Tungsten Oxide Films

DOI: 10.1002/anie.200502061

Controlling Wettability and Photochromism in a Dual-Responsive Tungsten Oxide Film**

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Control of the surface wettability of solid substrates has aroused great interest because of their importance in fundamental research and industrial applications.[1–4] Responsive materials have found extensive uses as controllable surfaces because of their intrinsic reaction to environmental stimuli such as light irradiation,[5] electric fields,[6] heating/cooling,[7] and solvent treatment.[8] However, the responsive surface wettability of smooth surfaces is usually very limited. For example, the reported maximum change in contact angle (CA) is only about 11° on flat surfaces coated with azobenzene.[5b] The introduction of surface roughness[9] has recently been used to enhance the responsive wettability of inorganic and organic materials between superhydrophilicity (CA less than 5°) and superhydrophobicity (CA higher than 150°).[10] This responsivity is due to a change of the chemical composition of the surface under an environmental stimulus. For multiresponsive materials, this change of chemical composition may induce multiresponsive properties by combining, for example, wettability conversion between two extreme states with photochromism,[11] which would be a promising starting point for the design of novel, artificial smart surfaces. Herein, we report an intelligent, dual-responsive tungsten oxide film that combines wettability conversion with photochromic behavior.

Tungsten oxide, which is an indirect, broad-gap semiconductor, has been extensively studied because of its unique physical/chemical properties and widespread applications. Tungsten oxide films have been prepared by a variety of methods, such as thermal evaporation, chemical vapor deposition, sputtering, and sol–gel methods.[12–16] Until now, nearly all of its applications are in photo- and electrochromic "smart" windows, erasable optical-storage devices, catalysts, gas sensors, and humidity and temperature sensors. The inorganic oxide film prepared by us shows both reversible wettability conversion between superhydrophobic and superhydrophilic states and photochromism upon alternating between UV irradiation and storage in the dark, and could lead to future uses for tungsten oxide in novel smart devices and help us to understand its chemical and physical properties better.

The rough tungsten oxide films were prepared by an inexpensive and simple electrochemical deposition process.[15] In a typical procedure, aqueous Na_2WO_4 solution was used as the electrolyte for electrodeposition of tungsten oxide films along with oxalic acid to adjust the solution pH in the range 3.1 to 8.6 (this is a suitable pH range for the electrochemical deposition of tungsten oxides; the influence of various experimental conditions on film formation will be discussed elsewhere). An indium tin oxide (ITO) glass was immersed in the electrolyte and electrochemical deposition was conducted at -1.5 eV in single-potential time-based mode with a platinum electrode as the counter electrode and Ag/AgCl as the reference electrode. The morphology of the deposited tungsten oxide film depends on the pH of the precursor solution (see the Supporting Information). Thus, a smooth film composed of nanoparticles is formed at low pH, whereas upon increasing the pH value the oxide films become rough with a remarkable increase of the size of the nanoparticles. When the pH of the precursor solution was about 8.6, a rough, brown film was obtained that exhibits a pebble-beach-like morphology made up of many nanoprotuberances with diameters in the range 40–350 nm (Figure 1). Energy-dispersive X-ray analysis confirmed that this rough film is tungsten oxide (see the Supporting Information).

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[**] The authors thank the National Nature Science Foundation of China (20125102, 90306011, 20421101) and the Innovation Foundation of the Chinese Academy of Sciences for funding this research.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

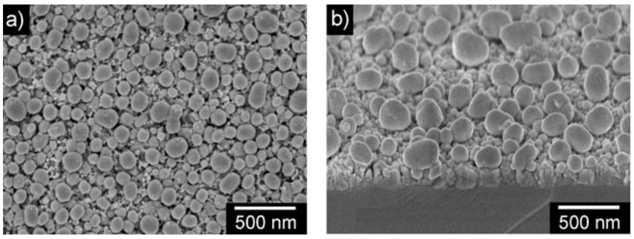

Figure 1. Typical SEM images of tungsten oxide films deposited from the electrolyte at a pH of about 8.6: a) top view; b) side view from 45°. The morphology of the nanostructures resembles a pebble beach.

The surface wettability of the as-prepared rough film was evaluated by water CA measurements. The CA on the film is 151.3 ± 2.9° (the left drop in Figure 2a), thus indicating that the surface is superhydrophobic. We believe that the rough nanostructures play an important role in the surface superhydrophobicity of the film.[2,3] Upon UV irradiation for three hours (a 500-W Hg lamp with a filter centered at 365 ± 10 nm was used as the light source), the water droplet spread out on the film with a CA of less than 5° (the right drop in Figure 2a). UV irradiation therefore induces a change in surface wettability to a superhydrophilic state. Storage of these irradiated films in the dark for 2 weeks caused them to become superhydrophobic again. This cycle was repeated several times, and a good reversibility of surface wettability was observed (Figure 2b).

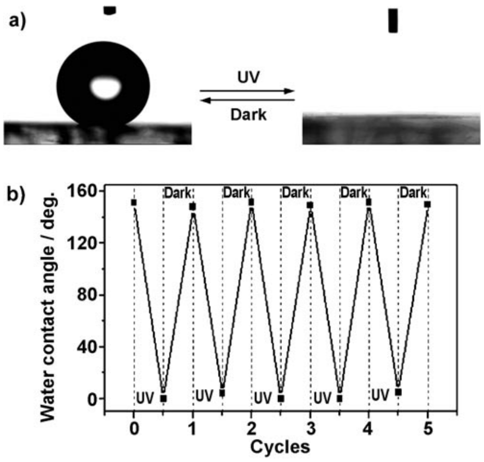

Figure 2. a) Water-drop profiles for the photoresponsive switch between superhydrophobicity and superhydrophilicity of the tungsten oxide film before (left) and after (right) UV irradiation. The water CAs are 151.3 ± 2.9° and less than 5°, respectively. b) Reversible water CA transition on the deposited tungsten oxide film upon alternating UV irradiation and storage in the dark.

Surface wettability is determined by the chemical composition of a surface and its nanostructure.[2–9] Our tungsten oxide film shows superhydrophobicity because of the air trapped in the interspaces of the rough surface.[2c] Upon UV irradiation, however, it becomes superhydrophilic. As tungsten oxide is a photosensitive material,[16] when the film is irradiated with UV light the photogenerated electrons will reduce part of the tungsten and the photogenerated holes will react with lattice oxygen to form oxygen vacancies. Water molecules from the air are adsorbed and coordinate kinetically to these oxygen vacancies, which greatly improves the surface hydrophilicity. The X-ray photoelectron spectra of the as-deposited film confirm that a reduction of tungsten to a mixed-valence state occurs (see the Supporting Information). For the as-prepared film, the peaks corresponding to the W 4$f_{7/2}$ and W 4$f_{5/2}$ orbitals are observed at 35.1 and 37.3 eV, respectively. These values are lower than those for tungsten(VI) trioxide powder (36.0 and 38.2 eV), which indicates that the tungsten in the electrodeposited film may be present as W^{6+}, W^{5+}, and W^{4+}. After UV irradiation, the peaks corresponding to W 4$f_{7/2}$ and W 4$f_{5/2}$ are observed at energy levels about 0.2 eV lower than those before UV irradiation, thus confirming that the tungsten atoms have been reduced to W^{5+}, W^{4+}, or even to W^{3+}.[15a]

In order to thoroughly understand the role of atmospheric water, the UV-irradiation experiment was also carried out under dry conditions. An evident difference of CA was observed when the sample was irradiated at different humidities (see the Supporting Information). For example, with an irradiation time of 3 hours under the standard conditions (relative humidity of 39–46 %), a superhydrophilic state appears, whereas under dry conditions (relative humidity of 9–12 %), the CA only changes from 152.3 ± 2.1 to 93.5 ± 12.4°. These results indicate that atmospheric water is important for the conversion into a hydrophilic state as water droplets can enter the spaces between the nanoprotuberances by a three-dimensional capillary effect.[17].

Adsorption of hydroxy groups formed in the photochemical surface reaction transforms the surface into an energetically metastable state. When the UV-irradiated film is placed under air in the dark the hydroxy groups are gradually replaced by atmospheric oxygen[18] and the surface evolves back to the initial state. To confirm the function of atmospheric oxygen we performed the following experiment: when the UV-irradiated samples were left under nitrogen in the dark for two weeks the CA only recovered to 30.2 ± 4.1°. This slight recovery may be due to oxygen contamination. When these samples were left under air or oxygen instead of nitrogen they returned to the superhydrophobic state. These results provide evidence for the dominant role of atmospheric oxygen in the recovery process[16] leading from superhydrophilicity back to superhydrophobicity. This reversible conversion proceeds only by adsorption and desorption of surface hydroxide ions at the outermost oxide layer.[1b,19] The stability of the surface nanostructures, free from changes in chemical conditions, explains why the reversible wettability switch can be repeated many times.

Since tungsten oxide is an excellent photochromic material, its photochromic behavior was also studied during the wettability conversion. After UV irradiation, the as-prepared film became yellowish green from the initial brown, and when this film was placed in the dark it recovered to brown. As shown in Figure 3, the UV spectra show a change in absorbance, with the greatest absorbance change of 0.34 occurring around 372 nm. In addition, a good reversibility was observed for many cycles of coloration and decoloration. The

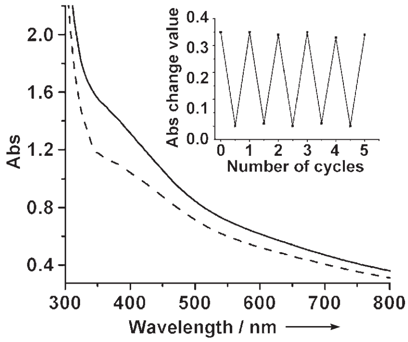

Figure 3. Absorption spectra of an electrodeposited tungsten oxide film before (solid line) and after (dashed line) irradiation with UV light at 365 ± 10 nm. The insert shows the photochromic switching of the absorption change (monitored at 372 nm) during consecutive cycles of UV irradiation and storage in the dark.

photochromic behavior of the as-deposited film is due to the variation of the tungsten valence and the number of oxygen vacancies and water molecules.[16] Importantly, the photochromic behavior and wettability change are linked by the adsorption of atmospheric water by the film.

In conclusion, nanostructured tungsten oxide films with wettability and photochromic dual-responsive properties have been prepared by a facile electrochemical deposition process. A reversible wettability conversion between superhydrophobicity and superhydrophilicity, which is accompanied by photochromism, can be realized for this tungsten oxide material by alternating UV irradiation with storage in the dark. The wettability interconversion and photochromism are coherent in nature and are due to changes in the redox properties of the metal ions and the number of oxygen vacancies and adsorbed water molecules. This study suggests that tungsten oxide materials and other semiconductor oxides with responsive redox properties have a promising future for use in dual- and multifunctional switches in new technological applications such as smart functional windows, microfluidic devices, and bioanalysis.

Experimental Section

The electrodeposition process was performed in a three-electrode system. An aqueous solution of Na_2WO_4 (0.5 M) was used as the electrolyte, and oxalic acid was used to adjust the pH of the solution in the range 3.1 to 8.6. A piece of ITO glass (area $2 \times 3\ cm^2$) was used as the cathode after it was cleaned with aqueous detergent, acetone, ethanol, and distilled water. The anode was a Pt plate ($1.5 \times 1.5\ cm^2$) and the reference electrode was a CHI110 Ag/AgCl electrode. The cathodic electrodeposition was performed at a constant potential of −1.5 eV for 1–3 min at room temperature. The deposited films were then removed from the solution, washed with distilled water, and blown dry with N_2.

A Hitachi S-4300F scanning electron microscope (SEM) equipped with an energy dispersive X-ray analyzer (Phoenix) was used to determine the morphology and the composition of the porous film. CAs were measured on a dataphysics OCA20 contact-angle system at ambient temperature. The average CA was obtained by measuring more than five different positions of the same sample. X-ray photoelectron spectra were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300-W $Al_{K\alpha}$ radiation. The base pressure was about 3×10^{-9} mbar. UV/Vis spectra were measured with a Hitachi U-4100 spectrophotometer. All measurements were performed at room temperature.

Received: June 15, 2005
Revised: November 28, 2005

Keywords: nanostructures · photochromism · surface chemistry · tungsten · wettability

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