With the development of smart devices, a great deal of attention has been paid to functional surfaces with tunable wettability. Recently, most studies have aimed to develop reversible control by applying external stimuli, including electrical potential, photoillumination, thermal energy, and changes to the surrounding environment such as the pH or the presence of organic or inorganic liquids. These techniques promise to stimulate the development of Microsystems, materials science, biotechnology, and medicine. Conventionally, wetting behavior can be controlled by modifying the surface with organic compounds. However, because of the poor chemical and thermal stabilities of organic coatings, it is difficult to achieve long-term durability. Additionally, variations in the geometrical structure of a solid surface can influence the contact angle of materials. In this case, however, the structures may be more susceptible to mechanical damage. Molecular-scale understanding and manipulation of the wetting behavior of water on solids remain fundamental challenges.

Various transition-metal oxides, such as TiO2, ZnO, WO3, and V2O5, have been known to exhibit photoinduced hydrophilicity as a result of UV irradiation. This type of reversible switching has aroused great interest in both fundamental research as well as practical applications. Hematite (α-Fe2O3), the most stable iron oxide under ambient conditions, is a good candidate for technological applications such as gas sensors, lithium battery electrodes, and field emission displays. Zhu and Lu employed different methods for the fabrication of Fe2O3 nanostructures, which all exhibited excellent wetting. Distinguished from these results, herein, we introduce a facile method to fabricate α-Fe2O3 surfaces with a wettability that can be switched from ultrahydrophobicity to superhydrophilicity and vice versa with UV irradiation and dark storage, respectively. Combined with the unique magnetic and electrical properties of α-Fe2O3, this type of interesting photoinduced wetting phenomenon probably opens a new field in multifunctional microfluidic devices and switches research.

A cleaned piece of Fe foil (10 × 10 × 0.25 mm3) with a purity of 99.99% (Aldrich) was heated on a hot plate under ambient conditions. The growth temperature was 350 °C, and the growth duration was fixed as 10 h. After being cooled to room temperature naturally, the materials produce a superhydrophilic surface. In this instance, the water droplet forms a contact angle of less than 5° within 0.5 s. This observation can be explained by the Wenzel equation as follows

\[
\cos \theta_A = r \cos \theta
\]

where θ and θ_A are the contact angles on a flat, rough surface, respectively. This equation indicates that the surface roughness, r, enhances the hydrophilicity of dewetting surfaces (θ > 90°) and the hydrophilicity of wetting surfaces (θ < 90°) because the magnitude of r is always greater than unity. As a polar material
with a water contact angle of 30° with the smooth surface, the α-Fe₂O₃ nanoflake film, possessing a large surface roughness that is confirmed by field-emission scanning electron microscopy (Figure 1a), displays the contact angle of water as 0°.

In addition, we found that the contact angle of the film gradually increases with time. The film became hydrophobic with a contact angle about 130° in 7 days. The origin of the contact angle increase with time is attributed to the adsorption of organic substances from the atmosphere. It is further proven when the contact angle increment rate was remarkably accelerated and the surface film was exposed to a vacuum chamber that the water contact angle was found to be about 0°.

The bouncing of a droplet is achieved on an ultrahydrophobic surface. The behavior of a water droplet falling freely on an α-Fe₂O₃ nanostructures surface is shown dynamically in Figure 1b. To the best of our knowledge, this is the first reported observation of the dewetting properties of α-Fe₂O₃ nanostructures.

In this work, in addition to the above-mentioned dewetting properties of the α-Fe₂O₃ nanofilm, we were surprised to find that the wettability can be reversibly switched by the alternation of UV (254 nm) irradiation and dark storage. After exposure to UV light (obtained from a 15 W Hg lamp centered at 254 nm) for 3 to 4 h, the contact angle was found to be about 0°, which shows that it has switched from the hydrophobic to the hydrophilic state. Besides, when the superhydrophilic substrate was kept in the dark for 7 days, its wettability recovered to its pristine hydrophobic state, and the reverse process took place with full reproducibility over four cycles (Figure 1c).

In general, the wettability conversion of inorganic materials is attributed to the material being naturally hydrophobic, becoming wetted after the UV-induced generation of free electrons or holes on the material surface, which results in hydroxyl adsorption. Surprisingly, we found that the sample maintains its hydrophobicity during water contact angle measurements for 3 to 4 h, which is attributed to the adsorption of organic molecules such as oil droplets from vacuum pumps on the surface, which will make the sample attain high hydrophobicity. The adsorption species are also confirmed by our X-ray photoelectron spectroscopy (XPS) study, which will be discussed later.

On the basis of the Young-Dupré equation,

\[ W_d = \gamma_{lv}(1 + \cos \theta) \]

where \( W_d \) and \( \theta \) refer to the work of adhesion and the contact angle between solid and liquid, respectively, and we denote the liquid–vapor interfacial energy as \( \gamma_{lv} \), for a given value of \( \gamma_{lv} \), the adhesion between the liquid and solid decreases as the contact angle increases. The bouncing of a droplet is achieved on an ultrahydrophobic surface. The behavior of a water droplet falling freely on an α-Fe₂O₃ nanostructures surface is shown dynamically in Figure 1b. To the best of our knowledge, this is the first reported observation of the dewetting properties of α-Fe₂O₃ nanostructures.

Figure 1. (a) FE-SEM image of the sample. (b) Photoresponsive wettability changes for water droplet profiles. (c) Reversible wettability transitions under the alternation of UV irradiation and dark storage.

Figure 2. Time-dependent change in the contact angle illuminated with different wavelengths of light. The contact angle of water droplets as a function of heating time at 90 °C is also shown in order to distinguish the thermal effect from the light-irradiation effect.
absorption peaks, C–H/C, C–O, and C–D, denoting the existence of organic pollutants. As shown in Figure 3b, the hydrocarbon band decreased dramatically compared to the band corresponding to the carbonyl. It is known that the hydrocarbon tail serves as a hydrophobic region and the carbonyl group serves as a hydrophilic region. Therefore, the ratio of C–H to C=O will influence the wettability of the sample.

To explore the effect of iron ions under UV irradiation, high-resolution XPS of Fe 2p\textsubscript{3/2} before and after UV irradiation was investigated (Figure 4). The spectral shape and its intensity in XPS indicate the character of chemical bonding or the degree of oxidation of the selectively probed atoms.\textsuperscript{(28)} It can be seen that the intensity of the shoulder at the higher binding energy of the peak was significantly increased after UV exposure. By the curve fitting of the spectra, Fe\textsuperscript{2+}/Fe\textsuperscript{3+} was found to be 0.173 after UV illumination compared to 0.448 before exposure to UV, and it is recoverable when the sample was stored in the dark for 7 days.

Figure 3. Peak deconvolution analysis of the background-subtracted X-ray photoelectron spectra before and after UV irradiation: (a) the O 1s level and (b) the C 1s peak region. The inset shows the calibrated spectra using the O 1s peak of 530.2 eV.

Figure 4. Peak deconvolution analysis of the background-subtracted XPS for Fe 2p\textsubscript{3/2}.
