ACS APPLIED MATERIALS & INTERFACES

Letter

www.acsami.org

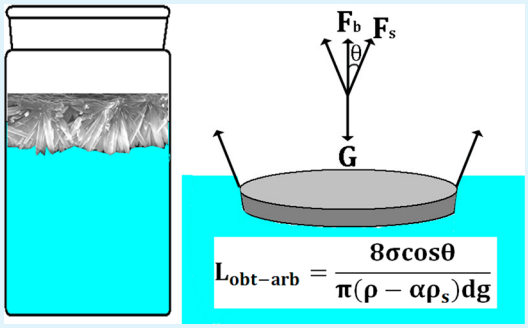
Self-Assembly of Large-Scale Floating TiO_2 Nanorod Arrays at the Gas–Liquid Interface

Hua-Rong Xia,[†,‡] Jia Li,[†,§] Chen Peng,[†,⊥] Long-Wei Li,[†,‡] Wen-Tao Sun,*[,†,‡] and Lian-Mao Peng*[,†,‡,§]

[†]Key Laboratory for the Physics and Chemistry of Nanodevices, [‡]Department of Electronics, [⊥]School of Software and Microelectronics, [§]Academy for Advanced Interdisciplinary Studies, Peking University, Beijing 100871, China

Supporting Information

ABSTRACT: This paper describes a facile one-step synthesis of large-scale floating TiO_2 nanorod arrays via a hydrothermal reaction without using any surfactants, which opens a new way to prepare floating photocatalysts for photodecomposition of floating organics and free-standing nanorod arrays for flexible dye-sensitized solar cells. A general model is developed to analyze the driving force for the floating TiO_2 film, which may be also useful for other two-dimensional materials to determine the obtainable size of an arbitrary shaped film floated by surface tension and buoyancy.



KEYWORDS: *floating, free-standing, nanorod arrays, flowerlike, surface tension, buoyancy*

As one of the most important wide-band-gap semiconductors, titanium dioxide (TiO_2) has many promising applications typically such as dye-sensitized solar cells (DSSCs), photocatalysts, and so on.[1,2] Because the density of TiO_2 is much larger than water,[3] it will sink when placed in water. However, for photodecomposition of floating organics such as crude oil floating on sea water, floating TiO_2 is essential.[4] To make TiO_2 float, one effective way is to attach it to floating substrates such as microbeads, pine wood chips, high-surface-area vermiculite, and so on.[5−7] Recently, Syoufian and Nakashima have succeeded in preparing floating submicrometer-sized hollow spheres in a different manner.[8] However, all of the above methods are multistep, and the TiO_2 film floats by buoyancy.

In another typical application, the use of one-dimensional crystalline nanorod arrays as photoanodes has been found to improve the charge collection efficiency by promoting faster charge transport and faster ion diffusion at the semiconductor–electrolyte interface in DSSCs.[9−11] What's more, free-standing nanorod arrays can be easily transferred onto flexible substrates for flexible electronics and DSSCs.[12] So far, many methods of synthesizing free-standing TiO_2 have been developed, but most of them are substrate-needed.[13,14] Most recently, Liu et al. have reported a seedless floating growth process in solution for the synthesis of crystalline ZnO micro/nanowire arrays on graphene, which may be used to prepare free-standing nanorod arrays.[15] However, to the best of our knowledge, large-scale floating TiO_2 nanorod arrays have never been reported before.

In this paper, we report a one-step synthesis of large-scale floating TiO_2 nanorod arrays via a high-temperature hydrothermal reaction without using any surfactants, which opens a new way to floating photocatalysts and free-standing nanorod arrays. The driving force for floating the TiO_2 film other than the above-reported buoyancy is found to be the surface tension. A general model is developed to determine the obtainable size of an arbitrary shaped film floated by surface tension and buoyancy, which may be useful for other two-dimensional (2D) materials.

In a typical synthesis, 20 mL of deionized water was mixed with 20 mL of concentrated hydrochloric acid (36.5–38% by weight) in a weighing bottle (3.5 cm diameter and 7 cm height) to offer the proper acidic reaction environment. The mixture was kept in a refrigerator for 1 h before the addition of 180 μL of $TiCl_4$, whose hydrolyzates are TiO_2 nanocrystals that can act as seeds for the growth of nanorods. After the solution reacted at 70 °C for 30 min and cooled down, 0.8 mL of tetrabutyl titanate was added dropwise to offer an adequate titanium source. Then the weighing bottle was placed in a Teflon-lined stainless steel autoclave (100 mL volume, Beijing STWY Equipment Co., Ltd.). The hydrothermal reaction was conducted at 160 °C for 12 h in an electric oven. After the reaction, the autoclave was naturally cooled to room temperature. The obtained film on the surface of the solution was taken out with a piece of glass slide, rinsed with deionized water, and dried in ambient air. The film is stable enough to be held by tweezers (Figure S1 in the Supporting Information, SI).

The morphology of the film was characterized by scanning electron microscopy (SEM). The SEM image of the film toward the solution, shown in Figure 1a, indicates that the bottom side is composed of large numbers of self-assembled

Received: July 6, 2013
Accepted: August 30, 2013
Published: August 30, 2013

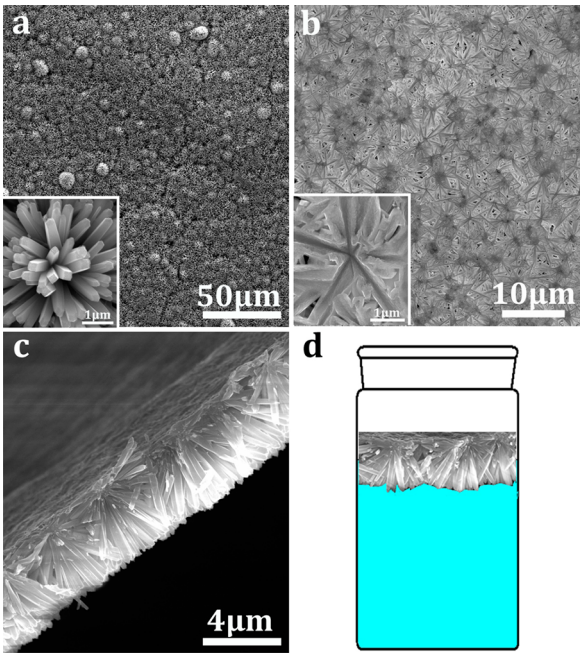
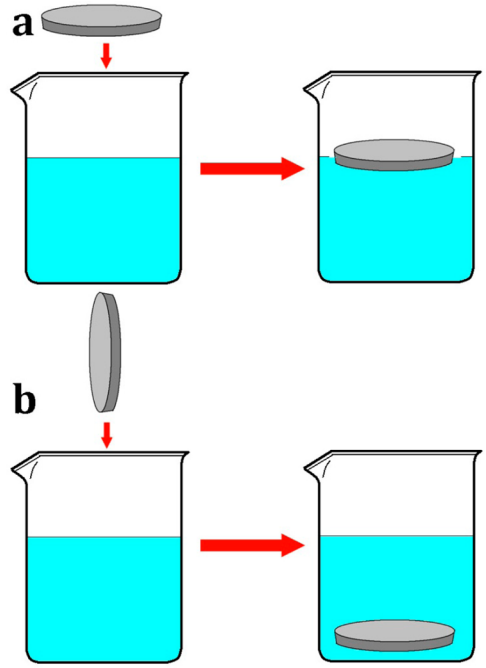


Figure 1. SEM images of the floating film: (a) bottom view (side toward the solution); (b) top view (side toward air); (c) sectional view; (d) enlarged sectional view in a weighing bottle.

flowerlike microstructures. The inset in Figure 1a shows an enlarged image of the microflower composed of nanorods, while the SEM image of the film toward the gas is shown in Figure 1b, from which we can see that the top is made up of many nanorods lying in a certain arrangement. Also, the inset in Figure 1b shows the enlarged image of the nanorods, which also corresponds to the other side of the microflower shown in Figure 1a. The sectional view in Figure 1c shows that one side of the film is a plane with many nanorods lying down, while the other side is rugged with many nanorods standing up. The X-ray diffraction (XRD) pattern of the floating film shows that it is rutile (Figure S2 in the SI). Figure 1d shows a film floating in a weighing bottle, while further work needs to be done to clarify the mechanism for the floating growth of the nanorod film, in which the interface may play a critical role.

Because the density of rutile TiO_2 is 4.3,[3] which is much larger than that of water, the buoyancy cannot float the film. To exclude the effect of any organics, which may offer a floating force like the above floating substrates, the film was annealed at 500 °C for 1 h first to remove possible organics. After that, the film was placed onto the surface of water, and it still floated steadily (video 1 in the SI). That is to say, the film does not float by the reported buoyancy from possible attached organics. Furthermore, because the nanorod is not hollow, it cannot float by buoyancy itself. Compared to the reported floating TiO_2, the film formed spontaneously at the liquid−gas interface and the high hydrophobicity of the rutile TiO_2 nanorods has also been reported.[16] In this way, another force, surface tension, caused by the cohesive forces among liquid molecules becomes important. To investigate whether the surface tension played an important role in the floating film, a straightforward test was to place them on the water surface in different ways, typically horizontally and vertically, as shown in Scheme 1. When the annealed film was placed onto water horizontally, with the surface of the film parallel to the water surface as shown in Scheme 1a, it would float onto the surface (Figure S3a in the SI). However, when it was placed onto water vertically, with the surface of the film perpendicular to the water surface as shown in Scheme 1b, it would sink to the bottom (Figure S3b in the SI). The main change in the forces applied to the film was that the surface tension placed horizontally was much larger than that placed vertically. Therefore, the surface tension may be the main driving force for floating the film.

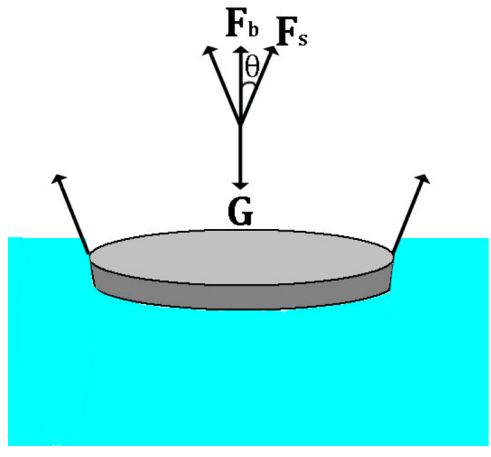
Scheme 1. Scheme of Films Placed onto the Liquid Surface: (a) Floating on the Surface When the Film Was Placed onto the Surface Horizontally; (b) Sinking to the Bottom When the Film Was Placed onto the Surface Vertically



To investigate whether the surface tension is large enough to float the film, the nanorod film is simplified as a 2D circular plate with a thickness of 3 μm. The forces applied to the film are shown in Scheme 2. In order to float the film, the sum of the buoyancy (F_b) and the component ($F_s \cos \theta$) of surface tension should not be less than the gravity (G).

$$F_b + F_s \cos \theta \geq G \quad (1)$$

Scheme 2. Schematic Forces of the Floating Film



dx.doi.org/10.1021/am4026938 | ACS Appl. Mater. Interfaces 2013, 5, 8850−8852

On the basis of the above simplification, the maximum size of a floating circular film is

$$L_{\max,\mathrm{cir}} = \frac{4\sigma \cos\theta}{(\rho - \alpha\rho_s)dg} \quad (2)$$

where $L_{\max,\mathrm{cir}}$ is the maximum length (the diameter here) between two arbitrary points on the surface of a circular film, σ is the surface tension coefficient of the solution, ρ and ρ_s are the densities of the film and solution, respectively, d is the thickness of the film, g is the gravity constant, and α is the volume fraction of the film immersed into the solution. If the surface tension is upright ($\theta = 0$) and the action of the buoyancy is left out ($\alpha = 0$), the maximum diameter of the floating circular TiO_2 film can reach 226 cm (Table S1 in the SI), which is much larger than that of the film (3.5 cm) here. Thus, the surface tension is large enough to float the film.

On the basis of the model, a general formula to calculate the obtainable size of a floating arbitrary shaped film is derived (details are given in the SI):

$$L_{\mathrm{obt,arb}} = \frac{8\sigma \cos\theta}{\pi(\rho - \alpha\rho_s)dg} \quad (3)$$

where $L_{\mathrm{obt,arb}}$ is the maximum length between two arbitrary points on the surface of an arbitrary shaped film. This formula can be used to account for why a 2D film can float and how large the floating film can reach, such as a titanium or aluminum foil (Figure S7 and videos 2 and 3 in the SI). Furthermore, the formula may be used to determine whether a 2D film of arbitrary shape with certain size can float or not, typically such as graphene, transition-metal dichalcogenides, transition-metal oxides, and graphene analogues.[17]

In summary, we have reported a one-step synthesis of floating nanorod arrays that are free-standing and can easily be transferred onto flexible substrates. These nanorod arrays may be used as floating catalysts for photodecomposition of some floating organics such as crude oil and as photoanodes for DSSCs, especially flexible DSSCs. We believe that this method will open a new way to fabricate floating photocatalysts and free-standing nanorod arrays. Besides, a general formula to determine the obtainable size of an arbitrary shaped floating 2D film, floated by surface tension and buoyancy, is put forward.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Photographs of the films, XRD pattern of the film, EDX spectra of the rods, transmittance spectra of the film, derivation details of the formula, and videos for the floating titanium dioxide film and titanium and aluminum foils. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: wtaosun@pku.edu.cn.
*E-mail: lmpeng@pku.edu.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Ministry of Science and Technology (Grants 2011CB933002 and 2012CB932702) and National Science Foundation of China (Grants 61306079 and 60871002).

■ REFERENCES

(1) Fujishima, A.; Honda, K. *Nature* **1972**, *238*, 37.
(2) Oregan, B.; Gratzel, M. *Nature* **1991**, *353*, 737.
(3) Rosenberg, I.; Brock, J. R.; Heller, A. *J. Phys. Chem.* **1992**, *96*, 3423.
(4) Berry, R. J.; Mueller, M. R. *Microchem. J.* **1994**, *50*, 28.
(5) Jackson, N. B.; Wang, C. M.; Luo, Z.; Schwitzgebel, J.; Ekerdt, J. G.; Brock, J. R.; Heller, A. *J. Electrochem. Soc.* **1991**, *138*, 3660.
(6) Magalhaes, F.; Lago, R. M. *Sol. Energy* **2009**, *83*, 1521.
(7) Holdich, R. G.; Ipek, I. Y.; Lazrigh, M.; Shama, G. *Ind. Eng. Chem. Res.* **2012**, *51*, 12509.
(8) Syoufian, A.; Nakashima, K. *J. Colloid Interface Sci.* **2007**, *313*, 213.
(9) Law, M.; Greene, L. E.; Johnson, J. C.; Saykally, R.; Yang, P. D. *Nat. Mater.* **2005**, *4*, 455.
(10) Liu, B.; Aydil, E. S. *J. Am. Chem. Soc.* **2009**, *131*, 3985.
(11) Feng, X. J.; Shankar, K.; Varghese, O. K.; Paulose, M.; Latempa, T. J.; Grimes, C. A. *Nano Lett.* **2008**, *8*, 3781.
(12) Wang, L.; Xue, Z.; Liu, X.; Liu, B. *RSC Adv.* **2012**, *2*, 7656.
(13) Zeng, T.; Tao, H.; Sui, X.; Zhou, X.; Zhao, X. *Chem. Phys. Lett.* **2011**, *508*, 130.
(14) Liu, Y.; Wang, H.; Li, H.; Zhao, W.; Liang, C.; Huang, H.; Deng, Y.; Shen, H. *J. Colloid Interface Sci.* **2011**, *363*, 504.
(15) Liu, J.; Lu, R.; Xu, G.; Wu, J.; Thapa, P.; Moore, D. *Adv. Funct. Mater.* **2013**, DOI: 10.1002/adfm.201300468.
(16) Peng, X.; Chen, A. *Appl. Phys. A: Mater. Sci. Process.* **2005**, *80*, 473.
(17) Wang, Q. H.; Kalantar-Zadeh, K.; Kis, A.; Coleman, J. N.; Strano, M. S. *Nat. Nanotechnol.* **2012**, *7*, 699.