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Self-assembled ZnO agave-like nanowires and anomalous superhydrophobicity

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Abstract
Thin films of ZnO agave-like nanowires were prepared on amorphous carbon thin layers on silicon substrates using thermal chemical vapour transport and condensation without any metal catalysts. The unusual superhydrophobicity of the fabricated surface was measured; the water contact angle reaches 151.1°. On the basis of experimental and theoretical analyses, it appears likely that the biomimetic microcomposite and nanocomposite surfaces of the prepared thin films of ZnO agave-like nanowires are responsible for the excellent superhydrophobicity.

1. Introduction

Surface wettability is an important property governed by the chemical composition and the geometric structure of solid surfaces [1, 2]. Generally, a surface with a water contact angle (CA) larger than 90° is called a hydrophobic surface. The surface is called superhydrophobic if the water CA is larger than 150°. Hydrophobic surfaces have been intensively investigated due to their importance in industrial applications. Recently, hydrophobic and superhydrophobic surfaces have usually been produced in two ways, on the basis of geometry and chemistry. In the geometric version, the method is to create a rough structure on a surface. The chemical route is to modify a rough surface with compounds with low surface free energy, such as fluorinated or silicon compounds [3–6]. Therefore, it is necessary to pursue a new production method and novel surface structure for industrial applications of hydrophobic and superhydrophobic surfaces. ZnO nanowire is an important functional material [7, 8]. Very recently, we fabricated ZnO nanowires on amorphous carbon thin layers on silicon substrates using thermal chemical vapour transport and condensation without any metal catalysts, and reported a remarkable enhancement of the field emission of the nanocomposites for ZnO nanowire covered amorphous carbon compared to that of the intrinsic amorphous

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diamond, suggesting the possibility of decorating amorphous diamond by fabricating one-dimensional nanostructures on its surface, which could substantially improve the field emission by modifying the surface microstructures [9]. Interestingly, thin films of ZnO nanowires are suggested to be good superhydrophobic coating candidates [10, 11]. In the study presented, we report on biomimetic microstructural and nanostructural thin films of ZnO agave-like nanowires fabricated on amorphous carbons, and the remarkable superhydrophobicity of the biomimetic microstructures and nanostructures measured.

2. Experimental details

In our experiment, the amorphous carbon thin layer is first deposited on single silicon substrates by using a magnetic field filtered ion deposition technique with the deposition pressure of 6.6 Pa and the substrate temperature of 320 K. Depending on the deposition time, the thickness of the prepared amorphous carbon films is controlled to be in the range from 30 to 150 nm. Then, ZnO nanowires are fabricated on the amorphous carbon by using thermal chemical vapour transport and condensation without any metal catalysts. In detail, a mixture source of ZnO powder (50 wt%) and graphite powder (50 wt%) is loaded in the higher temperature zone, and the amorphous carbon substrate is placed at the lower temperature of a horizontal tube furnace. The furnace is heated up to 1250 K and kept for 30 min under a pressure of 9.1×10^4 Pa and a constant argon gas flow of 800 sccm as the carrier gas. In our experiment, we take one thinner (30 nm) and two thicker (150 nm) substrates and place the thicker one (sample 1) close to the mixture source, and another thicker one (sample 2) and another thinner one (sample 3) 1 cm away from the close-to-source thicker one. Therefore, the growth temperatures of different substrates will be different. That of the one closer to the source will be higher than those for the other two. After the growth, the furnace is cooled down to room temperature. Grey films are observed on these substrates when the substrates are removed.

3. Results and discussions

Interestingly, a typical biomimetic microcomposite and nanocomposite surface is fabricated on amorphous carbon (sample 2) as shown in figure 1. In detail, the prepared thin film consisted of agave-like nanowires, and every agave-like structure was at the micrometre scale in figure 1(a). The needle-shaped petals of the agave-like structures are at the nanometre scale, their diameter is in the range from 30 to 50 nm and they are 15 μm in length, as shown in figure 1(b). The x-ray diffraction (XRD) pattern in figure 1(c) of the sample grown shows that the peaks can be indexed to typical hexagonal ZnO with lattice constants of $a = 3.2535$ Å and $c = 5.2056$ Å, which confirm that the samples are hexagonal ZnO. Further, the wettability of the biomimetic microcomposite and nanocomposite surface is evaluated from a water contact angle measurement. The value of the water CA reaches 151.1°, as shown in figure 1(d), which shows remarkable superhydrophobicity. The geometric structure of the biomimetic microsurface and nanosurface seems distinctly indicated as the physical origin for the superhydrophobicity.

To validate our proposed hypothesis, i.e. that the geometric structure of the surface seems likely to be the physical origin of the superhydrophobicity, we fabricate two other kinds of ZnO nanostructures. Figures 2 and 3 show ZnO nanostructures from samples 3 and 1. In detail, the array of ZnO nanowires with the diameter of 70 nm and lengths of 5–8 μm is approximately vertically grown from the substrate in figure 2(a), and the corresponding XRD spectrum is shown in figure 2(b). The array of ZnO nanocolumns with the diameter of 200 nm and length of 10 μm from sample 1 is shown in figure 3(a), and the corresponding XRD spectrum is

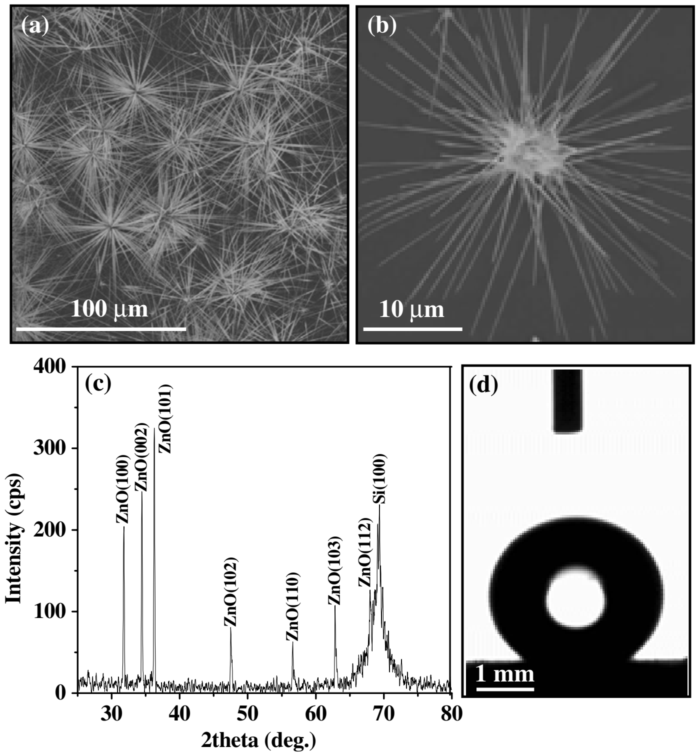

Figure 1. SEM morphologies, XRD spectra and a photograph of the water droplet shape for the ZnO agave-like nanowires fabricated on amorphous carbon films. (a) SEM image at lower magnification; (b) SEM image at high magnification; (c) XRD spectrum of ZnO agave-like nanowires; (d) photograph of the water droplet shape for ZnO agave-like nanowires.

shown in figure 3(b). The wettability of the two ZnO nanostructures is similarly evaluated, by water contact angle measurement, and the water droplet shapes are shown in figures 2(c) and 3(c), respectively. The water CAs of the two arrays of ZnO nanostructures are 106.7° and 94.4°, respectively. Clearly, these results show that both the surface morphology of the nanowire films and the size of the nanowires, i.e., the geometric factors, can greatly influence the hydrophobicity of the fabricated surfaces. Therefore, in our case, the remarkable enhancement of the superhydrophobicity seems likely to originate from the biomimetic microsurfaces and nanosurfaces of the prepared thin films of ZnO agave-like nanowires.

Jiang *et al* reported that the thin film consisted of a vertical and compact ZnO nanowire array showing excellent superhydrophobic [10]. However, in our case, the sparsely biomimetic microsurface and nanosurface meets almost the same standards of superhydrophobicity as were mentioned above. It is well known that the sparse structure is economical as regards materials. What induces the superhydrophobicity of the surface decorated with sparse ZnO agave-like nanowires in our case? Generally, the surface free energy and the surface roughness should be considered, because they are two important factors governing the surface wettability [2]. From the surface free energy viewpoint, in our case, most of the nanostructures above are oriented in the faceted (001) direction and have lower surface free energies than others, although they display different morphologies. Thus, there are different wettabilities of these surfaces decorated with three different ZnO nanostructures in our case. On the other hand,

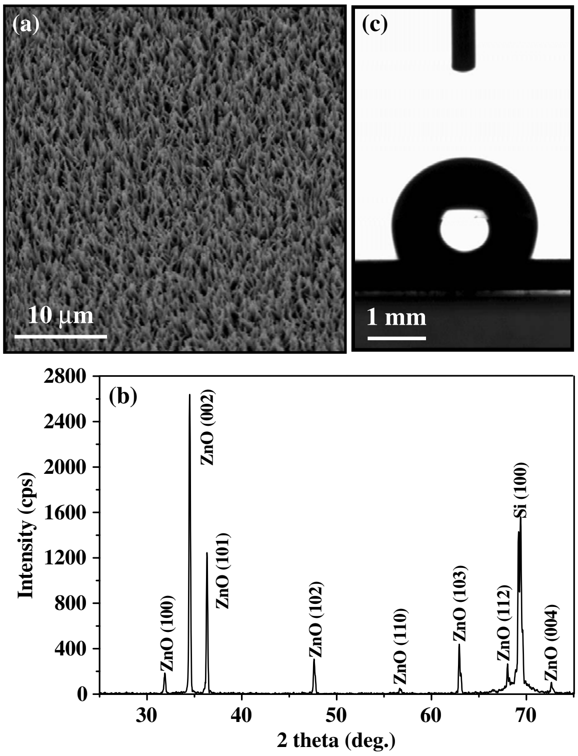

Figure 2. SEM morphologies, XRD spectra and a photograph of the water droplet shape for the ZnO nanowire arrays grown vertically from amorphous carbon films. (a) SEM image of ZnO nanowires; (b) XRD spectrum of ZnO nanowires; (c) photograph of the water droplet shape for ZnO nanowire arrays.

judging by the superhydrophobicity of biological surfaces [12–14], we consider that the air fraction between the microsurfaces and nanosurfaces and the water surface could influence the hydrophobicity of the fabricated surface, as the hydrophobicity of a rough surface can be enhanced by increasing the proportion of air/water interfaces [2]. For instance, the hierarchical microstructures and nanostructures of a water strider's leg surface are responsible for its water resistance and the supporting force [14]. Interestingly, the biomimetic microsurfaces and nanosurfaces of the prepared thin films of ZnO agave-like nanowires definitely display hierarchical structure and have larger proportions of air/water interfaces than samples 1 and 3. Additionally, the diameter, height and surface density of the agave-like nanowires can influence the hydrophobicity, because these factors can change the proportion of air/water interfaces. In detail, the relationship of the density and height of agave-like nanowires to the proportion of air/water interfaces is a direct ratio, and the diameter is in inverse proportion to the proportion air/water interface. Therefore, the hydrophobicity of sample 3 is better than that of sample 1. For sample 2, since agave-like structures are at the micrometre scale and petals of agave-like structures are at the nanometre scale, the agave-like structure with small diameter (30–50 nm) and large length (10–20 μm) produces a larger proportion of air/water interfaces than the other samples.

In order to check on the speculation above, we calculate the air/water proportions (f_{v}, i.e. water droplet occupied by air) for three ZnO nanostructures from the corresponding SEM images (figures 1–3). According to Cassie's law for the surface wettability, the microstructure

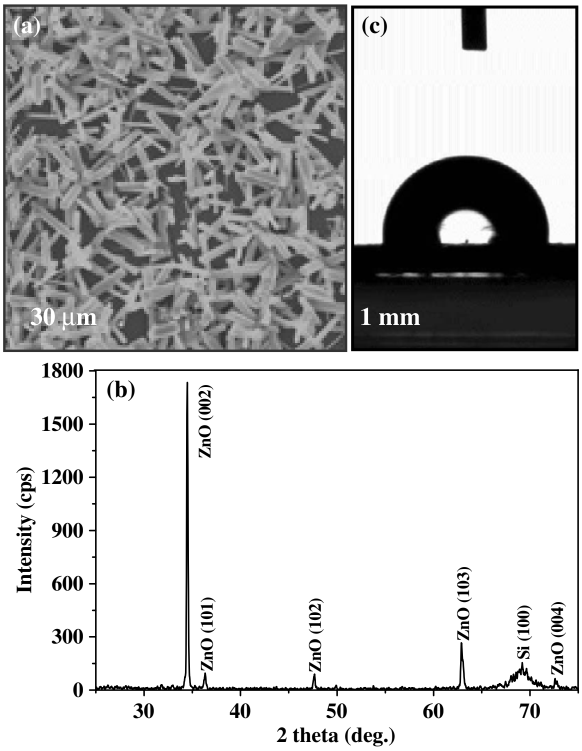

Figure 3. SEM morphologies, XRD spectra and a photograph of the water droplet shape of the ZnO nanocolumns fabricated on amorphous carbon films. (a) SEM image of ZnO nanocolumns; (b) XRD spectrum of ZnO nanocolumns; (c) photograph of the water droplet shape for the ZnO nanocolumns.

Table 1. A comparison between the f_v values and the water contact angles of three ZnO nanostructures.

Sample	1	2	3
Proportion of air/water interface (%)	46.13	91.8	84.71
Water contact angle (deg)	94.4	151.1	106.7

can be regarded as a heterogeneous surface composed of solid and air. f_s and f_v are the fractions of the surface under the water droplet occupied by solid material and air, and $f_s + f_v = 1$. In our case, the value of f_v for the agave-like nanostructure reaches 91.8%. A comparison of the f_v values among the three nanostructures is listed in table 1. Importantly, the experimental data support the theoretical deductions above, i.e., the high air/water interface of the agave-like nanostructure can enhance the hydrophobicity of the fabricated surface.

4. Conclusion

In summary, we have fabricated biomimetic microsurfaces and nanosurfaces consisting of ZnO agave-like nanowires on amorphous carbon. The prepared surface displays excellent superhydrophobicity due to the hierarchical microstructures and nanostructures, suggesting that biomimetic microsurfaces and nanosurfaces could be expected to be applicable in the design of dewetting surfaces and materials.

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