Roselike Microstructures Formed by Direct In Situ Hydrothermal Synthesis: From Superhydrophilicity to Superhydrophobicity

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We describe the fabrication of roselike microstructures by the direct in situ hydrothermal synthesis method. The as-prepared roselike microstructure film exhibits excellent superhydrophilic properties, absorbing a water droplet of 4 μL in less than 40 ms. Moreover, after a further modification with a self-assembled monolayer of octyltrimethoxysilane, the film changes its wetting properties from superhydrophilicity to superhydrophobicity with a contact angle as high as 154° and a tilt angle lower than 3°.

Introduction

Hydrothermal synthesis is a powerful method not only for preparation of three-dimensional zeolite crystals but also for fabrication of surface zeolite films.[1−3] Different hydrothermal methods have been developed to fabricate surface zeolite films, such as synthesis in the vapor phase,[4] template in situ growth,[5,6] seeding growth,[7] heteroepitaxial growth,[8] and the direct in situ crystallization method.[9] Their promising applications include catalysts in reactors, sensors for detection, and separation devices for gas or liquid separations.[3] However, to the best of our knowledge, there are few reports about the use of the direct in situ hydrothermal synthesis method to adjust the morphology and surface coverage of surface micro/nanostructures for mimicking the lotus effect.

The lotus effect concerns the self-cleaning property of lotus leaves, as first reported by Barthlott and Neinhuis.[10] Since the self-cleaning property has been revealed to be a cooperative effect of low surface energy and high surface roughness,[11,12] many interesting methods have been developed to mimic the lotus effect, including electrochemical deposition of metal aggregates,[13−16] arrays of carbon nanotubes, reconformation of polymers, plasma fluorination, the sol−gel method, TiO_2 coating by UV irradiation, and others.[17−21] Herein, we attempt to use the direct in situ hydrothermal synthesis method to fabricate surface microstructures with unique morphology, aiming at providing a strategy to generate superhydrophilic or superhydrophobic surfaces.

Experimental Section

The roselike microstructures were prepared according to the synthesis of mordenite (MOR) zeolite.[22] The reaction mixtures were prepared by slowly adding 0.107 g of $Al(NO_3)_3 \cdot 9H_2O$ into 5.7 mL of an aqueous solution of NaOH (the concentration was about 1.23 M), followed by adding 1.75 mL of colloidal silica (343.4 g/L SiO_2, 862.6 g/L H_2O) into the mixture. Finally, methanol was added into the mixture solution. A gel was formed and further stirred until it was homogeneous followed by aging for an hour at room temperature. Its final composition was $1SiO_2$:1/70Al_2O_3:7/20Na_2O:3/2methanol:40H_2O in molar ratio.

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After aging, the synthesis mixture was transferred into a Teflon-lined stainless steel autoclave, followed by immersion of a glass substrate in the reaction mixture. The glass substrate of 0.5 mm thickness was cleaned by immersing it in a mixed solution of H_2SO_4 and H_2O_2 (v/v = 7:3) for 30 min in advance. Then, the stainless steel autoclave was sealed and kept at 160 °C in a constant temperature oven for a given time. After it was taken out from the constant temperature oven, the stainless steel was cooled in the atmosphere, naturally.

The glass substrate with special microstructures was drawn out from the autoclave carefully and washed with distilled water. Before it dried, a homogeneous film formed on the glass substrate. After drying under atmosphere overnight, the unique film on the glass substrate was peeled off from the substrate. However, the special film without the glass substrate was still stable after drying.

The surface modification of the substrates covered with zeolites and roselike microstructures was carried out by immersing it in a toluene solution of octyltrimethoxysilane (1×10^{-3} M) for 24 h to form a self-assembled monolayer terminated with $-CH_3$ groups on the surface. Then the substrate was washed in turn with toluene, chloroform, ethanol, and distilled water, and then dried under atmosphere overnight.

The controlled experiments were carried on in a similar process, only changing the composition of the reaction mixture by taking out some components.

The measurements of static contact angles were carried out by commercial instruments (OCA 20, DataPhysics Instruments GmbH, Filderstadt). A distilled water droplet of 4 μL was used as the indicator. The filter paper for the controlled experiments of superhydrophilicity is qualitative filter paper (made in Hangzhou Fuyang Special Paper Industry Co., Ltd, P.R. China). The field emission scanning electron microscope (FE-SEM) images and energy-dispersive X-ray microanalysis (EDAX) patterns were obtained with a JEOL JSM-6700F scanning electron microscope at 10.0 kV.

Results and Discussion

The morphology of the surface microstructure formed on the glass substrate has been observed carefully with FE-SEM. With a reaction time of 6 h, very few roselike microstructures and some zeolite crystals are seen on the glass substrate, and most of the surface is covered with the reaction mixture, as shown in Figure 1a. When the reaction time is extended to 24 h, more roselike microstructures and crystal zeolites form on the substrate, as shown in Figure 1b, though the surface coverage is not very high. With further extension of the reaction time, more and more surface microstructures with different morphologies form on the substrate, and their size and density on the substrate increase, as shown in Figure 1c. However, after the glass substrate is dried under atmosphere, the surface microstructural films cannot adhere to the glass substrate stably. We presume that this is caused by the different surface properties of the surface microstructures and the glass substrate. We wonder if, when the reaction time is long enough to dissolve the glass substrate, the surface microstructures might form a stable free-standing film. When the reaction time is increased to 72 h and the glass substrate is dissolved, free-standing films are indeed obtained, which take the same shape and size as that of the glass substrate, as shown in Figure 1d.

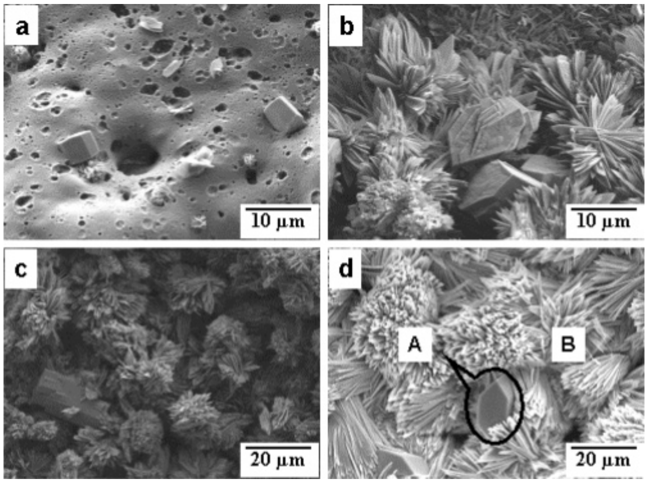

Figure 1. FE-SEM images of the surface structure formed by the direct in situ hydrothermal synthesis method. The reaction composition is $1SiO_2$:1/$70Al_2O_3$:7/$20Na_2O$:3/2methanol:$40H_2O$. The reaction time is 6 h (a); 24 h (b); 48 h (c); 72 h (d). A refers to the area covered by the zeolite crystal and B refers to the area covered only by roselike microstructures.

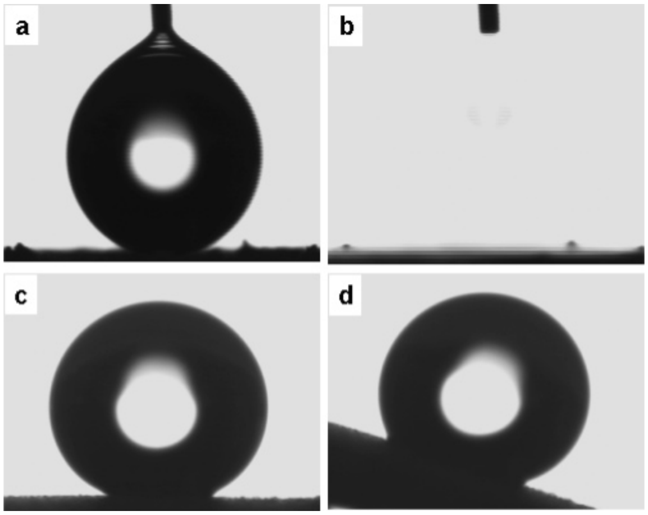

Figure 2. Shape of water droplets on the surface covered with both roselike microstructures and crystal zeolites (drop weight 4 mg) (a) before octyltrimethoxysilane modification; (b) 40 ms later than (a); (c) and (d) after octyltrimethoxysilane modification.

The wetting property of the free-standing film was studied by a contact angle instrument. When a water droplet (drop weight 4 mg) is placed on the surface, it is absorbed into the microstructure film in less than 40 ms, as shown in Figure 2, parts a and b. Forty milliseconds is the time limit of our contact angle instrument. We also find that hydrophilic filter paper absorbs a water droplet in more than 400 ms. This suggests that the surface, which contains both roselike microstructures and crystal zeolites, exhibits an excellent superhydrophilic property.

The surface of this substrate becomes superhydrophobic after immersing it in a toluene solution of octyltrimethoxysilane (1×10^{-3} M). The contact angle on this surface is about 153°, as shown in Figure 2c, suggesting that the surface changes from superhydrophilicity to superhydrophobicity. However, the tilt angle of the surface is more than 10°, as shown in Figure 2d, which indicates that water droplets do not easily run off. Therefore, such a surface bearing zeolite crystals and roselike microstructures is a superhydrophobic surface, but not a self-cleaning surface, which may be due to the presence of zeolite crystals on the surface.

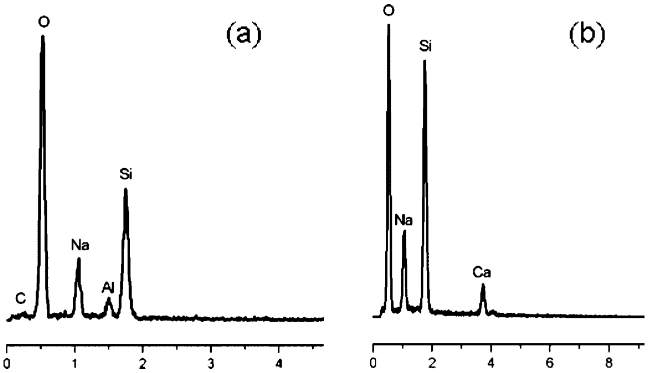

Figure 3. EDAX pattern of the film shown in Figure 1d; (a) is obtained from the crystal zeolite area (area A); (b) is obtained from the roselike microstructure area (area B).

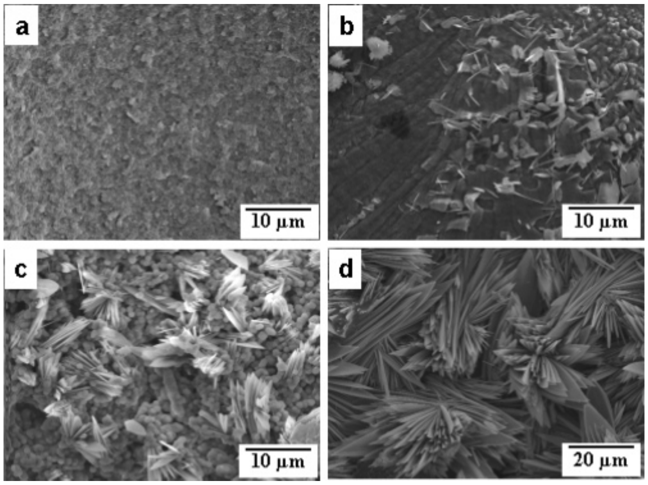

Figure 4. FE-SEM images of the surface with only roselike microstructure by the direct in situ hydrothermal synthesis method. The composition is $1SiO_2$:7/$20Na_2O$:3/2methanol:$40H_2O$. The reaction time is 6 h (a); 12 h (b); 24 h (c); 72 h (d).

To make the difference of areas A and B in Figure 1d clear, we used EDAX to characterize the composition of the zeolite crystal in area A and roselike microstructures in area B of Figure 1d. As seen in Figure 3a, a strong signal of the element Al is detected in the zeolite crystal area. However, in the roselike microstructure area, there is no signal of Al, as shown in Figure 3b. Moreover, we can see in Figure 1d, that there are more roselike microstructures than zeolite crystals on the surface, which may be due to the depletion of the $Al(NO_3)_3{\cdot}9H_2O$ in the reaction mixture. Thus we reason, if we do not add $Al(NO_3)_3{\cdot}9H_2O$ into the reaction mixture, we should be able to get a surface covered only with the roselike microstructures.

Indeed, by not adding $Al(NO_3)_3{\cdot}9H_2O$ into the reaction mixture, we obtain a surface only covered with the roselike microstructure as shown in Figure 4. As shown in Figure 4a, no zeolite appeared on the surface after 6 h of hydrothermal reaction. With an increase of the reaction time, there are more and more roselike microstructures formed on the substrate. When the reaction time reaches 12 h, there are some petal-like structures on the surface, as shown in Figure 4b. The roselike microstructures are observed when the reaction time is extended to 24 h, as shown in Figure 4c. However, just like before, the surface microstructure can come off the glass substrate after it is dried. So we choose to dissolve the glass substrate by increasing the reaction time to 72 h. Under this condition, we can obtain a stable free-standing film with only roselike microstructure, as shown in Figure 4d.

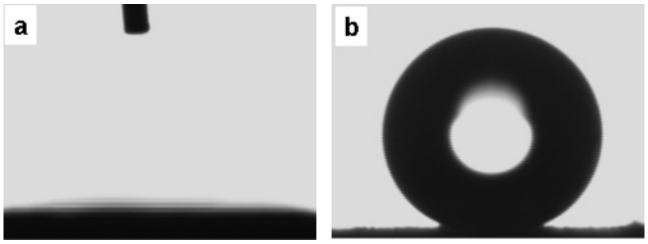

Figure 5. Shape of a water droplet on the surface only covered by the roselike microstructures (drop weight 4 mg) (a) before octyltrimethoxysilane modification; (b) after octyltrimethoxysilane modification.

We also studied the wetting property of this stable free-standing film with only roselike microstructures with the contact angle instrument. The free-standing film exhibits an excellent superhydrophilic property almost the same as that of the film containing zeolite crystals. It also absorbs a water droplet in less than 40 ms, as shown in Figure 5a. After the as-prepared film is modified with a self-assembled monolayer of octyltrimethoxysilane, the surface becomes superhydrophobic. The contact angle is about 156°, as shown in Figure 5b, and the tilt angle is lower than 3°, which means the water droplet can roll off the surface easily. So the roselike microstructure film is a self-cleaning surface with a “dirt repellent” or “dirt resistant” property.

To fully understand the self-cleaning property of the roselike microstructure film modified with a self-assembled monolayer of octyltrimethoxysilane, we describe the contact angle in terms of the Cassie equation:[23] $\cos\theta_r = f_1 \cos\theta - f_2$. Here, θ_r (156°) is the contact angle of the roselike film modified with a self-assembled monolayer of octyltrimethoxysilane; θ (80°) is the contact angle of the octyltrimethoxysilane monolayer on the glass substrate;[24] and f_1 and f_2 are the fractional interfacial areas of the roselike microstructures and of the air in the interspaces among the roselike microstructures, respectively (i.e., $f_1 + f_2 = 1$). This equation predicts that increasing the fraction of air (f_2) would increase the contact angle of the roselike film (θ_r). According to the equation, the f_2 value of the rough surface with roselike microstructures is estimated to be 0.93. This means that air occupies about the 93% of contact area between the water droplet and the roselike microstructures, which is responsible for the self-cleaning property of the surface.

In conclusion, we have extended the in situ hydrothermal synthesis method to fabricate a unique surface microstructure that is controlled by the reaction time and the composition. The relation of the surface microstructures with their wetting properties is discussed. Our results have demonstrated that the surface with only roselike microstructures has shown excellent properties of superhydrophilicity and superhydrophobicity after further chemisorption. Such a similar concept could be applied to synthesize many surface micro/nanostructures, combining the self-cleaning coatings with the

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unique properties of zeolites such as adsorption and separation.

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