

Correction to "Switchable Wettability in SnO₂ Nanowires and SnO₂@SnO₂ Heterostructures"

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Changes were made to the Abstract, Results and Discussion (last 7 paragraphs), Conclusion, and Acknowledgment to correct scientific errors. Changes in authorship were also made.

■ ABSTRACT

Tin oxide nanowires and heterostructures thereof were synthesized by sequential application of thermal and plasma-assisted chemical vapor deposition (CVD) methods. The wetting properties of surfaces based on individual nanowires, hyperbranched SnO₂@SnO₂ structures, and SnO₂@SnO₂@SiO_x core-shell heterostructures could be modulated from superhydrophilic to superhydrophobic by changing both chemical composition and the geometrical architecture of nanoheterostructures. Whereas the randomly grown SnO₂ nanowires with a contact angle of 3° exhibited superhydrophilicity, the contact angle of SnO₂@SnO₂ heterostructures synthesized by a two-step CVD process increased to 133°. The corresponding contact angle of SnO₂@SnO₂@SiO_x heterostructures was enhanced to 155.8° by a hydrophobic SiO_x coating. Switchable surface wettability in SnO₂@SnO₂@SiO_x heterostructures was observed by alternation of UV irradiation, storage in dark, and O₂ annealing, indicating that geometric microstructure was the major determinant in the switchable wettability. The significant change in the surface wettability upon changing the geometrical features is of potential interest in functional coatings such as antifinger print and self-cleaning surfaces.

■ RESULTS AND DISCUSSION

In the case of individual SnO₂ nanowires, the liquid completely penetrated into the vacancies among individual nanowire surfaces without being trapped into air pockets and nanovoids (Figure 6). Consequently, the water droplet rapidly spread over the surface, resulting in the superhydrophilic properties of the surface. In the case of SnO₂@SnO₂ heterostructures, the geometric surface area is maximized by the hyperbranching; however, the increase in the density of nanowire spikes considerably reduces the contact area of water droplets to the SnO₂ structures. The decrease in the contact area between the water droplet and the solid nanowire tips and the triple phase contact line (water/solid/air) prevents penetration of water into the grooves, leading to hydrophobic behavior. This effect could be further augmented by coating the hyperbranched SnO₂@SnO₂ structures with a hydrophobic SiO_x film via plasma-assisted chemical vapor deposition (CVD) of hexamethyldisiloxane. The synergy of both geometric (heterostructuring) and chemical (hydrophobic Si–O–C coating) approaches resulted in the observed superhydrophobicity.

To study the switchable surface wettability and to analyze the key factors involved in determining the surface wettability, the

samples were exposed to UV irradiation, stored under dark conditions, and annealed in O₂. The UV irradiation influenced wettability variation of the SnO₂@SnO₂@SiO_x heterostructure, which had a stable superhydrophobicity. The measurement of contact angle as a function of UV irradiation time under ambient conditions (Figure 7a) revealed that the CA of water was abruptly reduced in the beginning with increasing UV irradiation time, indicating the generation of electron–hole pairs in SnO₂ (SiO_x is transparent to UV) and their migration to the surface. Nevertheless, further UV illumination over 10 min and even longer (30 min) showed no substantial variation of CA that was maintained at ca. 133° and exhibited no further decrease. As known for TiO₂,³⁴ UV irradiation will generate electron–hole pairs in the metal oxide; the holes, due to their oxidative potential, can react with lattice oxygen and with adsorbed oxygen species to create surface oxygen vacancies (defect sites).³³ Water molecules preferentially coordinate into the oxygen vacancy sites, leading to the increase in the water adsorption. However, the oxygen adsorption is thermodynamically favored, and it is more strongly bonded on the defect sites than the hydroxyl group, and thus oxygen species can replace the hydroxyl groups adsorbed on the defective sites gradually when the UV-irradiated films are placed in the dark. This process is similar to the case of the TiO₂ film.³⁴ Subsequently, the surface evolves back to its original state (before UV irradiation), and the wettability is reconverted to superhydrophobicity.

Upon storing the sample in dark and heat-treating them in an O₂ atmosphere for a certain time, defective sites were gradually annealed, enabling the surface to recover the original superhydrophobicity.³⁵ Figure 7b shows the typical reconversion processes of UV-irradiated SnO₂@SnO₂@SiO_x heterostructured surface against storage in dark. During the first 3 storage days, water CA increased remarkably because of the fast adsorption of oxygen atoms to the surface defect sites at the beginning. In the next several days, the water CA increased slowly because of the gradually decrease in the defect sites. Further increase in CA was not observed after the water CA reached the values close to those at their original states (about 155°). There was no change in the case of SnO₂@SnO₂ heterostructure surface.

Figure 7c shows the reconversion processes of UV-irradiated SnO₂@SnO₂@SiO_x heterostructure surface with O₂ annealing time. The water CA increased sharply in the beginning and fully recovered to the original states (about 155°) in less than 6 h. This result implied that the oxygen adsorption was thermodynamically favored, and it was more strongly bonded on the defect sites than the hydroxyl group. The hydroxyl

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groups adsorbed on the defective sites will condense among themselves to create oxo-bridges atoms gradually when the hydrophilic samples were annealed in an oxygen atmosphere. Also, the parallel process of adsorption of oxygen species contributes to this process. Subsequently, the surface evolved back to its original state (before UV irradiation), and the wettability was reconverted to hydrophobicity. A similar observation was made in the case of $\text{SnO}_2@\text{SnO}_2$ heterostructure surface.

XPS analysis was used to characterize the surface composition to study the relationship between contact angle variation and surface composition. Figure 7d shows the XPS spectra of the O 1s peak region in $\text{SnO}_2@\text{SnO}_2$ and $\text{SnO}_2@\text{SnO}_2@\text{SiO}_x$ heterostructures under UV irradiation and O_2 annealing; the peak position was calibrated using the C 1s peak of 284.7 eV. It was observed that SiO_x coating led to a shift (0.3 eV) in the peak position toward lower binding energy possibly due to the dissociatively adsorbed water.³⁶ The O 1s peak of $\text{SnO}_2@\text{SnO}_2@\text{SiO}_x$ heterostructure further shifted to the lower binding energy side by 0.2 eV after UV irradiation due to the surface oxygen vacancies and recovered to the state before UV irradiation due to the oxygen adsorption.

It is noteworthy that there were no changes of the CA values of $\text{SnO}_2@\text{SnO}_2$ heterostructures surface under UV irradiation, in dark storage, or upon O_2 annealing, whereas the CA value of $\text{SnO}_2@\text{SnO}_2@\text{SiO}_x$ heterostructure was changed from superhydrophobic to hydrophobic under UV irradiation. This shows that the geometric features are the major determinant in the wetting behavior of our samples.

■ CONCLUSION

In summary, we have demonstrated the control of the wettability switching of SnO_2 nanowire-based surfaces modified by CVD. It was found that the hyper-branched nanostructures greatly enhanced the wetting properties verified in their superhydrophobic behavior. Also, switchable surface wettability of $\text{SnO}_2@\text{SnO}_2@\text{SiO}_x$ heterostructure was observed by alternation of UV irradiation, dark storage, and O_2 annealing, indicating that geometric microstructure was the major determinant in the switchable wettability from superhydrophilic to superhydrophobic. These studies provided valuable information for the design of a patterned superhydrophobic surface through a simple method, which has potential applications in industrial coatings and self-cleaning surfaces.

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