

# 热处理法实现 ZnO 纳米线表面润湿性的可逆开关转变

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**摘要:** 在紫外光或激光光照的作用下, 氧化锌纳米结构表面会在疏水和亲水性能之间发生可逆转变; 本文利用一种简单液相技术制备的氧化锌纳米线组成的表面, 通过热处理方式可以使其发生上述转变。实验结果表明, 在室温下, 刚获得的氧化锌纳米线表面显示了超疏水性能 (接触角为 151 度); 当经过 300 度高温处理 30 分钟后, 氧化锌纳米线表面从超疏水变为超亲水 (接触角小于 10 度); 当热处理温度高于 400 度后, 这种转变可以在少于半分钟时间内完成。获得的超亲水表面经过低于 100 度热处理数小时后可以恢复到起初的超疏水状态。这样, 就获得了氧化锌表面能可控的、具有开关作用的润湿性表面。这种润湿可控性与氧化锌在不同温度下产生的不同数量氧空位有关。本文的研究结果会有助于拓展氧化锌在微流器件、化学传感器和生物传感器等方面的应用。

**关键词:** 材料表面与界面; 氧化锌; 超疏水; 超亲水; 开关润湿性; 传感器

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## THERMAL ANNEALING TREATMENT TO ACHIEVE SWITCHABLE AND REVERSIBLE WETTABILITY ON ZNO NANOWIRES SURFACE

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**Abstract:** Zinc oxide (ZnO) nanostructured surfaces can be reversibly altered from hydrophobicity to hydrophilicity in response to ultraviolet light or plasma treatment. In this paper, a thermal annealing procedure was used to tune ZnO nanowires' surface wettability, and switchable and reversible wettability was achieved. ZnO nanowires were synthesized by a simple solution method. The surfaces of as-synthesized ZnO nanowires demonstrate a superhydrophobicity with water contact angle of 151 degree at room temperature. After a high temperature treatment (>300 degree C) for 30 minutes, their superhydrophobicity was transited to superhydrophilicity with water contact angle of < 10 degree. In addition, the properties of switchable wettability can be archived very shortly (less than half minutes) when the treatment temperature is more than 400 degree C. Also, the high-thermal annealed superhydrophilic ZnO surfaces can be recovered to superhydrophobicity after a low-temperature (~100 degree C) procedure for several hours. Thus, the tunable properties of ZnO surface energy result in reversibly switchable wettability between superhydrophobicity and superhydrophilicity. This tunable wettability can be explained based on ZnO as a semiconductor material, which provides different numbers of oxygen vacancies under different temperatures. This result will extend applications of ZnO nanomaterials to many important fields, such as microfluidic devices, chemical sensors and biosensors.

**Keywords:** Materials surface and interface; ZnO; superhydrophobic; superhydrophilic; switchable wettability; sensor

## 0 Introduction

Surface wettability is an important property for solid materials. Hydrophilicity (water contact

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angle  $<90^\circ$ ) and hydrophobicity (water contact angle  $>90^\circ$ ) are the two types of surface wettability. Both superhydrophilic and superhydrophobic surfaces are useful and desirable for many applications. Materials with superhydrophobic surfaces have attracted great interest in antifogging glass, self-cleaning and other applications<sup>[1,2]</sup>. On the other hand, it was reported that a superhydrophilic sensing surface could dramatically decrease the liquid required on the sensing area and significantly improve sensitivity<sup>[3]</sup>.

Zinc oxide (ZnO) has been widely studied as a functional semiconductor. It can be customized to obtain unique properties for many novel applications such as piezoelectric transducers, solar cells, and gas sensors<sup>[4]</sup>. In order to extend the application of ZnO nanostructures to chemical sensors or even biosensors, one important point is to change the wettability of ZnO from hydrophobic to superhydrophilic because all the biopolymers can be dissolved in water. By now, only a few papers were concerned with wettability conversion of ZnO nanostructures, in which they used ultraviolet illumination or oxygen plasma<sup>[5-7]</sup>. In this paper, we treated the as-synthesized ZnO nanostructure surface by thermal annealing. The ZnO surfaces demonstrated a different wettability under different temperatures. In addition, their switchable and reversible wettability between superhydrophobicity and superhydrophilicity were achieved when they were treated by low ( $\sim 100^\circ\text{C}$ ) or high ( $>300^\circ\text{C}$ ) temperature.

## 1 Experimental

A simple two-step approach was used for fabricating ZnO nanostructures. Firstly, a clean FTO (F-doped Tin Oxide-coated) glass substrate surface was modified by dip-coating using zinc acetate-2-methoxyethanol-monoethanolamine (MEA) solutions. The molar ratio of MEA to zinc acetate was kept at 1.0 and the concentration of zinc acetate was 0.75mol/l. The resultant solution was stirred at  $60^\circ\text{C}$  for 30 min to yield a clear and homogeneous solution. The gel films were fabricated on a FTO glass substrate with withdrawing rates of 1.5 cm/min. The gel films were then preheated at  $300^\circ\text{C}$  for 10 min and post-heated at  $600^\circ\text{C}$  for 50 min in order to obtain ZnO seeds coatings. Subsequently, the pretreated substrates were immersed into a chemical solution mixed by 0.1 mol/l  $\text{Zn}(\text{NO}_3)_2$  (99%) and  $\text{C}_6\text{H}_{12}\text{N}_4$  (99%). A little amount (600  $\mu\text{l}$ ) of hydrofluoric acid (HF, 1 mol/l) was added into the above 40 ml mixtures to tune the surface morphology. After heated in a laboratory oven under  $95^\circ\text{C}$  for 2 h, ZnO nanostructures were grown on the FTO glass substrate.

A scanning electron microscope (SEM, Hitachi 3500N) was used to observe the surface microstructures. X-ray diffraction (XRD, Bruker D8) was used to identify the crystalline phases. Surface wettability was investigated by a contact angle measurement (KSV CAM 101). De-ionized water was dropped onto the surface using a microsyringe

## 2 Results and discussion

Fig. 1a shows the SEM image of the ZnO nanostructure. They are nanowires with diameter of less than 100 nanometers. The nanowires cover almost all the surfaces of FTO glass substrate, although their orientations are to some extent unorderly. XRD analysis (Fig. 1b) indicates that the nanowires are ZnO wurtzite structures. The (002) diffractive peak is not stronger than others, illustrating that ZnO nanowires are not *c*-axes preferred orientation, which is in consistence with the SEM observation.

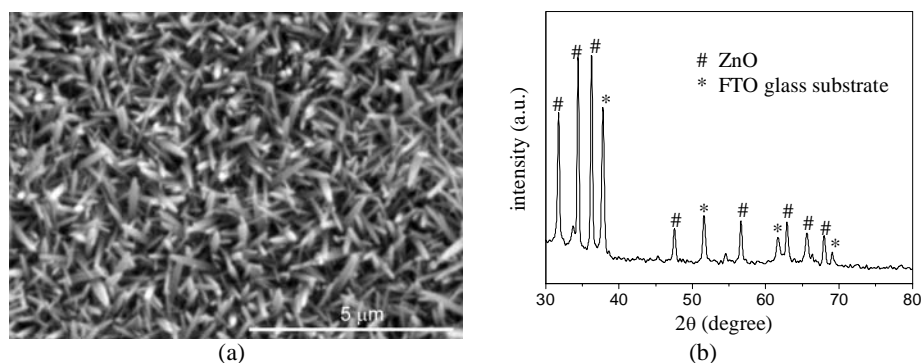


图 1 FTO 玻璃基底上 ZnO 纳米线的 SEM 形貌(a)和 XRD 分析图谱(b)  
Fig.1 SEM image (a) and XRD analysis (b) of ZnO nanowires on FTO glass substrate

Fig. 2a shows the superhydrophobic properties of the as-synthesized sample with a contact angle of  $151^\circ$ . Generally, there are two superhydrophobic states for a rough surface: Wenzel's state and Cassie's state<sup>[8]</sup>. The former represents a wet-contact mode and the latter represents a nonwet-contact mode. In the present work, when the sample was tilted to any angle, or even upside down, the water droplet on it stays pinned to it (see the inset of Fig. 2a). That is to say, the superhydrophobic ZnO surfaces provide a high adhesion to water, according with the character of Wenzel's state; water follows the solid surface textures and remains contact all the points of the solid surface below it. The roughness made from ZnO nanowires enhances water adhesive effect, and thus the ZnO nanowires surface show a strong sticky property.

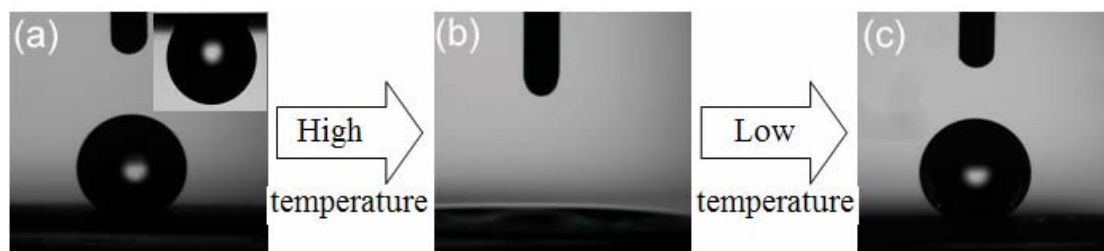


图 2 ZnO 纳米线表面上水滴的光学照片: (a)热处理前; 插图是把表面倒置后, 水滴继续粘附在表面上的照片。(b) 经  $400^\circ\text{C}$  高温处理后。(c) 经过  $100^\circ\text{C}$  低温处理后

Fig.2 Optical images of water droplets on the ZnO nanowires surface: (a) as-synthesized; (b) after a high temperature ( $400^\circ\text{C}$ ) treatment and (c) after a low temperature ( $100^\circ\text{C}$ ) treatment. Insert: a water droplet pinned to a surface upside down.

After the superhydrophobic ZnO nanowires surface was thermally treated at a high temperature more than  $300^\circ\text{C}$  for 20 minutes, the water contact angle changed from  $151^\circ$  to  $<10^\circ$ , demonstrating a superhydrophilic state (Fig. 2b). This result can be explained as followed. When the sample was annealed under a high temperature, the surface of ZnO nanowires would generate electron-hole pairs. Some of holes could react with lattice oxygen to form surface oxygen vacancies. These surface oxygen vacancies provide defect sites for chemisorption with hydroxyl groups, which induces superhydrophilic surfaces. When the temperature is higher, the amounts of oxygen vacancies are much more, and thus the water contact angle is much less. As shown in Fig. 3a, when the temperature is more than  $300^\circ\text{C}$ , the water contact angle falls dramatically from  $\sim 150^\circ$  to  $\sim 15^\circ$ . It is noted that the wettability can be transited from superhydrophobic to superhydrophilic in 30 seconds at  $400^\circ\text{C}$ . Thus the wettability can be switched in a very short time.

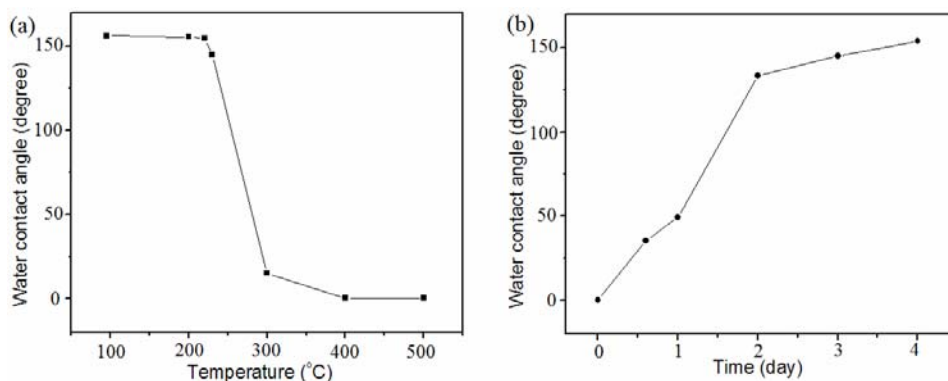


图3 水接触角随温度(a)和时间(b)的变化曲线  
Fig.3 Dependence of water contact angle of (a) temperature and (b) time.

Does the temperature always reduce the hydrophilicity? The answer is No. When a hydrophobic sample (as-synthesized ZnO nanowires) was annealed at a low temperature ( $<200$  °C), the wettability would keep their original hydrophobicity (see Fig. 3a). However, for a superhydrophilic sample (obtained by thermal annealing at high temperature  $>300$  °C), the wettability would vary from superhydrophilic to superhydrophobic when they were placed at a low temperature (100 °C) after 4 days (see Fig. 3b). The reversibility from superhydrophilicity to superhydrophobicity are corresponding to the energetically stability of oxygen vacancies<sup>[5]</sup>. The oxygen adsorption is thermodynamically favored, and it is more strongly bonded on the defect sites (i.e. oxygen vacancies) than the hydroxyl group. Oxygen atoms can replace the hydroxyl groups adsorbed on the defective sites gradually at low temperatures. Subsequently, the surface evolves back to its original state, and the wettability is reconverted from superhydrophilic to superhydrophobic.

### 3 Conclusions

In this work, switchable and reversible wettability are achieved by thermal annealing ZnO nanowires surfaces. The ZnO nanowires were fabricated by a simple solution method. Their wettability was dependent on the temperature. At high temperature ( $>300$  °C), they showed superhydrophilicity. At low temperature ( $<200$  °C), they showed superhydrophobicity. This can be explained based on ZnO as a semiconductor material, which provides different numbers of oxygen vacancies under different temperature. The results are expected to extend applications of ZnO nanomaterials, such as microfluidic devices, chemical sensors and biosensors

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