Surface modification of ZnO nanowire arrays with PTFE and their wettability property

Liqing Liu¹ · Yongtao Li¹ · Wei Ju¹ · Hongguang Zhang¹ · Xuemin He¹

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Abstract

Super-hydrophobic materials are important for their self-cleaning function which has become an increasingly popular research topic. This special surface in biologic world with super-hydrophobicity gives us a lot of inspiration to produce artificial hydrophobic materials to be applied in daily life and industry. Coating polytetrafluoroethylene (PTFE) on ZnO nanowire arrays is believed an ideal structure to produce a super hydrophobic surface layer. However, it is still a challenge to well combine PTFE and ZnO nanowires with high durability by a simple method. In this paper, we studied the wettability property of the surface modified ZnO nanowire arrays. These vertically ordered and well crystallized ZnO nanowire arrays were synthesized by a microwave-assisted hydrothermal method. After coating a thin layer of PTFE on those ZnO nanowire arrays by a simple vapor deposition method, the surface of samples has excellent super hydrophobicity with extremely low water rolling angle. The experimental results testify the modified ZnO nanowires have a good self-cleaning surface.

Keywords ZnO nanowire arrays · Nanocomposites · Physical vapor deposition · Superhydrophobicity

1 Introduction

In recent years, the hydrophobic surface has attracted extensive researches for practical applications. In particular, the research about super-hydrophobic materials with self-cleaning function raised a considerable interest [1–3]. Naturally, a lot of biological materials show their excellent surface hydrophobicity [4–6], such as the lotus leaf which benefits from its cellular micro bulge and biological wax crystals coating surface to meet self-cleaning function. This special surface has a certain biological function in protecting themselves from being polluted, which draws our attention to produce artificial hydrophobic materials which would be applied in daily life, industry and agriculture [7–9]. To obtain super-hydrophobic surface, fundamentally it needs low surface energy and high surface roughness [10–12]. It is known that polytetrafluoroethylene (PTFE)

has low surface energy [13, 14] while ZnO nanowire arrays [15] have high surface roughness. So ZnO nanowire arrays coated PTFE are believed to be an ideal structure to produce a super hydrophobic surface [16–19]. However, the methods reported are either RF magnetron sputtering a PTFE target [16, 17] or spin/dip coating [19] a film from a PTFE emulsion [18]. The former needs complex equipment such as magnetic sputter while as for the latter the thickness of the film is frequently non-uniform and thick. Moreover, because of the weak interaction between PTFE and ZnO nanowire by dipcoating [18, 20], the durability of the surface is also weak, which limits the application of super-hydrophobic surfaces.

In this paper, the super-hydrophobic ZnO nanowires with high contact angle and the minimum rolling angle were prepared by a simple and inexpensive method. After coating a thin layer of PTFE on these ZnO nanowire arrays

✉ Liqing Liu, liuq@njupt.edu.cn; Yongtao Li, liyt@njupt.edu.cn; Wei Ju, 1297049471@qq.com; Hongguang Zhang, Zhanghongguang2003@126.com; Xuemin He, zspohexuemin@163.com | ¹New Energy Technology Engineering Laboratory of Jiangsu Province, School of Science, Nanjing University of Posts and Telecommunications (NJUPT), Nanjing 210023, People's Republic of China.

by a vapor deposition method, the surface of the samples has excellent super hydrophobicity with extremely low water rolling angle. The wetting property shows that the modified ZnO nanowires have a good self-cleaning surface.

2 Experimental section

At first, the ZnO nanowires were synthesized by a hydrothermal method similar to our previous report [21], by immersing a fluorine doped tin oxide (FTO) glass with ZnO seed layer into a mixture solution of zinc nitrate ($\text{Zn}(\text{NO}_3)_2$) and hexamethylenetetramine (HMTA, $\text{C}_6\text{H}_{12}\text{N}_4$) in deionized (DI) water and being heated for 2 h. Then PTFE was deposited on ZnO nanowires to get a low surface energy coating. In a typical process, the FTO glass with ZnO nanowires was inserted in the center of a conventional horizontal tube furnace with a quartz working tube, which was placed face down 5 mm above 0.1 g PTFE power in a sapphire boat. Then the sample was heated at 360 °C for 45 min under air atmosphere of 100 Pa. The temperature cooled down to room temperature naturally. To compare, the pure FTO glass was treated using the same method. The samples were characterized by field emission scanning electron microscopy (FESEM, FEI Inspect F50), and X-ray diffraction (XRD, Rigaku smartlab) was used to investigate the structural properties of ZnO NWs and PTFE growth orientation. Energy dispersive X-ray spectrometer (EDX, Oxford X-act) was attached to the SEM to determine the element composition of the samples.

3 Results and discussion

Figure 1 shows the SEM images of the as-synthesized nanowire arrays. Figure 1a shows the morphology of the top of unmodified ZnO nanowires. The ZnO nanowires are grown vertically on the FTO substrates. The morphology of the nanowires can be seen clearly in the inset of Fig. 1a. The average spacing between nanowires is about 300 nm. Such structure provides enough interspaces between each nanowire to offer high surface roughness which is ideal for superhydrophobicity. Figure 1b presents the SEM image of the ZnO nanowires coated with PTFE. It shows that there are only a little morphology changes after PTFE coating. After checking the morphology in detail, it can be seen that there are some subtle changes at the top of these nanowires. The top of the nanowires without PTFE is flatter than those coated. This feature can be observed in the image shown in the inset of Fig. 1b, in which the spacings between nanowires are filled by PTFE and the nanowires

Fig. 1 SEM images of ZnO nanowire arrays grown on FTO substrate. **a, b** are the unmodified and modified samples, respectively. The inserts are the larger magnification of images

Fig. 2 XRD and EDX patterns of the ZnO/PTFE nanowire arrays

shows a curved surface. Obviously, there is a thin layer of PTFE on the top of nanowires.

Figure 2 shows the XRD pattern of the as-prepared ZnO/PTFE nanowire arrays. The weak peak located at 18.1° is the main diffraction peak of PTFE (JCPDS card No. 472,217). The peaks at 26.8°, 38.3° and 52.0° correspond to the FTO, which come from the diffraction of the FTO substrate. The other peaks shown in Fig. 2 can be well indexed to hexagonal ZnO with lattice constants of $a = 3.263 \text{ \AA}$ and $c = 5.178 \text{ \AA}$. The peak corresponds to 002) plane of ZnO is very strong, which means these ZnO nanowires are well crystallized and highly oriented in the c-axis direction. The EDX spectrum inset of Fig. 2 indicates that these nanowires are comprised of Zn, O and F elements, accompanied with molar ratio of $\text{F}:\text{Zn}:\text{O} = 0.05:1:1.12$. In addition, it is noted that PTFE is somewhat unusual in having an as-polymerised melt temperature of 341 °C and 340 °C while the subsequent melting temperature is 328 °C, respectively

Fig. 3 The water droplet shape on FTO substrate before (a) and after (b) modified with PTFE; c water droplet spread on the pure ZnO nanowires, and d a water droplet standing on a PTFE-modified ZnO nanostructured surface

[20, 22]. The heating temperature of 360 °C is just a little higher than the melting point of PTFE. From the XRD and EDX results, it is believed that these PTFE were indeed deposited on the surface of ZnO nanowire arrays to reduce the surface energy [16].

Figure 3 shows images of a water droplet on different types of substrate. The water droplet contact angles (CA) on pure FTO substrate were around 30° and 115° before and after modification with PTFE, as shown in Fig. 3a, b, respectively. The improvement of the contact angle after PTFE coating owns to the low surface energy of sample. However, lacking of roughness leads to the contact angle can only reach 115° which can't meet the requirement of super-hydrophobic surface. When the droplet is on ZnO nanowire arrays, as indicated in Fig. 3c, the surface shows super-hydrophilicity with a contact angle less than 5°. This super-hydrophilic surface comes from the super high roughness of ZnO nanowire arrays and hydrophilic property between ZnO and water. When the ZnO nanowire arrays were coated with PTFE, the wettability of the surface has an obvious change, exhibiting a high CA up to 160°, as shown in Fig. 3d. This value is close to those in the reported works [16, 23]. In addition, the water rolling angle is lower than 5°, indicating an extreme low adhesive force.

Compared with the sample without coating, these coated ZnO nanowire arrays with a low surface energy layer of PTFE were contributed to super-hydrophilicity of the surface. It is well known that super-hydrophobic surface needs high surface roughness and low surface energy. Though the FTO glass after being treated with PTFE has an improved contact angle, the value is not large enough for the low surface roughness. However, high surface roughness of ZnO nanowire arrays is helpful

to its superhydrophilicity. The treated ZnO nanowire arrays meet well the two conditions of super-hydrophobic, thus super-hydrophobic ZnO nanowires formed with the contact angle transformed from 0° to 160°.

4 Conclusions

In this paper, superhydrophobic ZnO/PTFE nanowires arrays have been successfully fabricated by a two-step growth method. After coating a thin layer of PTFE on these ZnO nanowire arrays by a vapor deposition method, the surface has a very high contact angle and an extremely low rolling angle. The whole process was simple, controllable, timesaving and free of complex equipment. The experimental results show the modified ZnO nanowires have a good self-cleaning surface. This work gives us a new inspiration to learn from natural phenomena and extends the fields of the new super-hydrophobic surface.

Acknowledgements This work was supported by Natural Science Foundation of Jiangsu Province of China (Grant Nos. BK20141337, BK20150829), and Large Equipment Grants of Southeast University, China.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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