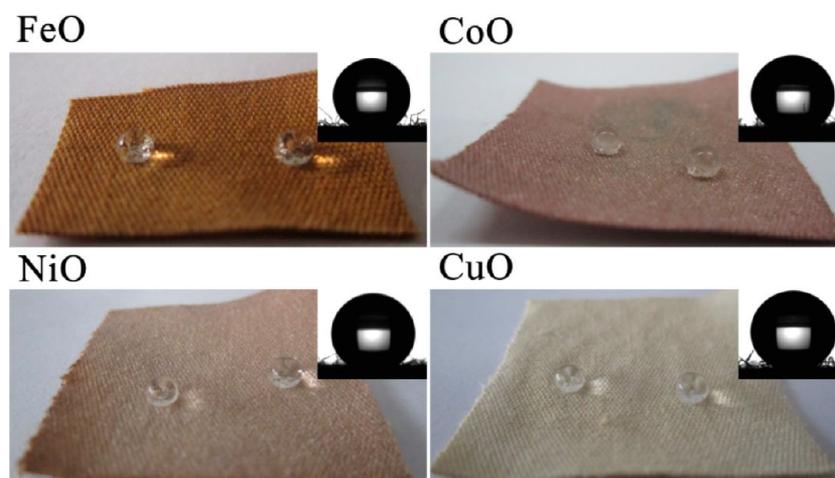


Figure 2. Optical images of superhydrophobic fabric formed via the in situ growth of Group VIII and IB metal-oxide nanoparticles. The inset images in the upper right-hand corner of each panel are images of the static water droplets ($5 \mu\text{L}$).

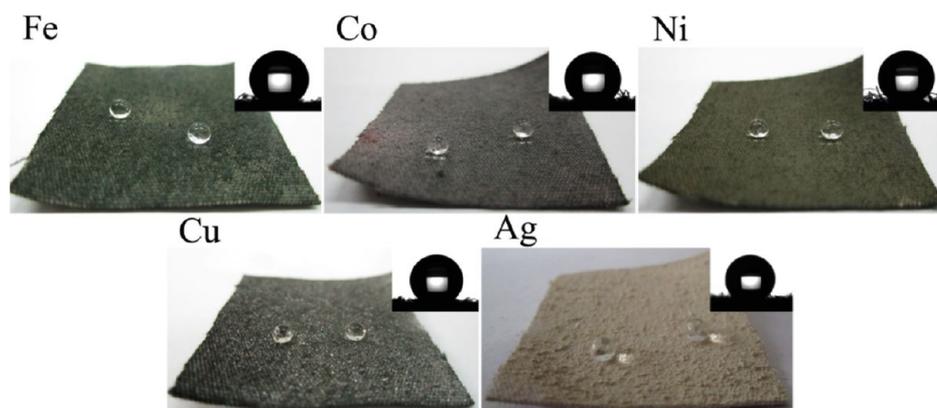


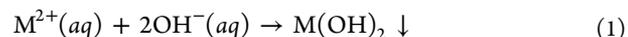
Figure 3. Optical images of superhydrophobic fabric from the in situ growth of Group VIII and IB metal nanoparticles. The inset images in the upper right-hand corner of each panel are images of the static water droplets ($5 \mu\text{L}$).

sodium dodecyl benzene sulfonate) as capping agents to stabilize the aqueous dispersions of metal/metal oxide nanocrystals; it is just growing on a fabric. Finally, the dip coating method is limited to its coefficient of utilization of the nanocrystals suspension, since the nanoparticles suspended in the solvent are limited to its saturation value and the physical adsorption behavior of the fabric, because of the fact that the intermolecular van der Waals force is quite mild. As the adsorption equilibrium is reached, the fabric eventually will not absorb nanoparticles anymore. Nonetheless, the in situ growth method may avoid precursor waste and directly control the amount of nanoparticles loaded on the fabric via adjustment of the precursors.

Here, the in situ growth method was used to have both metal oxides and simple metallic substances grown on them. As is our expectation, the fabrics with metals/metal oxides grown on them were successfully modified with thiols (*n*-octadecyl thiol and 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol) that possess low surface free energy. The water droplets remained on the fabric surfaces after thiols' modification remain almost spherical and easily roll off. The contact angles are larger than 150° , and the sliding angles are smaller than 10° (see Figures 2 and 3). The contact angles of the oil droplet on the fabric surfaces are superoleophilic after the modification of *n*-octadecyl thiol and oleophobic with CA values approximate to $>150^\circ$ after the modification of 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol.

3.2. In Situ Growth of Metal-Oxide Nanocrystals on Fabrics. The in situ growth of metal-oxide nanocrystals is,

in essence, an acid–base neutralization. It can be considered that the precursors (i.e., FeSO_4 , $\text{Ni}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2$ and $\text{Cu}(\text{CH}_3\text{CO}_2)_2$) provided the transition-metal ions and reacted with the bases (such as NaOH and NH_4OH) as the Lewis acid. The aqueous solution of precursors was neutralized by bases (NaOH and NH_4OH) and formed their corresponding metal oxides, according to the following reactions:



where M represents transition-metal elements such as Fe, Co, Ni, and Cu. In the process of the growth of NiO, a sodium hydroxide (NaOH) solution was used to substitute for a weaker base (ammonia solution), to avoid the complexation reaction between $\text{Ni}(\text{OH})_2$ and the ammonia solution, which can lead to the effect of dissolving the precipitate.

As graphically shown in Figure 2, the fabrics from the in situ growth of metal-oxide nanoparticles exhibit good superhydrophobic properties and stability after modified with *n*-octadecyl thiol. The morphologies of the native fabric and the fabrics coated with metal oxides of Fe, Co, Ni, and Cu after surface modification was studied by SEM (see Figure S2 in the Supporting Information and Figure 4). In addition, XPS measurements were proposed to confirm the existence of

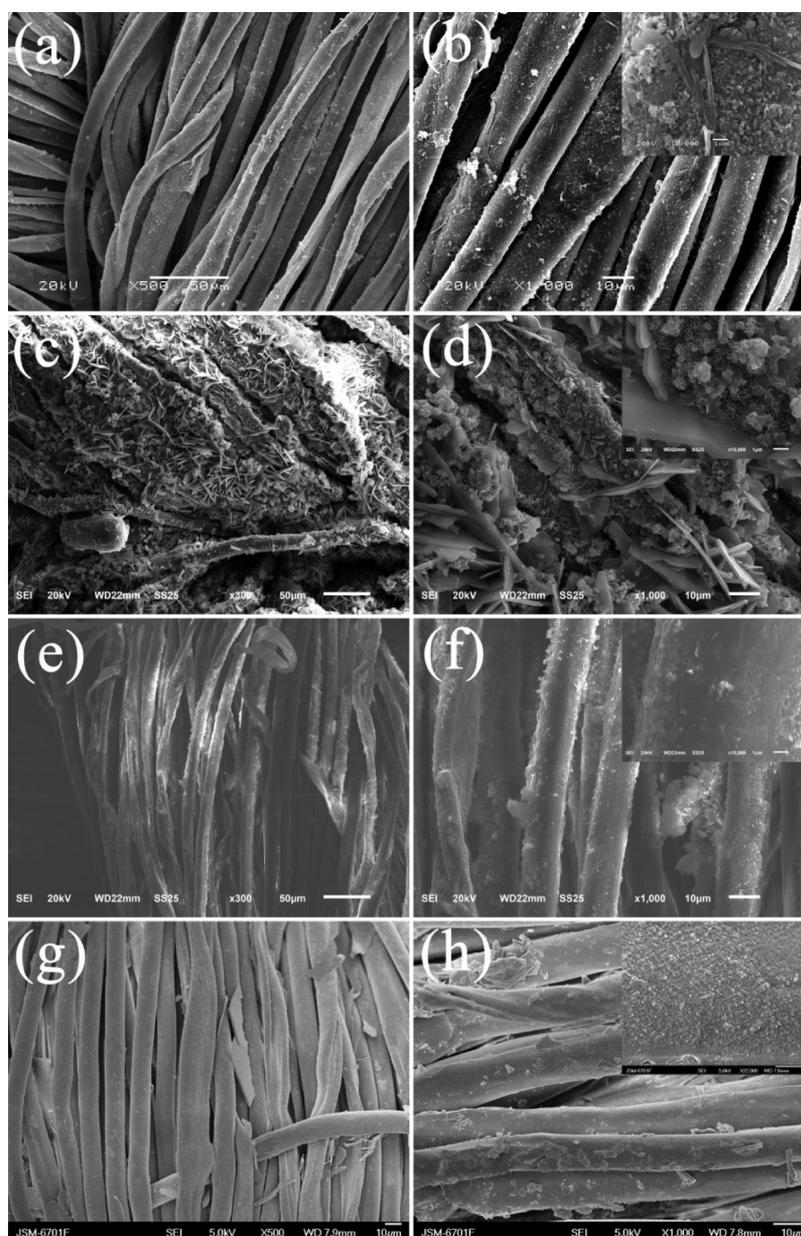


Figure 4. SEM images of fabrics coated with (a, b) iron oxides, (c, d) cobalt oxides, (e, f) nickel oxides, and (g, h) copper oxides nanoparticles after surface modification with *n*-octadecyl thiol.

Group VIII and IB metal elements on the fabrics, as schematically shown in Figure S3 in the Supporting Information.

In some chemical experiments, the drop sequence of reagents plays a very important role to the experimental success. It is notable that the wettability of the modified fabric with the in situ growth of iron oxides is strongly related to its drop sequence of reagent. In our experiment, the FeSO_4 solution was added dropwise into the highly concentrated ammonia aqueous solution (3 M) with the fabric immersed in it. This highly concentrated ammonia solution can inhibit the oxidation of Fe(II) of FeO to Fe(III), which can result in invalidity of the surface modification with thiol.²³ After the neutralization reaction finished, the fabric that was coated with FeO nanoparticles was quickly rinsed with water and absolute alcohol three times sequentially, then rapidly transferred to the *n*-octadecyl thiol anhydrous ethanol to avoid its oxidation.

3.3. In Situ Growth of Metal Nanocrystals on Fabrics. The fabrics that came from the same textile were all tailored into

squares with the same areas (29 mm \times 29 mm). The original weights were slightly different from each other (see Table S2 in the Supporting Information). The precursors have the same concentrations and the same volumes, which denote that the amounts of transition-metal ions are the same. While excess reductive agent (sodium borohydride and ascorbic acid) was added in the solutions contained different precursors, different kinds of ions of equal amount can be reduced fully. The net weight increases (see Table S2 in the Supporting Information), as well as the color changes of the fabrics before and after the in situ growth of different transition-metallic simple substances (see Table S3 in the Supporting Information), provided direct evidence that all of the transition-metal nanocrystals have grown on the fabric. The fabric with Ag nanocrystals grown on it has a relatively more remarkable net weight increase; this may be due to the bigger atomic weight and the thorough reduction of Ag.

The aqueous solution of precursors (i.e., FeSO_4 , $\text{Ni}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2$, CuSO_4 , and AgNO_3) is reduced to their corresponding

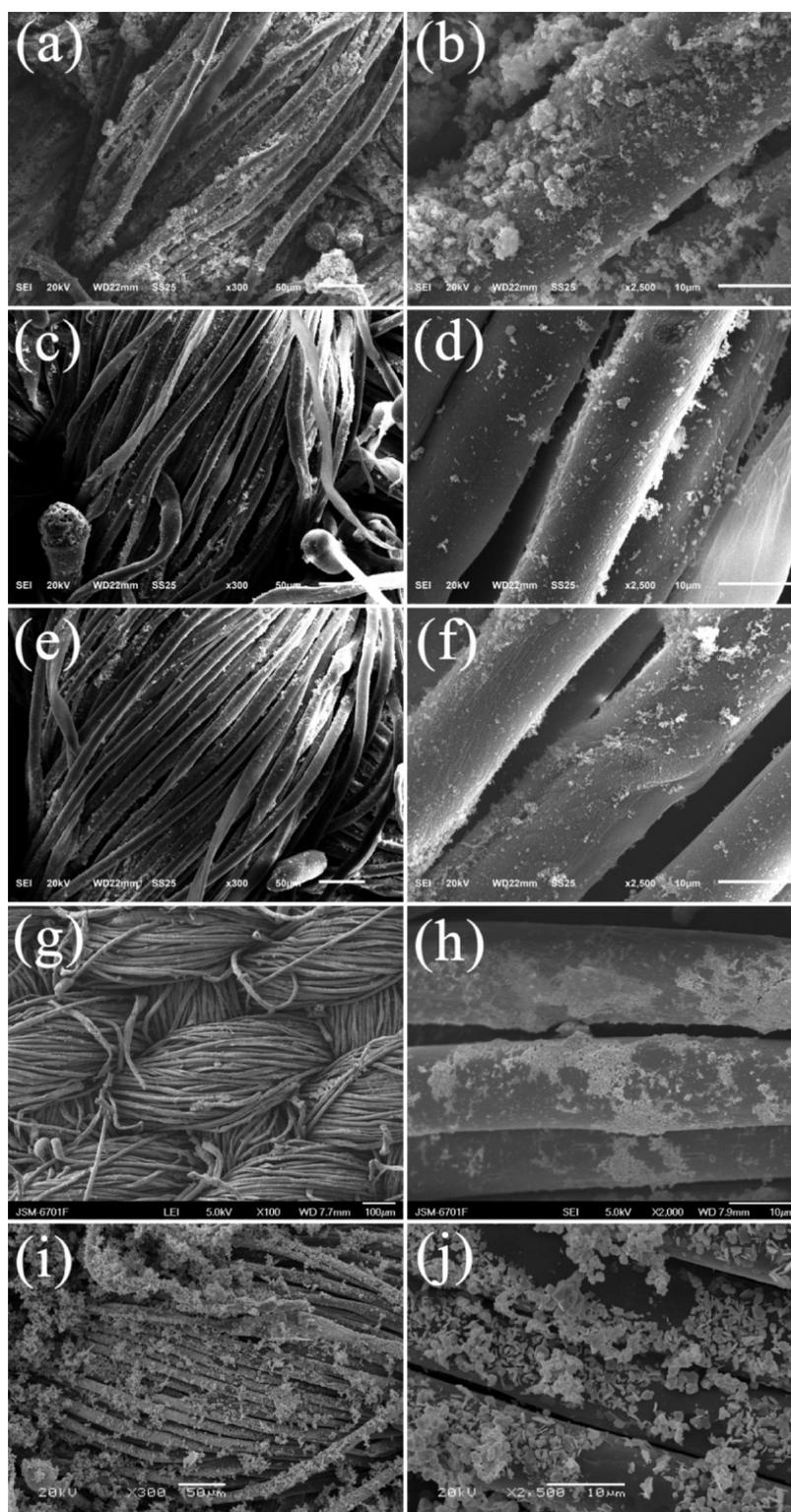
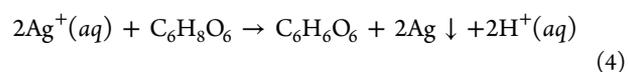


Figure 5. SEM/FESEM images of fabrics coated with (a, b) Fe, (c, d) Co, (e, f) Ni, (g, h) Cu, and (i, j) Ag nanoparticles.

metallic simple substances, using sodium borohydride or ascorbic acid. The reactions involved can be described as follows:



where M represents transition-metal elements such as Fe, Co, Ni, Cu, and Ag. Figure 5 shows typical SEM/FESEM images of fabrics respectively coated with Fe, Co, Ni, Cu, and Ag nanoparticles, which demonstrate the surface roughness constructed by both microscale fibers and nanoscale metal nanoparticles. XPS measurements confirmed the presence of corresponding Group VIII and IB metals, carbon, and oxygen on the coated fabrics, as schematically shown in Figure 6.

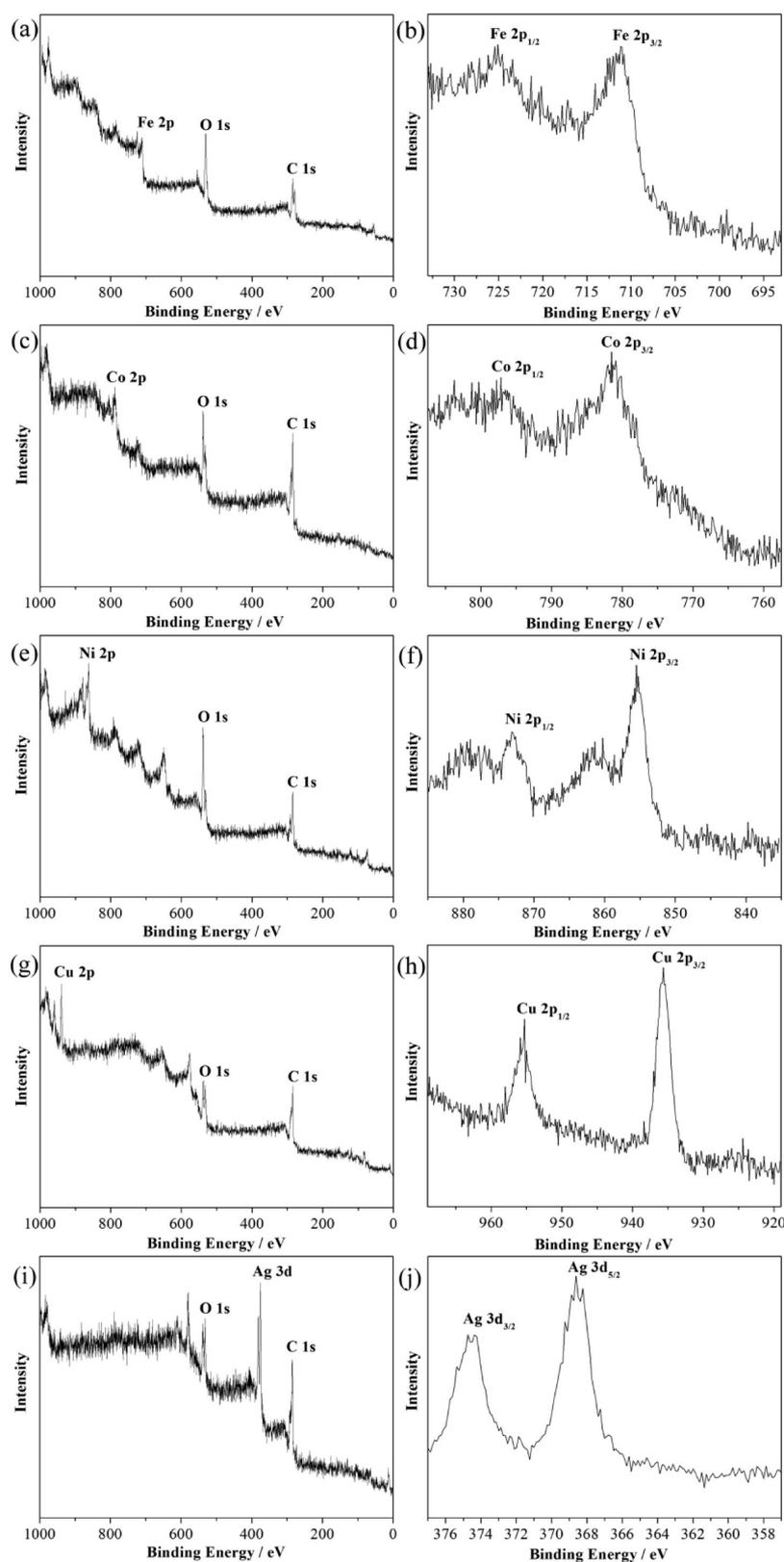


Figure 6. XPS spectrum of fabrics coated with (a, b) iron, (c, d) cobalt, (e, f) nickel, (g, h) copper, and (i, j) silver nanoparticles. The panels on the left show the integrated spectra of each fabric, whereas the panels on the right show the high-resolution spectra that correspond to every metal.

The interaction between the transition metal and *n*-octadecyl thiol is essentially the interaction between the transition-metal atoms and the S atoms in the *n*-octadecyl thiol molecule, resulting in coordination complexes. The pK_{sp} values are found

from *Lange's Chemistry Handbook, 15th Edition*. For iron, we can only find the pK_{sp} value of FeS (Fe(II)) ($pK_{sp} = 17.20$); both elemental Fe and Fe(III) are vacant. Experimentally, on one hand, the as-prepared FeO nanoparticles on the fabric are likely

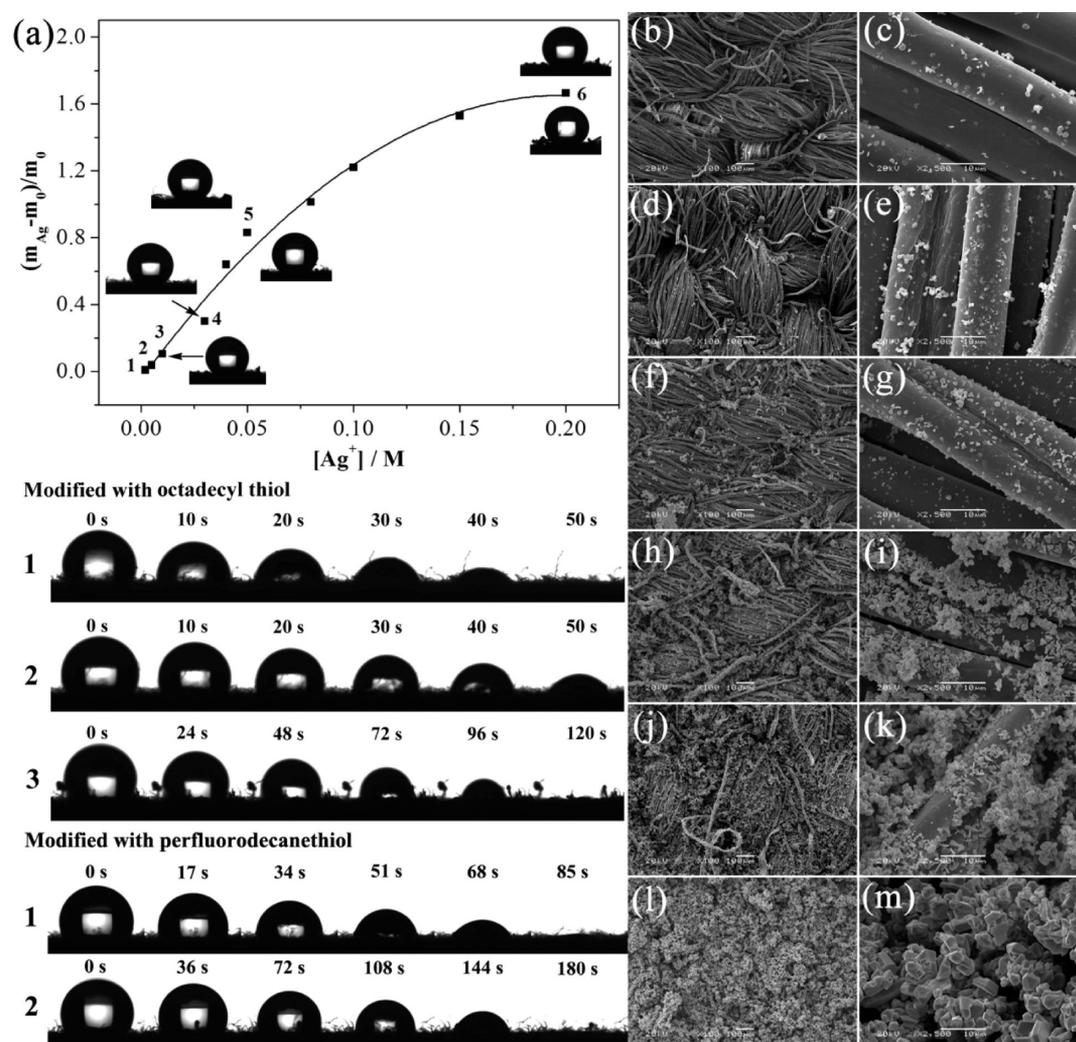


Figure 7. (a) Relationship between the proportion of weight increase $((m_{Ag} - m_0)/m_0)$ and the Ag^+ concentration. The images of contact angle (CA) modified with both *n*-octadecyl thiol (upper left) and perfluorodecanethiol (lower right) at different concentrations are presented near the curve. The contact behaviors of water droplet at lower concentrations were proposed underneath. Panels (b)–(m) are SEM images that correspond to different concentrations of Ag^+ as labeled with dots 1–6 in panel (a): (b, c) dot 1 (0.002 M), (d, e) dot 2 (0.005 M), (f, g) dot 3 (0.01 M), (h, i) dot 4 (0.03 M), (j, k) dot 5 (0.05 M) and (l, m) dot 6 (0.2 M). Images in the far right column are high-resolution SEM images.

to be oxidized; after it was dried in a air-drying oven, the color of the fabric changed from black to rusty red. After the treatment of *n*-octadecyl thiol, the fabric is still superhydrophilic. On the other hand, the fabric with as-prepared elemental iron grown on it was immersed in an *n*-octadecyl thiol solution of ethanol. Then, it is clear that the fabric is still superhydrophilic. However, when the as-prepared fabric coated with Fe nanoparticles was rinsed with sodium borohydride and then immersed in distilled water for 24 h, it became superhydrophobic ($CA \approx 150^\circ$) after surface modification. Accordingly, the experiments have demonstrated that it is the Fe(II) that interacted with *n*-octadecyl thiol, instead of the metallic iron and Fe(III). Other transition metals, such as Co, Ni, Cu, and Ag, might possess the similar property that the as-prepared metallic simple substances cannot be modified by thiol. This may be due to the atmospheric reaction conditions, which can inevitably induce the oxidation of the transition metals, especially nanoscale nanocrystals with high specific surface area. It can be deduced that the transition-metal oxides at the outermost nanoparticles play an important role to interact with thiol. In more detail, it is the transition-metal ions with a specific valence state (such as Fe(II), Co(II), Ni(II), Cu(II) and

Ag(I)) that can efficiently coordinate with thiol and form the coordinate bonds; neither simple transition-metal substances (such as Fe) nor ions with any other valence states (such as Fe(III)) can be modified with thiol.

To the best of our knowledge, the coating capacity of in situ-grown nanoparticles (defined as a weight ratio, $(m_{Ag} - m_0)/m_0$), and the wettability, are related to many factors, such as the initial concentration, reaction rate, external environment, and so forth. This ratio was determined by weighing the original fabrics, and nanocrystal-coated fabrics immediately after being removed from the drying oven. As the most important factor, the precursor concentrations can influence not only the weight of nanoparticles coated on the fabric, but also the wettability of both water and oil in a certain range. As graphically shown in Figure 7a, the coating capacity increases after the in situ growth of nanoparticles, which is correlates positively with the concentration of the precursor. After the precursor concentration surpasses one value, the weight will no longer increase, indicating that the in situ growth of nanoparticles reaches its dynamic equilibrium. The wettability of the water droplet modified with two types of thiols are presented via CA images corresponding to

definite concentrations beside the curve and underneath it in Figure 7a. When the concentration of Ag^+ is quite low, which can induce a low coating capacity, the fabric is hydrophobic (the CA value at 0 s is $>90^\circ$) but unstable (water spreads on the film and permeates through the film within 180 s, even for the fluoric surface at a concentration of 0.005 M), indicating insufficient surface roughness to realize a stable superhydrophobicity. As the concentration of Ag^+ increases and when the coating capacity is $\sim 30\%$ of the original fabric (the corresponding concentration of Ag^+ is $\sim 0.2\text{--}0.3$ M), the stable superhydrophobic fabric is obtained from the modification of *n*-octadecyl thiol, which can shed water effortlessly and the CA value will change slightly while the concentration continues to increase. When the coating capacity of Ag reaches its extreme (~ 1.6 times of the weight of the original fabric), the coating capacity will no longer increase as the concentration of Ag^+ increases. In addition, it is obvious that the fabrics with the modification of fluoric thiol possess lower surface free energy, which can reduce the concentration threshold of Ag^+ , forming a superhydrophobic surface. The gradient increases in coating capacity can be observed intuitively from the SEM images, as schematically shown in Figures 7b–m. Among them, Figures 7h and 7i specifically give both the integrated and high-resolution morphology of the lowest coating capacity (dot 4 in Figure 7a), forming a superhydrophobic surface with modification of *n*-octadecyl thiol, which might also be the optimal one, because the lower coating capacity can best retain the native properties of the fabric. While the coating capacity reaches its upper extreme (dot 6 in Figure 7a), it is difficult to recognize the fibers that compose the fabric, as graphically shown in Figures 7l and 7m. Moreover, with the increase of the coating capacity, the nanoparticles will obviously grow (see Figure S4 in the Supporting Information). The oversized nanoparticles will not contribute to the surface roughness anymore. A similar conclusion is observed for the other transition metals, such as Fe, Co, Ni, and Cu, having the same variation tendency. Unfortunately, with the increase of the in situ growth of nanocrystals, the fabric may lose its original functions and utility. Therefore, it is important to control the weight of fabrics coated with the appropriate amount of nanocrystals that will endow the fabric with multifunctional properties (superhydrophobic and self-cleaning properties coordinate with the daily use) without losing their original functions and utility.

3.4. Mechanisms of In Situ Growth of Metal Oxides and Metals. In situ growth of metal/metal oxide nanocrystals on the fabric allow it to participate in the entire reaction process. In turn, the participation of the fabric allow the generated nanocrystals to easily grow on the fabric beforehand, because of the competition of homogeneous nucleation and heterogeneous nucleation. In the process of homogeneous nucleation, the molecules randomly diffuse throughout the solution, meet, and coalesce into the newly formed particle in the interior of the liquid; in contrast, in the process of heterogeneous nucleation, the new molecules selectively rely on the heterogeneous nucleation sites and gradually grow and transform into crystals.^{25,26} Both the in situ growth of metal oxides and metals can provide enough energy to overcome the nucleation energy (ΔG^*), which depends on the interfacial energy of the metals formed in the reaction medium.²⁵ The homogeneous nucleation and heterogeneous nucleation in certain systems can be related by their nucleation energy:

$$\Delta G_{\text{het}}^* = \Delta G_{\text{hom}}^* f(\theta) \quad (5)$$

where $f(\theta)$ represents the reduction factor ($f(\theta) = \frac{1}{4}(2 + \cos \theta) - (1 - \cos \theta)^2$) and θ is the contact angle (CA), which is a

measure of the interfacial energy between the nucleating metal nanocrystals and the heterogeneous site surface. The term $f(\theta)$ is always <1 in the nonextreme cases ($\theta < 180^\circ$). In the presence of heterogeneous mediums, the nucleation of metal nanocrystals is preferred on these mediums, since $\Delta G_{\text{het}}^* < \Delta G_{\text{hom}}^*$. As a heterogeneous medium, the original fabric possesses a certain amount of surface roughness; thus, its participation will decrease the nucleation energy to form the critical nucleus. The nucleation will first occur on the outer surface of the fabric under the conditions of a sufficiently low solution concentration and a sufficiently slow dropping rate. The faster reaction rate is beneficial for the nanocrystals to nucleate in solution, whereas the slower reaction favors nucleation on the fabric, because of the abundant time available for the nanocrystals to shift to the heterogeneous surface and grow in situ. The growth of transition-metal oxides on fabric is essentially the neutralization reactions, whereas the growth of elemental transition metals is essentially the oxidation–reduction reactions. From a kinetics point, the reaction rate of the neutralization reaction is so quick that the metal oxides are most likely to form in the solution instead of growing on the fabric. A relatively small part of metal oxides is growing on the fabric, and the vast majority has precipitated adequately before they arrive at the fabric. However, the reaction rate of the oxidation–reduction reactions is relatively slow and the elemental metals, being reduced, have sufficient time to grow on the fabric, resulting in the prevailing of heterogeneous nucleation. The elemental metals grown on the fabric are evenly distributed and are more remarkably stable than the as-prepared metal oxides formed via neutralization reactions.

In addition, another advantage for the in situ growth of transition metals is that it can be easily converted to their corresponding oxides via the easy-to-manipulate water-soak treatment (or hydrogen peroxide treatment), which can deeply oxidize the metal nanocrystals. After immersion in distilled water (keep ventilating) for ~ 24 h, the metallic nanocrystals coated on the fabrics were partially or completely converted to the oxides, while leaving the fabric intact. After surface modification with the *n*-octadecyl thiol, the colors of the fabrics change very much, whereas the superhydrophobicity remains unchanged (see Figure S5 in the Supporting Information). The intuitive difference between Figure 2 and Figure S4 in the Supporting Information is the color difference. It might be ascribed to the degree of oxidation of the metal nanoparticles and the ingredients of the oxidized nanoparticles by the water-soak treatment. The gradient variations of fabric color is occur by applying different water-soak times of thiol-modified fabrics coated with Fe nanoparticles as schematically shown in Figure S6 in the Supporting Information. In summary, by combining the relatively time-lapse advantage of the oxidation–reduction reaction with the strong interaction between transition metals and thiol, we provided the universal method to prepare a stable and evenly distributed surface for oil/water separation.

3.5. Surface Modification with Thiols. Surface modification was proposed for the purpose of reducing the surface free energy from the perspective of altering surface chemical composition. Because of the strong covalent bond between sulfur and the transition-metal element, thiols that have a strong interest in reacting with the transition-metal element are selected as modifying agents. The direct evidence is the change of the color of fabrics before and after thiol modification (see Tables S3–S5 in the Supporting Information). Here, two types of thiols, i.e., *n*-octadecyl thiol and 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol, are used to modify the fabrics that have been coated with

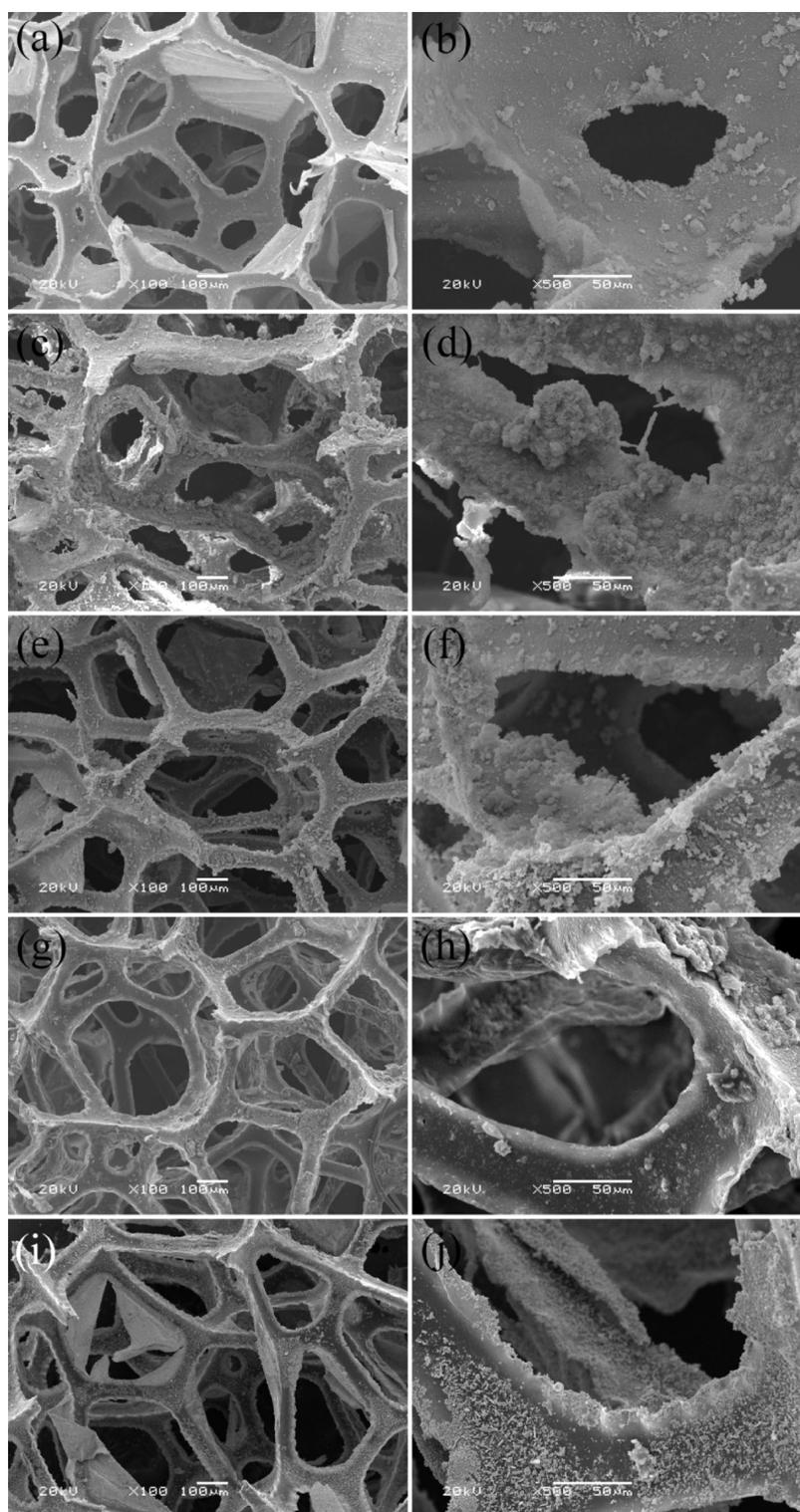


Figure 8. SEM images of sponges coated with (a, b) Fe, (c, d) Co, (e, f) Ni, (g, h) Cu, and (i, j) Ag nanoparticles.

transition metal/metal oxide nanoparticles. Both of them can realize the property of superhydrophobicity. However, only the fabric modified with the fluoric *1H,1H,2H,2H*-perfluorodecane-thiol can induce an oleophobic property (see Figure S7 in the Supporting Information).

3.6. Superhydrophobic and Superoleophilic Sponge.

Sponge is a type of very rough surface material with a porous structure and a large internal surface area; it is known as a strong absorbing medium for both oils and water. Therefore, the coating

of transition-metal nanocrystals with *n*-octadecyl thiol modification on the sponge skeletons is expected to invert the wettability of the sponge from superhydrophilic to superhydrophobic while maintaining its capacity of absorbing oils, thus realizing its application for removing oils from water. Similar to the fabric, the porous sponge can not only adsorb the metal nanoparticles via van der Waals forces, but also bond with the metal nanoparticles through the polar ligands widely distributed both inside and outside the sponge. It makes the nanoparticles be

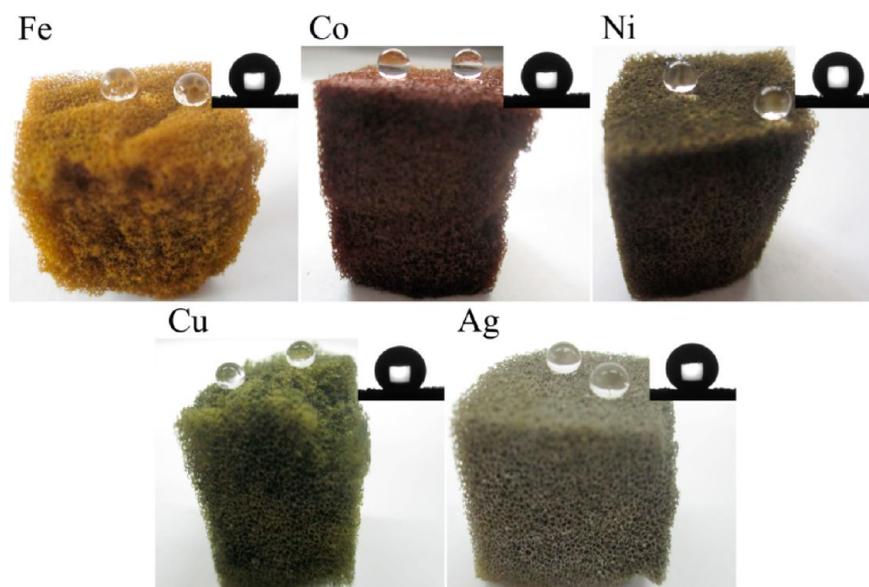


Figure 9. Optical images of superhydrophobic sponges from the in situ growth of Group VIII and IB metal nanoparticles. The inset images in the upper-right-hand corner of each panel are the images of static water droplets ($5 \mu\text{L}$).

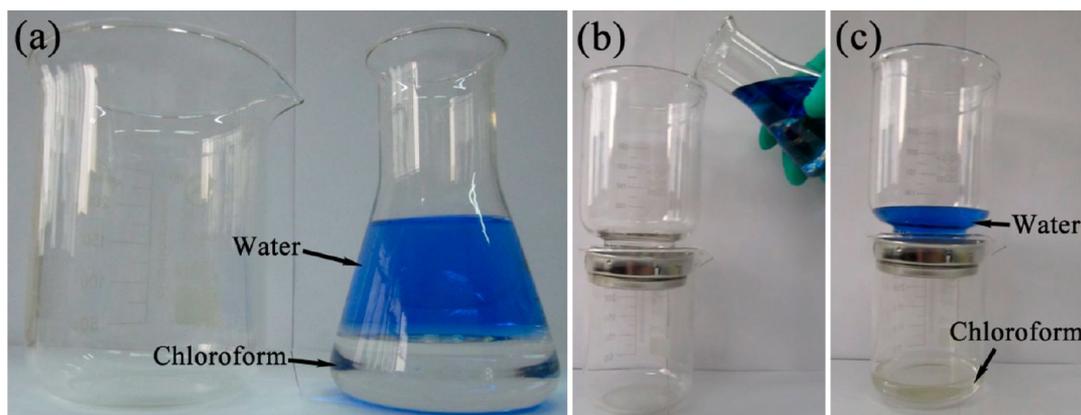


Figure 10. Photograph of the fabric-based oil/water separation process of water and chloroform (see the video file provided in the Supporting Information). The water was dyed with Methylene Blue for clear observation.

deeply absorbed and well fixed with the sponge skeleton, forming the microscale and nanoscale rough surface, as graphically shown in Figure 8 (the original sponge is shown in Figure S8 in the Supporting Information), thus improving the stability of its superhydrophobicity and the working life for its application in oil–water separation. Different loadings of the transition-metal nanocrystals on the sponges can be controlled by using the same strategy of altering the concentration of the precursors, and it has a variation trend similar to the in situ growth on the fabric. As is graphically shown in Figure 9, superhydrophobic/superoleophilic sponges from the in situ growth of different transition metals have been realized.

3.7. Oil/Water Separation. The surface free energy (tension) of water is commonly much greater than that of oil. Therefore, solid surfaces possess the proper surface free energy (between those of water and oil) such that both hydrophobicity and oleophilicity might be exhibited. Combined with an appropriate surface morphology, porous superhydrophobic and superoleophilic materials can be prepared. By combining superhydrophobicity with superoleophilicity, a porous surface that possesses special wettability is introduced, intended to be used to separate oil from water.

Fabrics/sponges coated with Group VIII and IB metal/metal-oxide nanoparticles form the microscale and nanoscale hierarchical rough structure. While they are modified with *n*-octadecyl thiol, which possesses the proper surface tension (between those of water and oil), they show very different wettability to water and oil droplets. For the water droplets, the fabric/sponge surface shows superhydrophobicity, and thus water cannot permeate the porous surface, which should be attributed to the large negative capillary effects resulting from the nanostructures. For the oil droplets, the surface is superoleophilic, and thus the oil can permeate the film smoothly. Since the microscale and nanoscale hierarchical structure can magnify the wettability of the surfaces to their extremes,^{27,28} it can be concluded that both the antipermeability of water and the permeability capacity of oil can be remarkably amplified by the coordination effect of the microscale fibers (sponge skeleton) and the nanoscale nanocrystals.²⁹ The wetting difference between water and oil on the porous surface provide a strategy to separate a water-and-oil mixture effectively.

The separation experiments of a water-and-oil mixture, using both fabrics and sponges, have been realized, as graphically shown in Figures 10 and 11a–c (video files are provided in the

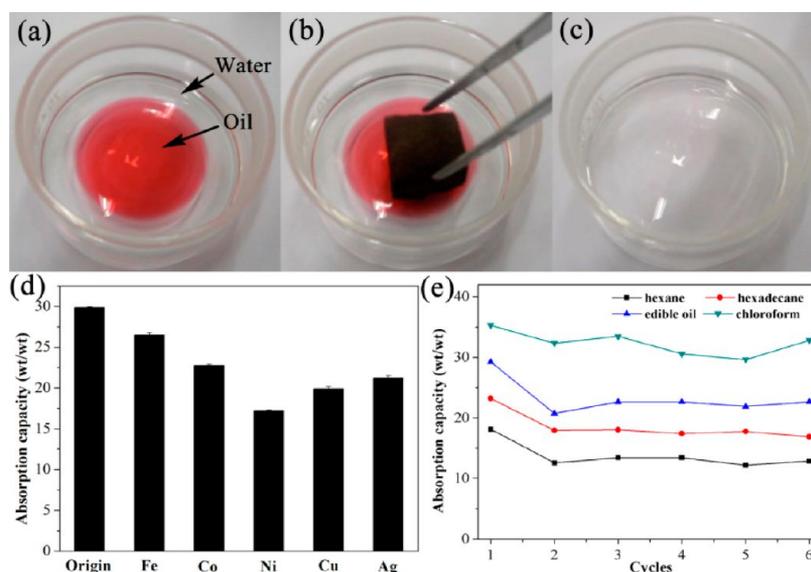


Figure 11. (a–c) Snapshots of the removal process of hexadecane (dyed with oil Red Dye 24 for clear observation) from the distilled water surface by an as-prepared sponge coated with cobalt nanoparticles (see the video file provided in the Supporting Information). (d) Bar graph showing the absorption capabilities of as-prepared sponges coated with different metal nanoparticles. (e) Line graph showing the absorption capabilities of as-prepared sponges coated with copper nanoparticles for different types of oil or organic solvent.

Supporting Information). In the fabric-based oil/water separation device, the as-prepared fabric coated with silver nanoparticles was fixed to the bottom of a bottle that is open at both ends. As expected, while a mixture of water (dyed with Methylene Blue for clear observation) and chloroform was poured into the fabric-based oil/water separation device, the chloroform was absorbed and permeated through the fabric and rapidly dropped into the beaker underneath, whereas water could not penetrate the film and still resided on the fabric. Superhydrophobic/superoleophilic sponges from our approach can separate oils from water surface easily. By dipping the sponge that was coated with cobalt nanoparticles into a water-and-oil mixture, the oils were quickly absorbed by the sponge. While the sponge was pulled out of the water, the oils were completely drawn and the water became clear, as illustrated in Figure 11.

The absorption capacity, which is defined as $(m_{\text{saturated}} - m_{\text{initial}})/m_{\text{initial}}$, was used to measure the weight of oils and other nonpolar organic liquids that can be captured by the as-prepared sponges with an in situ growth of Group VIII and IB metals. As schematically shown in Figure 11d, the absorption capacity of hexane for the native sponge and sponges respectively coated with Fe, Co, Ni, Cu, and Ag are slightly different from each other. However, the sponges coated with metal nanoparticles always possess lower absorption capacity than the native one, indicating a damping effect on the oil/water separation efficiency. This might be because the as-coated metal nanoparticles inside the porous sponges more or less fill the interspace, thus partially occupying the space, which is prerequisite for the absorption of oils. Therefore, a proper loading of metal nanoparticles is indispensable so that it is possible to form a stable superhydrophobic surface (as illustrated in Figure 7a), otherwise saving as much storage space inside the sponge as possible. In addition, the absorption capacity of superhydrophobic/superoleophilic sponges for different types of oils and organic solvents were investigated for the purpose of measuring the practical capability for various oil/water separation systems and the recyclability of the sponges. In typical absorption measurements, as schematically shown in Figure 11e, the superhydrophobic/

superoleophilic sponges coated with copper nanoparticles were used to absorb the as-selected oils (i.e., hexane, hexadecane, edible oil, and chloroform). The absorption capabilities vary from individual to individual; the bigger the specific gravity, the larger the absorption capability. The primary absorption capabilities are obviously larger than the subordinate one; this is because the virgin sponges are much more lightweight than the as-used ones, since the oils inside the sponges cannot be completely squeezed out. Moreover, as-prepared sponges from our method show excellent recyclability for different types of oil, since the absorption capabilities after the first cycle remain unchanged.

4. CONCLUSIONS

In conclusion, the objective of this work was to report on a general methodology for the in situ growth of both metals and their oxides on fabrics, as well as sponges, which can be modified with thiols, instead of proposing a limited method for designated metal/metal oxide. The Group VIII and IB metal oxides, as well as simple metallic substances, such as Fe, Co, Ni, Cu, and Ag, were successfully fabricated via the simple and available methods using the in situ growth with metals/metal oxides on the fabric/sponge substrate. Different transition-metal elements, as well as the same transition metal with different valence states, could provide the porous fabric/sponge with different colors. The as-selected transition-metal element can not only strongly bond with thiols, but also possess some special properties that can be utilized to realize multifunctional integration.³⁰ These transition-metal nanoparticles were all prepared via a coprecipitation method. Furthermore, taking Ag nanoparticles as an example, the relationship between the precursor concentration, the coating capacity, and the wettability was investigated in details. We have not only presented the optimum consumption of the precursor that can retain the native properties of the fabric, based on the premise of realizing its stable superhydrophobicity, but we have also revealed its microscopic morphology contrasting with the surface morphology with both insufficient and superfluous nanoparticles from the in situ growth method. The in situ growth

of metal oxides is essentially the neutralization reactions, since the precursors can be recognized as Lewis acids. In addition, the in situ growth of metals is essentially the oxidation–reduction reaction. Since the redox potentials are different for individual transition metals, the appropriate reducing agent is indispensable (such as sodium borohydride and ascorbic acid) to reduce the metal ions to their simple substances. In addition, our strategy is also available for other thiols, such as 1H,1H,2H,2H-perfluorodecanethiol. After being modified with fluoroalkyl thiol, the fabric/sponge could realize superhydrophobic properties, as well as oleophobic properties.

The oil/water separation experiments demonstrated that the as-obtained superhydrophobic/superoleophilic fabrics and sponges can be effectively used to separate both heavy oils (greater density than water) and light oils (lower density than water). The as-prepared metal-nanoparticle-based sponge can absorb a broad variety of oils with high selectivity, enormous absorption capacities, and excellent recyclability. It shows promise for developing an environmental friendly and cost-effective strategy for advanced liquid–liquid separation or water treatment technology.

■ ASSOCIATED CONTENT

📽 Supporting Information

Movies of oil/water separations via both the fabric-based device and sponge-based device (Movies 1 and 2), pK_{sp} values of different sulfides (Table S1), optical images of the hydrophilic fabrics and sponges (Figure S1), SEM images of the original fabric (Figure S2) and the original sponge (Figure S8), XPS spectrum of fabrics coated with metal-oxides (Figure S3), high-resolution SEM images of fabrics coated with Ag nanoparticles at the different concentrations of Ag^+ (Figure S4), weight variations of fabrics coated with different transition metal nanoparticles (Table S2), color changes of fabric coated with metal/metal-oxides nanoparticles over the entire fabrication process (Tables S3–S5), optical images of superhydrophobic fabrics coated with metal nanoparticles that experience the water-soak treatment (Figure S5), wettability of thiol-modified fabrics with iron growth on possessing different water-soak times (Figure S6), wettability comparison of water/oil on the alkyl and perfluoroalkyl thiols (Figure S7), and optical images of robust superhydrophobic fabric and sponge (Figure S9). These materials are 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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■ REFERENCES

- (1) Guo, Z. G.; Zhou, F.; Hao, J. C.; Liu, W. M. *J. Am. Chem. Soc.* **2005**, *127*, 15670–15671.
- (2) Feng, X. J.; Jiang, L. *Adv. Mater.* **2006**, *18*, 3063–3078.

- (3) Guo, Z. G.; Liu, W. M.; Su, B. L. *J. Colloid Interface Sci.* **2011**, *353*, 335–355.
- (4) Bhushan, B. *Langmuir* **2012**, *28*, 1698–1714.
- (5) Choi, C.-H.; Kim, C.-J. *Phys. Rev. Lett.* **2006**, *96*, 066001.
- (6) Lee, C.; Choi, C.-H.; Kim, C.-J. *Phys. Rev. Lett.* **2008**, *101*, 064501.
- (7) Xu, W.; Choi, C.-H. *Phys. Rev. Lett.* **2012**, *109*, 024504.
- (8) Wang, C. X.; Yao, T. J.; Wu, J.; Ma, C.; Fan, Z. X.; Wang, Z. Y.; Cheng, Y. R.; Lin, Q.; Yang, B. *ACS Appl. Mater. Interfaces* **2009**, *1*, 2613–2617.
- (9) Tian, D. L.; Zhang, X. F.; Wang, X.; Zhai, J.; Jiang, L. *Phys. Chem. Chem. Phys.* **2011**, *13*, 14606–14610.
- (10) Xue, Z. X.; Wang, S. T.; Lin, L.; Chen, L.; Liu, M. J.; Feng, L.; Jiang, L. *Adv. Mater.* **2011**, *23*, 4270–4273.
- (11) Ookawara, S.; Ishikawa, T.; Ogawa, K. *Chem. Eng. Technol.* **2007**, *30*, 316–321.
- (12) Choi, C.-H.; Ulmanella, U.; Kim, J.; Ho, C.-M.; Kim, C.-J. *Phys. Fluids* **2006**, *18*, 087105.
- (13) Blossey, R. *Nat. Mater.* **2003**, *2*, 301–306.
- (14) Xue, C. H.; Jia, S. T.; Chen, H. Z.; Wang, M. *Sci. Technol. Adv. Mater.* **2008**, *9*, 035001.
- (15) Xu, B.; Cai, Z. S. *Appl. Surf. Sci.* **2008**, *254*, 5899–5904.
- (16) Liu, Y. Y.; Wang, X. W.; Qi, K. H.; Xin, J. H. *J. Mater. Chem.* **2008**, *18*, 3454–3460.
- (17) Liu, Y. Y.; Tang, J.; Wang, R. H.; Lu, H. F.; Li, L.; Kong, Y. Y.; Qi, K. H.; Xin, J. H. *J. Mater. Chem.* **2007**, *17*, 1071–1078.
- (18) Nguyen, D. D.; Tai, N.-H.; Lee, S.-B.; Kuo, W.-S. *Energy Environ. Sci.* **2012**, *5*, 7908–7912.
- (19) Wang, H. X.; Fang, J.; Cheng, T.; Ding, J.; Qu, L. T.; Dai, L. M.; Wang, X. G.; Lin, T. *Chem. Commun.* **2008**, 877–879.
- (20) Leng, B. X.; Shao, Z. Z.; With, G. de; Ming, W. H. *Langmuir* **2009**, *25*, 2456–2460.
- (21) Wang, T.; Hu, X. G.; Dong, S. J. *Chem. Commun.* **2007**, 1849–1851.
- (22) Zhu, X. T.; Zhang, Z. Z.; Yang, J.; Xu, X. H.; Men, X. H.; Zhou, X. Y. *J. Colloid Interface Sci.* **2012**, *380*, 182–186.
- (23) Li, J.; Shi, L.; Chen, Y.; Zhang, Y. B.; Guo, Z. G.; Su, B. L.; Liu, W. M. *J. Mater. Chem.* **2012**, *22*, 9774–9781.
- (24) Kida, T.; Oka, T.; Nagano, M. *J. Am. Ceram. Soc.* **2007**, *90*, 107–110.
- (25) Narula, G. K.; Narula, K. S.; Gupta, V. K. *Materials Science*; McGraw–Hill: New York, 1988; p 157.
- (26) Boistelle, R.; Astier, J. P. *J. Cryst. Growth* **1988**, *90*, 14–30.
- (27) Wang, B.; Zhang, Y. B.; Shi, L.; Li, J.; Guo, Z. G. *J. Mater. Chem.* **2012**, *22*, 20112–20127.
- (28) Bhushan, B.; Jung, Y. C. *Prog. Mater. Sci.* **2011**, *56*, 1–108.
- (29) Zhang, Y. B.; Chen, Y.; Shi, L.; Li, J.; Guo, Z. G. *J. Mater. Chem.* **2012**, *22*, 799–815.
- (30) Liu, K. S.; Jiang, L. *ACS Nano* **2011**, *5*, 6786–6790.