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UV-Driven Reversible Switching of a Roselike Vanadium Oxide Film between Superhydrophobicity and Superhydrophilicity

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In recent years, functional surfaces with reversibly tunable wettability have become much sought after because of their usefulness in fundamental research and industrial applications.[1] The wettability of solid surfaces is influenced by both the surface geometry and the chemical composition. Various transition-metal oxides, such as ZnO, TiO_2, WO_3, and SnO_2, are well-known to exhibit photoinduced hydrophilicity as a result of UV light irradiation.[2] Moreover, although most metal oxide surfaces with controllable wettability exhibit only minor changes in water contact angle (CA) when prepared on smooth substrates, hierarchically nanostructured metal oxide substrates exhibit large changes in their responsive wettability, from superhydrophobic to superhydrophilic states.[3] Various studies have shown that the variation of the surface wettability can be intensified by generating a local structure with a large geometric area relative to the nominal area.[4]

Vanadium pentoxide (V_2O_5) is a well-known transition-metal oxide that has been extensively studied and widely used in many applications such as catalysts, electrochemical devices and functional ceramics.[5] Further, V_2O_5 exhibits photoinduced hydrophilic properties as a result of UV light irradiation.[2] After dark storage for a certain time, the hydrophilicity of V_2O_5 substrates is significantly reduced and the water CA is restored to its initial value. Most previous research into V_2O_5 has mainly aimed at the fabrication of nanostructured forms with anisotropic morphology,[6] gas sensors,[7] optical switches,[8] and electrodes in Li rechargeable batteries,[9] but its surface wettability has been insufficiently studied. In particular, a V_2O_5 substrate that can be switched between superhydrophobicity and superhydrophilicity with UV irradiation has not previously been reported.

In this paper, we present the fabrication of a roselike nanostructured V_2O_5 film with a wettability that can be reversibly switched between superhydrophilic and superhydrophobic through UV irradiation and dark storage, respectively. This study might provide a general method for fabrication systems with desirable properties, that is, by delivering a suspension of roselike V_2O_5 particles onto a substrate, which can be achieved with a number of current technologies including inkjet printing, micropipetting, and microcontact printing.

Porous nanostructured V_2O_5 films were obtained by drop-casting an ethanolic suspension of V_2O_5 particles, which were synthesized with the sol−gel method,[10] onto Si wafers. Vanadium triisopropoxide was mixed in an ethanolic−aqueous medium together with hexadecylamine as an organic templating agent and the mixture was stirred for 24 h in air. The resulting orange suspension was then heat-treated in a Teflon-lined autoclave at 180 °C for about a week. The final product was washed with pure ethanol and distilled water, then dried under vacuum at room temperature. The V_2O_5 particles were redissolved in ethanol, and the ethanolic suspension was used to fabricate nanostructured V_2O_5 films by drop-casting onto Si wafers.

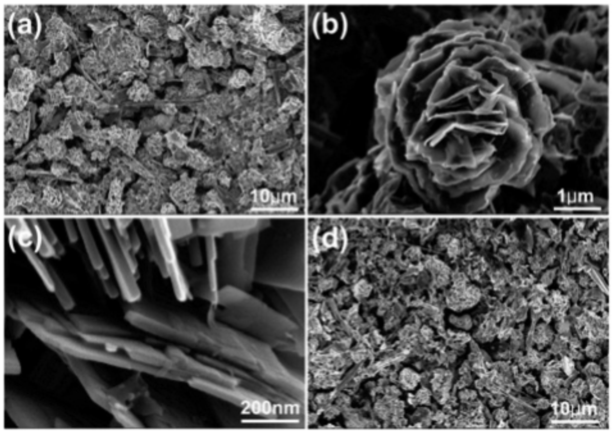

Figure 1. (a) SEM image of a rose-garden-like nanostructured V_2O_5 substrate. (b) Close-up image of an individual roselike spherical structure. (c) Magnified image of panel b. (d) SEM image of a nanostructured V_2O_5 substrate after calcination at 400 °C.

The morphologies of the V_2O_5 films can be seen in the SEM images in Figure 1. The films have an interesting rose-garden-like morphology, which results from the aggregation of the nanoporous spheres on the substrate. The close-up image shows that the morphology of roselike spheres is composed of smooth petal-like structures, which presumably arise from the layered structure of V_2O_5. The spherical structures are several micrometers ($3\sim5\ \mu$m) in diameter. Figure 1c shows a highly magnified image of an individual roselike sphere, with its multilayered structure consisting of hierarchically densely packed radially oriented nanoslices. The thickness of the layered structures and the crevices between them were found to be ∼40 nm. Therefore, this substrate should have superhydrophobic properties, as observed in nature on lotus leaves, owing to its nanoporous structure with submicron- to micron-scale apertures.[11]

The surface wettability of the V_2O_5 substrate was studied by measuring the water CA. Watanabe and co-workers reported that a smooth and pure V_2O_5 substrate has a water CA of 50°, that is, it exhibits hydrophilic behavior.[2] However, we found that the water CA of the nanostructured V_2O_5 film was about $156 \pm 2°$, with the water droplet riding on top of the surface, which indicates the presence of a superhydrophobic state (Figure 2a). To explain this phenomenon, X-ray diffraction (XRD) analysis was carried out on the deposited V_2O_5 film (Figure 2c). It is noticeable that the V_2O_5 film produces an XRD pattern characteristic of a mesophase with an interlaminar distance of 2.1 nm, corresponding to its (001) reflections. These coincide with the intercalation of the amine into the V_2O_5. This result suggests the presence of a double layer of the amine perpendicularly oriented to the V_2O_5 planes with interpenetrated alkyl chains.[12] The dense packing of the alkylchains thus renders the V_2O_5 surface hydrophobic, then the superhydrophobicity of the nanostructured V_2O_5 film arises because the nanoporous network structures trap air in the apertures.[11b] The hierarchical roughness of the nanostructured V_2O_5 film enhances

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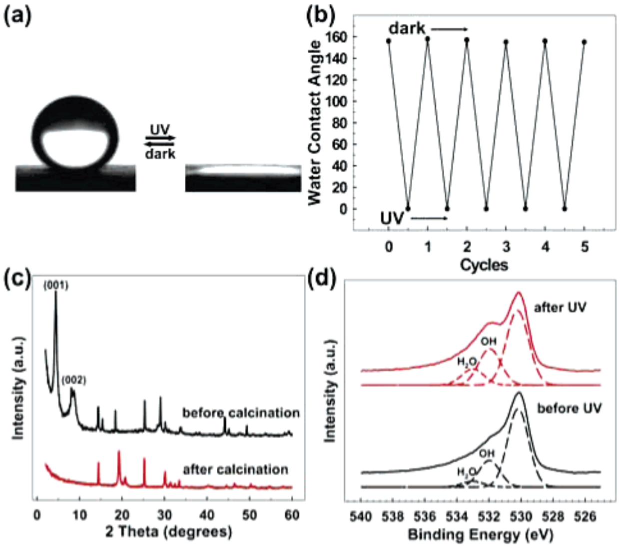

Figure 2. Photoresponsive wettability changes in the nanostructured V_2O_5 substrate: (a) water droplet profiles and (b) reversible wettability transitions through UV exposure and dark storage, respectively; (c) X-ray diffraction analysis before and after calcination; (d) X-ray photoelectron spectroscopy spectra of the O 1s level before and after UV irradiation.

the hydrophobic behavior, so that water droplets on the surface tend to become perfectly spherical (Figure 2a). In addition, the alkyl chains were removed by carrying out calcination in air to verify their effect on the water-repellency of the nanostructured V_2O_5 film. Even though the nanostructured V_2O_5 surface maintains its configuration without severe damage after calcination at 400 °C (Figure 1d), its water CA becomes almost zero, so water spreads very rapidly over the surface. The calcinated V_2O_5 film maintains superhydrophilicity even after the dark storage for 6 months and it does not show photoreversible water CA change. As expected, the XRD reflections related to the alkyl chains disappear after calcination at high temperatures as shown in Figure 2c. From this result, we speculate that the intercalated alkyl chains render the initially hydrophilic V_2O_5 surface hydrophobic.

The nanostructured film behaves interestingly when exposed to UV light (365 nm) with an intensity of 2 mW/cm^2, as shown in Figure 2b. When the prime V_2O_5 substrate was exposed to UV light for 2 h, the water CA was found to be about 0°, that is, it was switched from the superhydrophobic state to the superhydrophilic state (Figure 2a). The water droplet quickly spread out over the surface. When the superhydrophilic substrate was kept in the dark for a certain time, its wettability recovered to its pristine superhydrophobic state, and the reverse process took place with full reproducibility over ten times (Figure 2b). These results provide evidence that the surface wettability conversion can be reversibly produced on a V_2O_5 film surface, with little damage after many switching cycles. At this time, no orientation changes of hexadecyl chains were observed after UV exposure and dark storage, respectively.

The generation of superhydrophilicity by exposure to UV light is closely related to the preferential adsorption of water on the photogenerated surface defect sites. It is well-known that UV exposure generates electron−hole pairs in V_2O_5.[2] The holes react with lattice oxygen, leading to the creation of surface oxygen vacancies, while the electrons react with lattice metal ions, inducing conversion of V^{5+} sites to V^{3+} defect sites. Hydroxyl adsorption on the defect sites is kinetically more favorable than oxygen adsorption, which leads to dissociative adsorption of water molecules at these sites. This renders the V_2O_5 films hydrophilic. To confirm the increased adsorption of water, the V_2O_5 films were analyzed by carrying out X-ray photoelectron spectroscopy (XPS) before and after the UV irradiation (Figure 2d). No substantial changes were observed in the binding energy of the V 2p peak after UV exposure (data not shown), since the V^{3+} defects easily give electrons to adsorbed oxygen, which reconverts V^{3+} species to V^{5+}.[2] However, the shoulder at the higher binding energy of the O 1s peak is significantly broader after the UV exposure, and its intensity is increased. This broader shoulder is ascribed to the dissociative and physical adsorption of water molecules, which means that the V_2O_5 surface is highly hydrophilic. Water will fill the apertures of a rough surface, owing to the three-dimensional capillary effect, resulting in a water CA of about 0°.[11c] During the storage in the dark, since the exposure of the surface to air tends to increase the thermodynamically preferred oxygen adsorption, the hydroxyl groups adsorbed on the defect sites are gradually replaced by oxygen atoms, and the hydrophobicity of the V_2O_5 surface increases, that is, the surface recovers to the superhydrophobic state.[2]

In conclusion, we have presented a facile method for the fabrication of roselike nanostructured V_2O_5 films that are photoswitchable between superhydrophobicity and superhydrophilicity, which carries out the simple drop-casting of a suspension of V_2O_5 particles synthesized with the sol−gel method. This is ascribed to the conjunction of the surface roughness and the photosensitivity of V_2O_5. Our approach enhances the possibility of producing large homogeneous or patterned surfaces with tunable wettability, which could be used in a wide range of applications such as catalysts, electrodes, switchable smart devices, etc.

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