Journal of Experimental Nanoscience
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t716100757

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Online publication date: 31 January 2011

To cite this Article Zhang, Zhao-Zhu , Xu, Xiang-Hui , Yang, Jin and Zhu, Xiao-Tao(2011) 'Fabrication of hierarchical structures on alumina plate and its nonwetting property', Journal of Experimental Nanoscience, 6: 1, 29 — 37

To link to this Article: DOI: 10.1080/17458081003752996

URL: http://dx.doi.org/10.1080/17458081003752996

Journal of Experimental Nanoscience
Vol. 6, No. 1, February 2011, 29–37

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(*Received 30 December 2009; final version received 5 March 2010*)

We have fabricated a micro- and nano-hierarchical structure on an alumina plate by a simple hydrothermal method. Hexafluorophosphate octahedrons with nanoparticles on each of the eight plane surfaces were obtained. After self-assembling of a film of perfluorooctanoic acid, the Al plate with a high contact angle of $160 \pm 2^\circ$, exhibited a nonwetting property.

Keywords: engineering materials; hierarchical structures; superhydrophobic; temperature

1. Introduction

Considerable attention has been paid recently to the fabrication of metal nanoparticles and the induced potential applications in photography, optoelectronics, biological labelling and so on. Metal nanomaterials possess many properties, such as size-related optical, adsorbents, electronic and catalytic properties. Three-dimensional nanomaterials with various morphologies, nanoholes [1], nanorods [2], nanotubes [3], nanowires [4] and nanoflowers [5] have been previously reported, most of which were fabricated in a single scale. Recently, hierarchical structures [6] are becoming an effective way to obtain a functional nanomaterial, such as superhydrophobic material.

Superhydrophobic surfaces with a contact angle (CA) greater than 150°, inspired by lotus leaves, are characterised by some amazing properties, such as self-cleaning, anticorrosion, antipollution [7–9]. It has drawn much attention from both fundamental research and practical applications. In practice, a material is hydrophilic when the intrinsic water CA (CA on its flat surface) is less than 90°, while a material is hydrophobic when the intrinsic water CA is greater than 90°. To fabricate a superhydrophobic surface, it is essential to create a rough structure, especially micro- and nano-hierarchical structures.

There are many reports on fabricated nanosized structures on the surface of copper, zinc and so forth [10–13]. The literature about fabricating of hierarchical structures on aluminium substrate by hydrothermal method is scarce, though aluminium and its alloys

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ISSN 1745–8080 print/ISSN 1745–8099 online

DOI: 10.1080/17458081003752996
http://www.informaworld.com

are important engineering materials. Here we report the fabrication of superhydrophobic aluminium surface with octahedron hierarchical structures by a simple hydrothermal method, and its nonwetting properties after surface modification.

2. Experiment and characterisation

2.1. *Preparation of hierarchical structure on alumina plate*

Aluminium (Al) plates sized $2 \times 2 \times 0.1$ cm (width $\times$ length $\times$ thickness) were used as a substrate. About 0.4 g of ammonium hexafluorophosphate was added to 30 ml of deionised water and then stirred to form a uniform solution. Having been washed with absolute ethanol and deionised water, the Al plates were put into the solution and maintained in Teflon-lined stainless steel autoclave of 50 ml capacity and then sealed or maintained in a sealed flask at 90°C, 100°C and 120°C, respectively. Afterwards, it cooled to room temperature naturally. The products were collected and washed with deionised water thoroughly, and then dried in air.

2.2. *Preparation of superhydrophobic self-assemble film on alumina plate*

The as-prepared samples were immersed in an ethanol solution of perfluorooctanoic acid (0.1 M) for 60 min, and finally were dried in vacuum.

2.3. *Characterisation*

The surface chemical compositions of the as-prepared sample were analysed with a VGESCALAB210 X-ray photoelectron spectroscope (XPS). The microstructure is determined by an X-ray diffractometer (XRD) (Philips Corp., The Netherlands) operating with Cu-Kα radiation at a continuous scanning mode and an omega angle of 1.0°. The morphological structures of the as-prepared Al surface were examined with a field emission scanning electron microscope (JSM-6701F, FE-SEM). The sessile drop method was used for water CA measurements with a CA-A contact angle meter (Kyowa Scientific Company, Ltd., Japan) at an ambient temperature. The water droplets (about 5 μl) were dropped carefully onto the surface. The average CA value was determined by measuring at five different positions of the same sample.

3. Results and discussion

3.1. *Effect of temperature and time on the hierarchical aluminium surface*

The resulted Al surface was examined by FE-SEM. The surface topography of the Al plates in an autoclave for 6 h is shown in Figure 1(a)–(d). Uniform octahedrons are on the surface at 100°C (Figure 1(a)). On each of the eight plane surfaces, nanoparticles of about 10–20 nm dispersed uniformly. On the contact area of each two planes there is a 'channel' of about 20 nm width. The 'channels' are pointed by arrows in Figure 1(a) and (b). It is obvious that temperature has great impact on the formation of aluminium hexafluorophosphate octahedron. And a few octahedrons are found on the Al surface fabricated at 90°C, which is shown in Figure 1(c). Figure 1(d) shows the surface topography of the Al plates at 120°C, on which the octahedron does not grow completely. It is apparently clear that

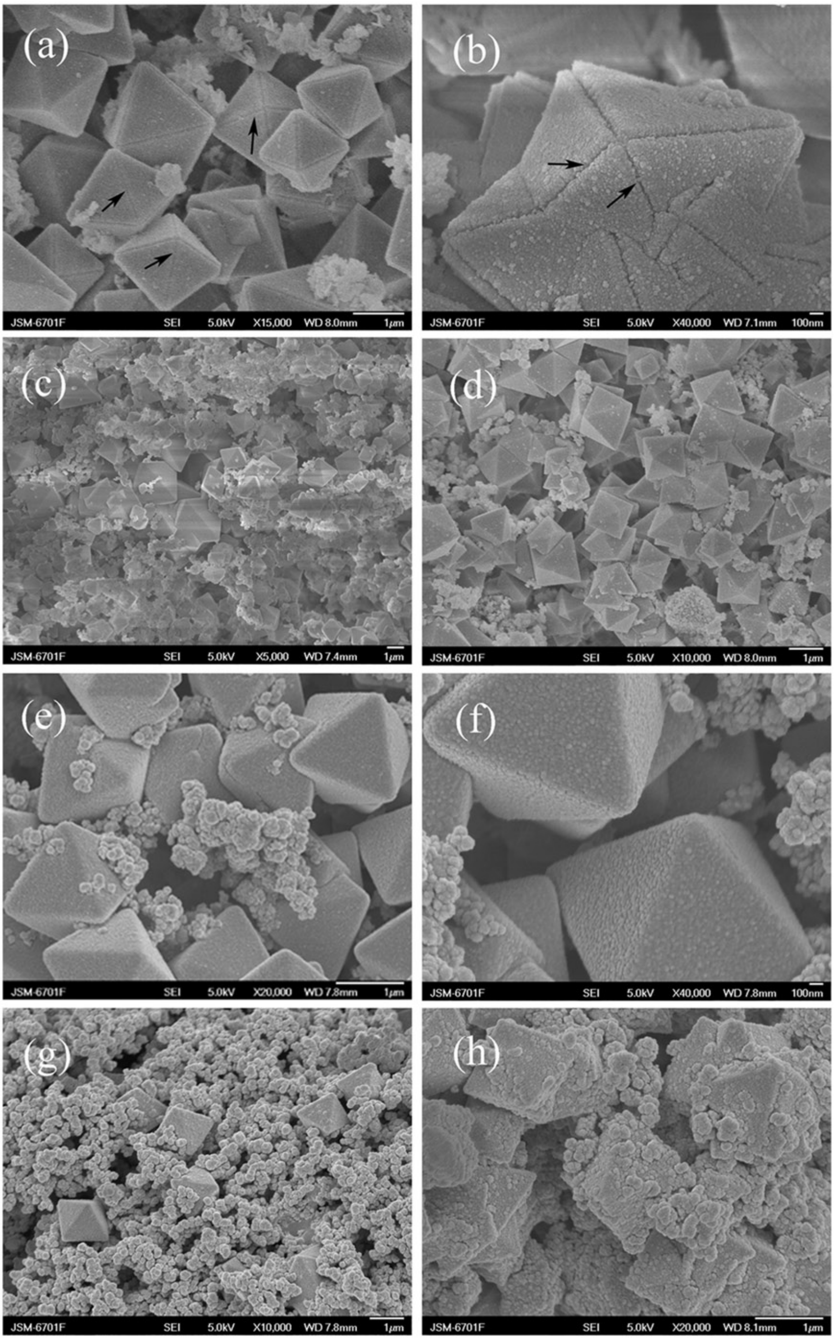

Figure 1. Effect of temperature on the morphological structure of the Al sample at different conditions: (a)–(d) maintained at water-jacked kettle, (e)–(f) maintained at flask, (a), (e) at 100°C for 6 h, (b), (f) larger magnification of (a) and (e), (c), (g) at 90°C for 6 h and (d), (h) at 120°C for 6 h.

the sample at 90°C, 100°C and 120°C are different. The 'channel' was only found at 100°C. The image from Figure 1(e)–(h) shows the surface structure of the Al plates in flask. It can be seen that the uniform octahedron can be found on the sample 100°C as well (Figure 1(e)), on which nanoparticles of about 10–20 nm dispersed, but with no special 'channel'. The samples at 90°C and 120°C are almost the same as these in autoclave. Therefore, we draw the conclusion that the proper temperature to fabricate uniform octahedrons is at 100°C. Figure 2 shows the FE-SEM images of Al plates kept in an autoclave for different times. In the case of the Al plate maintained for 3 h (Figure 2(a)), there were only nanosized particles on the surface. When the time was extended to 6 h (Figure 1(a)), uniform octahedrons grew on Al plates. When the Al plate was maintained for 7 h, the octahedrons were incomplete (Figure 2(b)). And if the experiment time further extended to 9 h, no octahedrons can be found (Figure 2(c)) and only micro-sized particles appear on the surface. From the FE-SEM image described above, we can conclude that the proper condition to obtain the special octahedrons was maintaining the Al plates in an autoclave at 100°C for 6 h.

By comparison of the samples fabricated in different conditions, it is clear that we can only get the complete octahedrons at 100°C for 6 h. And the special 'channel' can only appear in the autoclave at 100°C for 6 h exclusively. It may be the result of the proper temperature gradient and the high pressure in the autoclave. The heat convection, resulting from temperature difference in the autoclave, brought the ions from high-temperature

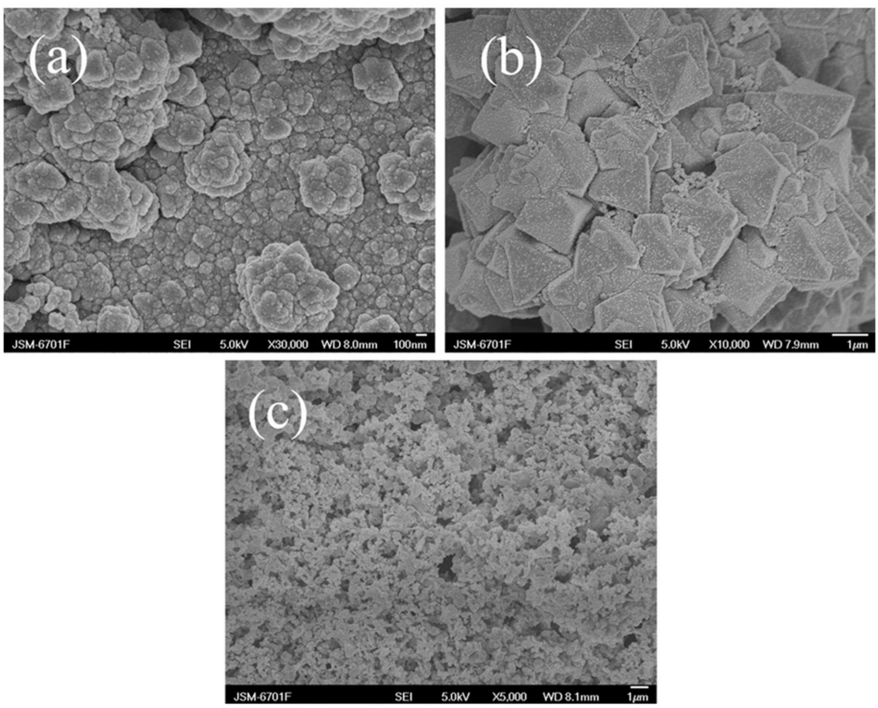

Figure 2. FE-SEM images of the Al plates maintained in an autoclave for different times, (a) 3 h, (b) 7 h and (c) 9 h.

region to low-temperature region. In the low-temperature region, the solution became supersaturated and finally crystallised.

3.2. *Surface composition and X-ray diffraction patterns of the hierarchical aluminium surface*

The surface compounds can be identified by XPS measurements. Figure 3 shows the XPS spectra of the Al sample in the autoclave at 100°C for 6 h. The peaks located at 74.7, 137.1 and 685.5 eV are attributed to aluminium (Al), phosphorus (P) and florin (F) elements in the hexafluorophosphate, respectively. They indicate that a film of aluminium hexafluorophosphate grew on the Al plate. The PF_6^- ion has a certain complexing ability to metal ions. So, the Al^{2+} ions in the solution were captured by PF_6^- to form the octahedron hexafluorophosphate. The possible growth mechanism of the aluminium hexafluorophosphate is described as follows:

$$2Al + 3H_2O \rightarrow Al_2O_3 + 3H_2 \uparrow$$
$$NH_4^+ + H_2O \rightarrow NH_4OH + H^+$$
$$Al_2O_3 + 6H^+ + 6PF_6^- \rightarrow 2Al(PF_6)_3 + 3H_2O.$$

Figure 4 shows the XRD spectra of Al sample in the autoclave at 100°C for 6 h. The peaks located at 19.34° and 22.38° [14] are the characteristic diffraction peaks of hexafluorophosphate, and the diffraction peaks of 31.85°, 44.95°, 73.71° and 79.45° [15] are ascribed to the Al element. The XPS and XRD spectra of Al sample in the flask at 100°C for 6 h are the same as those in the autoclave. Both the XRD and the XPS spectra demonstrate that a film of aluminium hexafluorophosphate grew on the Al plate.

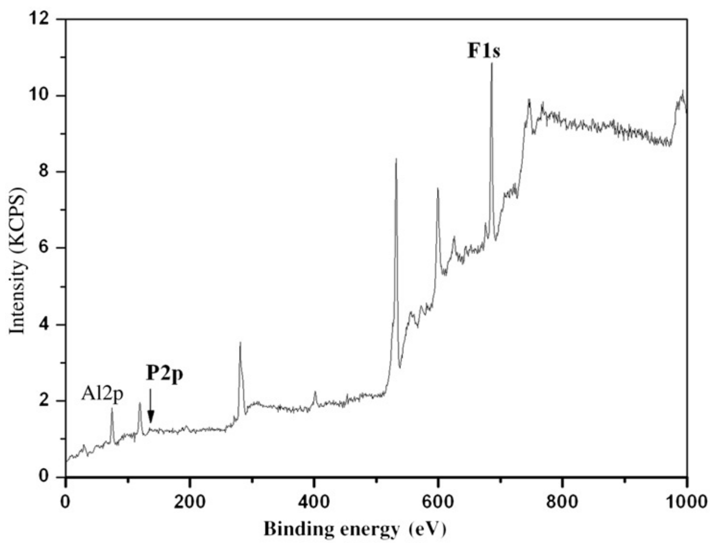

Figure 3. XPS spectra of Al sample maintained in an autoclave at 100°C for 6 h.

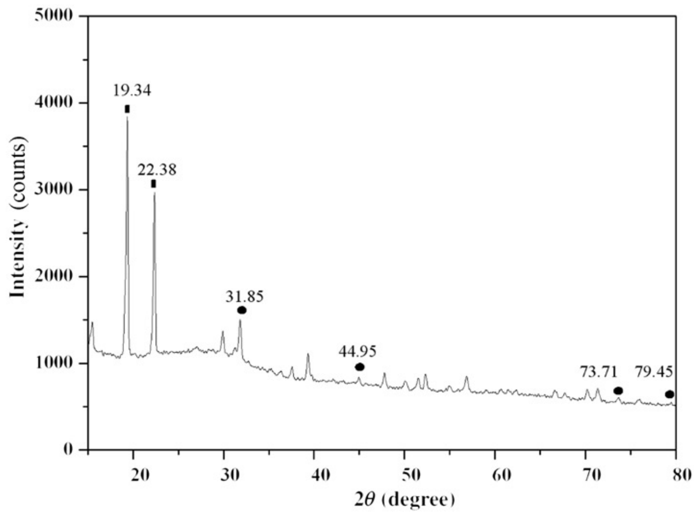

Figure 4. XRD spectra of Al sample maintained in an autoclave at 100°C for 6 h.

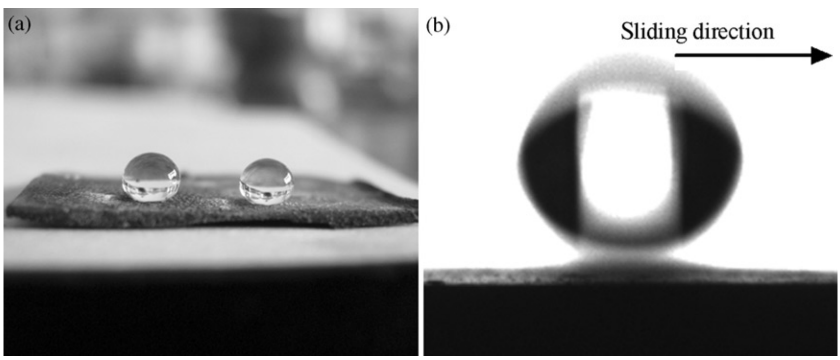

Figure 5. Photographs of water droplet on the prepared Al surface (a) and sliding angle ($5 \pm 2°$) of water on the as-prepared surface (b).

3.3. *Wetting property of the superhydrophobic surface*

It is well-known that the methods to fabricate a superhydrophobic surface can be mainly reduced to two approaches: either create a rough structure on a hydrophobic material surface or modify the rough surface with a special low surface energy material [16,17]. In the experiment reported here, we created a rough structure on the Al substrate and then modified the rough surface with a special low surface energy material.

The surface wettability of the as-prepared substrates has been studied by CA measurements. Figure 5(a) shows the image of water droplet on the prepared Al surface in an autoclave at 100°C for 6 h. After having been modified by perfluorooctanoic acid, the Al plate shows a high CA of $160 \pm 2°$ and exhibited a nonwetting property. Hardly are the water droplets able to stick to the surface, as a sliding angle of around $5 \pm 2°$ on the

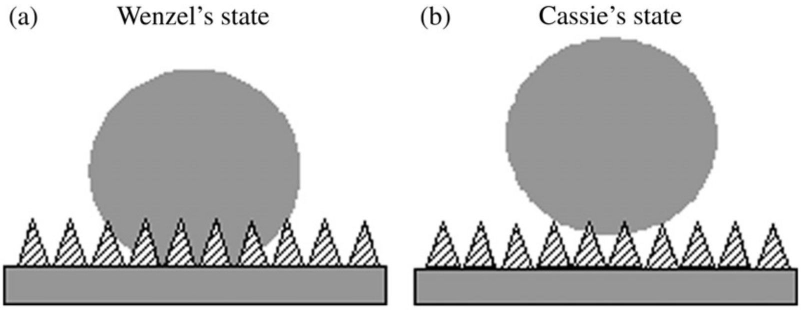

Figure 6. Two superhydrophobic states: Wenzel's state (a) and Cassie's state (b).

surface allows the droplets to roll off quite easily (the sliding angle of water on the as-prepared surface is shown in Figure 5(b)). Additionally, the CA is almost unchanged at ambient temperature for one week, which means that the prepared surface has a certain extent of durability in this condition.

3.4. *Theory analysis of the superhydrophobic surface*

Usually, on a rough surface there are two superhydrophobic states: Wenzel's state and Cassie's state [18]. In Wenzel's state (Figure 6(a)), the water droplets pin the surface in a wet-contact mode. Since the water droplets are unable to slide on the surface, a surface with high adhesion is observed [19]. In contrast, in Cassie's state (Figure 6(b)), the water droplets adopt a nonwet-contact mode on solid surfaces and can roll off easily due to their low adhesive force [20]. It is believed that the water droplets on the Al plate are in Cassie's state described by the Cassie–Baxter equation [21]

$$\cos\theta r = f_1 \cos\theta - f_2,$$

where f_1 and f_2 are the fractions of solid contact area and air contact area with water, respectively (i.e. $f_1 + f_2 = 1$) and θ and θr are the CA of a smooth surface and that of a rough surface. We can get the f_2 value of the structured alumina surface, which is about 0.965 (the CA of flat alumina plate was 45°). It means that when the water droplet dropped onto this surface, sufficient air was trapped to space between the micro- and nano-hierarchical structure, which can prevent water from intruding into spaces. Combined with the self-assembling film of perfluorooctanoic acid, the surface exhibited a remarkable nonwetting property.

Lotus leaves, showing a high CA and very low CA hysteresis, are the typical examples of superhydrophobic surfaces in Cassie's state. Due to the low CA hysteresis, the droplets can roll off quite easily, which has a self-cleaning effect. It is well-known that micro- and nanoscale hierarchical surface topographies, such as those found on lotus leaves are critically important. On the Al plate with hierarchical structures, the three-phase contact line (air–liquid–solid) [22] on the surface are contorted and unstable because of the hierarchical structures, which can trap sufficient air to prevent water from intruding into the spaces, and finally produce large CAs and low CA hysterics. Therefore, we are positive that the prepared surface structure is an essential factor to obtain the nonwetting property on the alumina plate.

4. Conclusions

In summary, we fabricated the micro- and nano-hierarchical structures on the aluminium plates by an easy but effective method. The morphologies were controlled by the temperature. The hierarchical structures were obtained at 100°C both in the autoclave and in the flask. The aluminium plates, which were modified by perfluorooctanoic acid, exhibited a notable nonwettting property. Such plates may have a variety of applications in industry for its antipollution, self-cleaning and antiicing properties.

Acknowledgements

The authors acknowledge the financial support of the National 973 Project of China (grant no. 2007CB607601) and the National Science Foundation of China (grant nos. 50835009, 50773089 and 50721062).

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