

Electrochemically generated super-hydrophilic surfaces†

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The control of surface wettability of indium tin oxide ($\text{In}_2\text{O}_3\text{-SnO}_2$) coated glass surfaces is studied. We report here the first observation of purely electrochemical generation of super-hydrophilic surfaces at $\text{In}_2\text{O}_3\text{-SnO}_2$ electrodes in the absence of an ultraviolet illumination source. This is achieved by the application of high anodic potentials for a prolonged period. Such surfaces are reversibly converted back to their original hydrophobic state on storage in air (one or two days) or water (a week) (and *vice versa*). The unique character of these surfaces can be attributed to the surface structure of the hydrophilic phase.

Surface wettability is one of the important parameters in many solid samples. Controlling and/or modifying the surface wettability of solid substrates is important for fundamental understanding of surface structure and behavior as well as in many applications.¹⁻⁴ For practical applications, both super-hydrophilic (water contact angle less than 5°)⁴ and super-hydrophobic (water contact angle greater than 150°)⁴ materials are particularly desirable. Although there have been many reports concerning the preparation of super-hydrophobic surfaces, which are usually achieved by use of low-surface energy coatings (fluorine-containing polymer coatings) combined with specially designed surface textures (fractal surfaces),²⁻⁴ there are far fewer reports on super-hydrophilic materials. In recent years, it has been reported that highly hydrophilic TiO_2 surfaces can be achieved by ultraviolet (UV) illumination.⁵⁻⁹ Several commercial products (antifogging glass, self-cleaning construction materials *etc.*) have been designed and produced on the basis of this phenomenon.⁹ Due to the diversity of the potential applications of this photoinduced surface wettability conversion phenomenon, this discovery has further aroused research interest in TiO_2 , which can potentially play an important role in environmental purification and solar energy conversion.⁹⁻¹¹ However, for production of super-hydrophilic surfaces with TiO_2 coated materials, illumination with UV light (380 nm) is necessary. In this work, we have successfully created such super-hydrophilic surfaces on conductive indium tin oxide ($\text{In}_2\text{O}_3\text{-SnO}_2$) coated glass surfaces without the use of such an illumination source. Thus, we report what we believe to be the first instance of purely electrochemical generation of super-hydrophilic surfaces, at $\text{In}_2\text{O}_3\text{-SnO}_2$ coated glass by application of high anodic potentials resulting in $\text{In}_2\text{O}_3\text{-SnO}_2$ coated glass which has an antifogging and highly cleaned surface for at least a few days.

The $\text{In}_2\text{O}_3\text{-SnO}_2$ (weight ratio of 10% SnO_2 to 90% In_2O_3) coated glass plate was purchased from Precision Optical Systems Singapore, Singapore. Its specifications are: specific surface area, $40\text{--}80\text{ m}^2\text{ g}^{-1}$; purity, 99.5%; bulk density, 0.2 g cm^{-3} ; true density, 7.1 g cm^{-3} ; and the refractive index, 2.0 at 500 nm. Millipore water ($18.2\text{ M}\Omega\text{-cm}$) was used for experiments. A three-electrode set up was employed for electrochemical studies. The $\text{In}_2\text{O}_3\text{-SnO}_2$ was utilized as the working electrode and a platinum disk was used as the counter electrode. The reference electrode was Ag/AgCl , saturated KCl. Electrochemical experiments were carried out using the EG&G Princeton Applied Research, Potentiostat/Galvanostat Model 273A (USA) controlled by ECHM software. The Digilab Excalibur Series, Model FTS 30000 Fourier transform spectrophotometer was employed for IR spectroscopy (FT-IR). The IR experiments were carried out using the transmission mode with a solid sample holder (this is possible due to the transparency of the $\text{In}_2\text{O}_3\text{-SnO}_2$ plate). Atomic force micrographs (contact mode) of the electrodes were obtained using a Burleigh Instruments (New York, USA) Metris-2001 Atomic Force Microscope (AFM).

The water contact angle showed more than 80° before potential treatment (Fig. 1a) on $\text{In}_2\text{O}_3\text{-SnO}_2$ coated glass. After application of a high positive potential (2.0 V for 60 min in aqueous 0.1 mol dm^{-3} phosphate buffer or 0.01 mol dm^{-3} H_2SO_4 solution), water droplets spread out as a film, resulting in contact

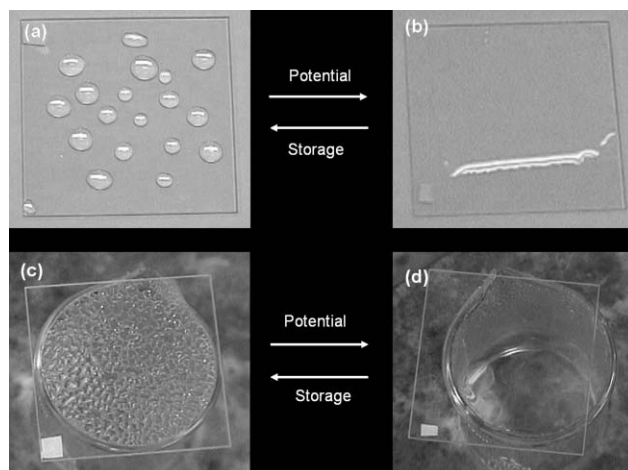


Fig. 1 (a), A hydrophobic surface of $\text{In}_2\text{O}_3\text{-SnO}_2$ coated glass before treatment. (b), A highly hydrophilic surface on application of 2.0 V for 60 min; white line shows the edge of the water film. (c), Exposure of a hydrophobic $\text{In}_2\text{O}_3\text{-SnO}_2$ coated glass to water vapor. The formation of fog (small water droplets) hindered the view of the bottom of the beaker. (d), Creation of an antifogging surface after potential application, as before. The formation of a water film, arising from the super-hydrophilic surface, gives a clear view of the bottom of the beaker.

† Electronic supplementary information (ESI) available: AFM images of $\text{In}_2\text{O}_3\text{-SnO}_2$ coated glass before and after potential (2.0 V for 60 min) application. See <http://www.rsc.org/suppdata/cc/b4/b414418j>
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angle of less than 1° or 2° (Fig. 1b). This change of wettability was clearer when the $\text{In}_2\text{O}_3\text{-SnO}_2$ coated glass was exposed to water vapor. Without treatment, the $\text{In}_2\text{O}_3\text{-SnO}_2$ coated glass fogged (Fig. 1c), but on potential application the $\text{In}_2\text{O}_3\text{-SnO}_2$ glass became transparent (Fig. 1d), showing a remarkable antifogging effect.

The potential application created a surface that was super-hydrophilic. Even after storage in air at room temperature, the super-hydrophilicity is maintained for one or two days (storage under water maintained the super-hydrophilicity for a week). A longer storage period induced a gradual increase in the water contact angle, revealing a gradual loss of the super-hydrophilic characteristic. However, the hydrophilicity was repeatedly generated by applying high anodic potentials. We checked the hydrophilicity development by applying various potentials from 1.0 V to 3.0 V. The hydrophilicity commenced from 1.9 V onwards after applying the potential for more than one hour, but super-hydrophilicity was not achieved under this condition. Super-hydrophilicity started after applying 2.0 V for 10 minutes. The development of super-hydrophilicity by application of potentials above 2.0 V achieved the same results as obtained for 2.0 V. Our results suggest that 2.0 V is the approximate threshold potential to generate super-hydrophilicity on the $\text{In}_2\text{O}_3\text{-SnO}_2$ coated glass plate.

To gain information on the surface wettability, we used FT-IR spectroscopy and atomic force microscopy. From the FT-IR data, we observed an increase in hydroxyl groups on the surface after potential application. Fig. 2 shows the FT-IR spectra for the $\text{In}_2\text{O}_3\text{-SnO}_2$ coated glass plate both before and after potential (1.9 V and 2.0 V separately) applications. There are increased absorbances at the OH group stretching frequency (3695 cm^{-1})^{6,12} with potential applications. This may be the main factor giving rise to the super-hydrophilicity of the $\text{In}_2\text{O}_3\text{-SnO}_2$ coated glass plate. After potential application, the intensity of the absorbance peak is higher due to the hydroxyl groups from both dissociated water and molecularly adsorbed water¹³ (Scheme 1a and 1b). The IR experiments were carried out under carefully controlled conditions, with both the hydrophobic and super-hydrophilic glass plates handled and stored identically. In this manner, reproducible results were obtained. Considering Fig. 2, the increase in absorbances of the peak with potential applications are not due to baseline shift, as is evident from the fairly constant level of the baseline absorbances at the beginning of the scan, from 4000 cm^{-1} . The attainment of the electrochemically generated super-hydrophilicity can be attributed to the following: (a) when applying higher anodic

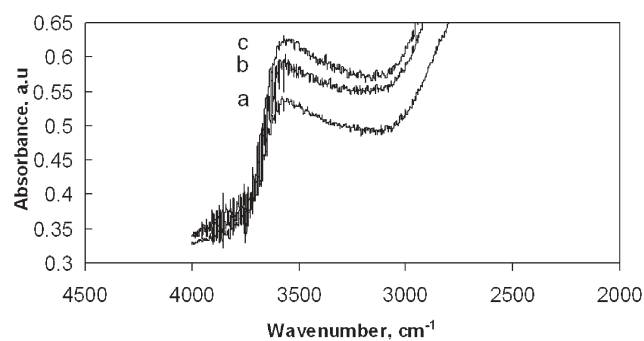
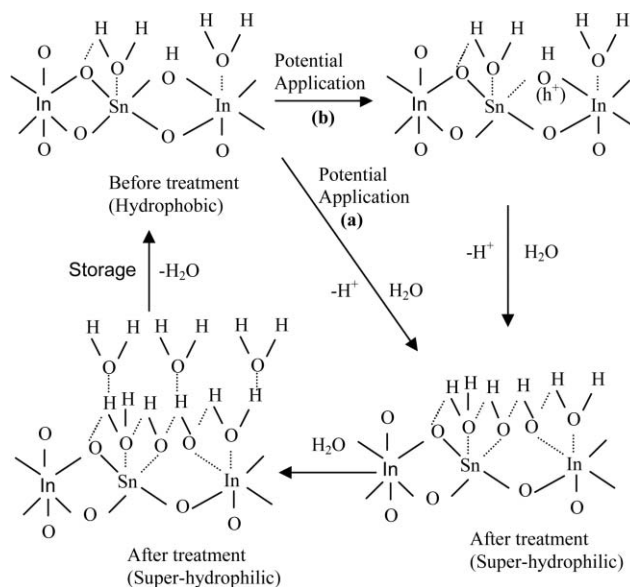


Fig. 2 FT-IR spectra of $\text{In}_2\text{O}_3\text{-SnO}_2$ coated glass (a) before potential and (b) after potential (1.9 V for 60 min) and (c) after potential (2.0 V for 60 min) application.



Scheme 1 Schematic view of the $\text{In}_2\text{O}_3\text{-SnO}_2$ surface before and after potential application.

potentials, water oxidation leads to the formation of hydroxyl groups on the surface of $\text{In}_2\text{O}_3\text{-SnO}_2$ layer, (b) since $\text{In}_2\text{O}_3\text{-SnO}_2$ behaves as a partial semiconductor and partial conductor, the tin oxide doped indium oxide layer has valence band (VB) and conduction band (CB) energy levels. When applying higher anodic potentials, the energy level of the CB may be lowered and matched with the energy level of the VB. As a result, electrons can move from VB to CB forming holes (h^+) on the surface of the VB. These holes (h^+) are responsible for the generation of super-hydrophilicity through oxidative decomposition of water, forming hydroxyl groups accompanied by layers of adsorbed water. Some of the holes^{7,14} can react with lattice oxygen to form surface oxygen vacancies. Meanwhile, water and oxygen may compete to dissociatively adsorb on the oxygen vacancies. The defective sites are kinetically more favorable for hydroxyl adsorption than oxygen adsorption. As a result, the surface hydrophilicity is drastically improved and the water contact angle of the surface changes from 80° to less than 5° . In addition to the hydroxyl group formation on the $\text{In}_2\text{O}_3\text{-SnO}_2$ surface, organic contaminants present were also decomposed with the high potential treatment which contributed to the development of super-hydrophilicity. At this point, it is not certain which of the two possibilities above predominates or whether both play significant roles. Further study of the detailed mechanism is in progress.

The Atomic Force Microscope (AFM) image of the $\text{In}_2\text{O}_3\text{-SnO}_2$ surface is changed after conversion to super-hydrophilicity by applying 2.0 V. The AFM measurements were made on an indium tin oxide plate (1 cm width \times 3 cm length \times 1 mm thickness) whereby about half its length had been made super-hydrophilic electrochemically whereas the other half remained hydrophobic (not dipped into the electrolyte solution during electrolysis). Therefore AFM images (available as electronic supplementary information)[†] were taken for the hydrophobic and super-hydrophilic surfaces on the same plate. In this way, any differences likely arose from the electrochemical surface treatment and not from differences between different plates. The results of

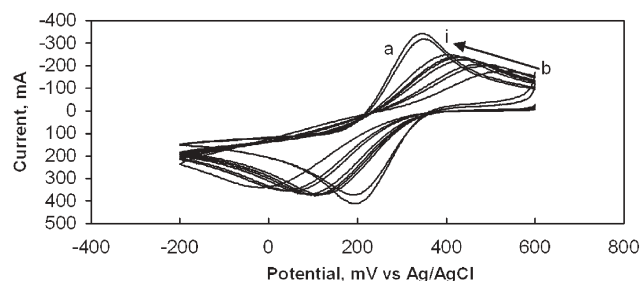


Fig. 3 Cyclic voltammogram of (a) hydrophobic and (b) super-hydrophilic $\text{In}_2\text{O}_3\text{-SnO}_2$ coated glass in $1 \text{ mmol dm}^{-3} \text{ K}_3\text{FeCN}_6$ and $1 \text{ mol dm}^{-3} \text{ KCl}$ solution. (b–i) changing from super-hydrophilic to hydrophobic status of the $\text{In}_2\text{O}_3\text{-SnO}_2$ coated glass surface after storage in water for (b) 0, (c) 10, (d) 20, (e) 80, (f) 200, (g) 380 min, (h) 1 day and (i) 1 week. Scan rate: 50 mV s^{-1} .

these measurements show that the image is changed in the surface structure height (surface structure height determined from the 3D images from the AFM data). The hydrophobic surface structure gives a height of 122.4 nm and the super-hydrophilic surface structure gives a height of 169.7. The increase in height of the surface structure is due to increase in number of hydroxyl groups, with molecularly adsorbed water layers. On storage in air (about two days), the chemisorbed hydroxyl groups were replaced with oxygen from the air,^{14,15} converting back to the original hydrophobic state. However, it took at least a week of storage in water to regain its full original status prior to potential application. The surface becomes energetically unstable after the hydroxyl adsorption;¹⁵ the oxygen adsorption is thermodynamically favored, and oxygen is more strongly bonded on the defect sites than the hydroxyl group. A similar⁷ result has also been observed on the TiO_2 surface. Therefore, the hydroxyl groups adsorbed on the defective sites can be replaced gradually by oxygen atoms when the super-hydrophilic surfaces are stored in air or water under normal room conditions. We observed that when the super-hydrophilic surface was stored in an aqueous 0.5 mmol dm^{-3} ruthenium(II)bipyridyl complex solution, the super-hydrophilicity was maintained for at least three months. The cause of phenomenon is not clear but experiments are continuing. Such highly hydrophilic surfaces may have practical applications. Arising from the antifogging, cleaning effects, they may be used in lenses of medical devices for invasive procedures.

The electrochemical behaviors of $1 \text{ mmol dm}^{-3} \text{ K}_3\text{FeCN}_6$ in $1 \text{ mol dm}^{-3} \text{ KCl}$ were studied at the hydrophobic (Fig. 3a) and super-hydrophilic $\text{In}_2\text{O}_3\text{-SnO}_2$ surfaces (Fig. 3b). Continual changes from the super-hydrophilic to the hydrophobic surface (Fig. 3b to 3i) on storage in water are demonstrated. The super-hydrophilic $\text{In}_2\text{O}_3\text{-SnO}_2$ surface shows the broadened

voltammogram of the $\text{Fe}(\text{CN})_6^{3-/4-}$ redox couple. This broadening may be due to the negative charges of some dissociated hydroxyl groups acting as repulsive sites to the redox species $\text{Fe}(\text{CN})_6^{3-/4-}$ and/or due to the resistance or slow electron-transfer kinetics caused by the hydroxyl group with adsorbed water molecules on the super-hydrophilic surface of the $\text{In}_2\text{O}_3\text{-SnO}_2$. The re-establishment of the reversibility of the redox couple (Fig. 3b to 3i) after storage in water clearly indicates the recovery from super-hydrophilic to hydrophobic character. While the electrochemical results do not constitute proof, they do provide an additional support for our suggested mechanism.

The results here clearly establish the attainment of super-hydrophilic surfaces at $\text{In}_2\text{O}_3\text{-SnO}_2$ coated glass solely from the application of high anodic potentials. Hitherto, such surfaces have only been observed through illumination with UV radiation (e.g. TiO_2 coated surface).

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