Research Article

Highly Ordered TiO₂ Macropore Arrays as Transparent Photocatalysts

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Highly ordered transparent TiO₂ macropore arrays were synthesized via a simple glass-clamping method at room temperature. The as-synthesized TiO₂ macropore arrays show high transmittance in the visible light region and can be used as transparent photocatalysts for degradation of organic dyes.

1. Introduction

Transparent devices have received considerable attentions in recent years due to their potential applications in fields where traditional silicon-based technique could not approach, such as transparent displays, transparent transistors, solar cells, transparent supercapacitors, and ultraviolet (UV) detectors [1–5]. TiO₂, as one of the most important wide bandgap semiconductors, has been studied to be used as transparent device because of its outstanding physical and chemical properties. For example, TiO₂ transparent thin films would make great impact in fields like photoelectrodes [5], antireflection films [6], self-clean glass [7], and nonlinear optical devices [8].

Two-dimensional (2D) ordered arrays are of great significance in many research areas of modern science and technology, with the applications including optical and optoelectronic devices [9], dye-sensitized solar cells [10], surface-enhanced Raman spectroscopy [11], catalysis [12], and sensors [13, 14]. Recently, 2D TiO₂ ordered arrays, combining the outstanding properties of TiO₂ with their 2D ordered assembling, have gained great research interests, and many kinds of methods have been developed to synthesize 2D TiO₂ ordered arrays. For example, Wang et al. described an atomic layer deposition (ALD) method to fabricate TiO₂ ordered nanobowl arrays, which can be used to separate monosized submicron spheres [15]. Yang et al. reported

an rf-sputtering method to synthesize ordered hollow TiO₂ hemisphere films [10], and described their applications in dye-sensitized solar cells (DSSCs) as high-efficiency photoelectrodes. Kannaiyan et al. developed a method to fabricate 2D hybrid CdS/TiO₂ composite nanodot arrays [16] and studied the photocatalytic properties of the hybrid thin film. However, complicated procedures or expensive equipments are usually required, and it is still quite desired to develop simple method to synthesize 2D TiO₂ ordered arrays. On the other hand, it would be more desired to make the 2D TiO₂ ordered arrays transparent to fit special applications in transparent electronics.

In this paper, we developed a simple and low-cost glass-clamping method to synthesize highly ordered TiO₂ macropore arrays by using hexagonally arranged PS sphere monolayer as the sacrificial mask. As-synthesized highly ordered TiO₂ macropore arrays showed high transmittance as approximately 92% in the visible light region and can be used as interesting transparent photocatalysts for the degradation of polluted organic dyes.

2. Experimental

Monodispersed polystyrene (PS) spheres were first synthesized via the emulsifier-free method developed by Holland et al. [17]. The corresponding SEM images of the as-obtained PS can be seen in Figure S1 (see Supplementary Material

FIGURE 1: (a) SEM of PS sphere monolayer on glass substrate, the inset image is FFT of the SEM image of PS monolayer. (b, c, and d) SEM images of 2D TiO₂ ordered arrays with magnification of 2500x, 40000x, and 140000x, respectively. The inset image of Figure 1(b) is FFT of the SEM image of the TiO₂ arrays. (e, and f) Photographs of large-scale 2D TiO₂ ordered arrays under different incident angles of light.

available online at doi:10.1155/2012/762510). The second step is to assemble a PS monolayer on a cleaned glass substrate. During this step, a piece of glass substrate was used, which was precleaned by boiling in piranha solution ($\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2 = 7:3$ v/v). After being cleaned, the glass substrate was put in the bottom of a Petri dish ($\Phi = 5$ cm), which was filled with deionised water until the level of the water equals to the upper surface of the glass substrate. Then, 15 μL monodispersed PS spheres suspensions (wt 5%; water:ethanol = 1:1) were dropped onto the glass, which were found to rapidly spread and form a PS spheres monolayer on the glass substrate (Scheme 1(a)).

After putting another piece of the precleaned glass substrate on the surface of the PS spheres monolayer, a syringe was utilized to drain the Petri dish, resulting in the formation of dried PS spheres monolayer between the two pieces of glass substrates (Scheme 1(b)). To get highly ordered TiO₂ macropore arrays, a drop of tetra-n-butyl-titanate (TBT) solution was then dripped from the edge of the PS spheres monolayer as shown. Stored in air for several days, the TBT solution slowly spread and filled the cavities of the PS spheres monolayer, where it homogeneously hydrolyzed and formed into amorphous $\text{Ti}(\text{OH})_4$ (Scheme 1(c)). After completely hydrolyzed, the upper glass substrate was peeled off, and

SCHEME 1: Schematic representation of the procedures employed for the fabrication of 2D TiO_2 ordered arrays.

FIGURE 2: Transmittance spectra of 2D TiO_2 ordered arrays on glass substrate. The inset image is photograph of 2D TiO_2 ordered arrays on glass (top) and bare glass (bottom).

the bottom glass substrate with $\text{Ti}(\text{OH})_4/\text{PS}$ spheres was annealed at 450°C for 5 hours, resulted in the formation of the final highly ordered TiO_2 macropore arrays.

3. Results and Discussion

After annealing, the product was first characterized by using X-ray diffraction (XRD) to get information about its composition. Figure S2 is the corresponding XRD pattern of the product, which can be easily indexed to crystalline TiO_2 with the anatase phase (JCPDS Card, number 89-4203). No peaks from other impurities were detected, indicating the formation of pure TiO_2 product.

The PS spheres used in the work have diameters of about 500 nm (Figure S1). Figure 1(a) is a typical SEM image of the as-synthesized PS spheres monolayer, which

is found to be hexagonal arranged on the glass substrate on a large scale. The inset fast Fourier transform (FFT) pattern of the PS monolayer shows regularly arranged spots, confirming its uniform hexagonal arrangement. By using the PS spheres monolayer as the templates, highly ordered TiO_2 macropore arrays were obtained on a large scale, as can be seen from Figure 1(b). The SEM image in Figure 1(c) also reveals that the TiO_2 product consists of highly ordered TiO_2 hemispheres with diameters of around 500 nm, similar to the PS spheres. The thickness of the TiO_2 hemisphere is around 30 nm (Figure 1(d)). Confined by the PS spheres monolayer templates, all the TiO_2 hemispheres arranged hexagonally on the substrate, forming into the final TiO_2 macropore arrays. The FFT pattern inset in Figure 1(b) confirms its regular hexagonal arrangement.

Due to the regular macropore structures of the TiO_2 product, it is interesting to find that the TiO_2 film on glass substrate exhibited different colours upon different tilts to the illuminated solar light. Figures 1(e) and 1(f) are the photographs of the TiO_2 film to solar light with the tilt angles of around 20° and 30° , respectively. Under such angles, the film exhibited sky-blue and light green colors, respectively. This phenomenon can be well explained by the grating model suggested by Billon et al. [18], which indicates that highly ordered hexagonal pattern would behave as gratings. Thus, the structures would obey the Grating equation:

$$m\lambda = d(\sin \alpha + \sin \beta), \quad (1)$$

where m is the diffraction order, λ is the wavelength, d is the distance between centres of two adjacent hemispheres, α is the incident angle, and β can be considered as the observation angle. In this case, if we keep m , d , and α as constants, then when the observation angle β is changed, we can observe that the colour perception of the surface will be changed. Such highly angular dependence character demonstrates that the synthesized TiO_2 arrays film from the simple glass-clamping method has very good uniformity and regularity.

Due to the superior uniformity, regularity, and homogeneous thickness of the TiO_2 ordered arrays, the TiO_2 films synthesized by the glass-clamping method show very good transparency in the visible light region. Figure 2 is the transmittance spectrum of the 2D TiO_2 ordered arrays on glass substrate, while a cleaned glass was also used to check as baseline during the testing. For comparison, the transmittance spectrum of a clean glass substrate was also depicted in Figure 2. From the spectrum, we can easily find out that the 2D TiO_2 ordered arrays have great transparency, with a transmittance value of approximately 92% (transmittance value was measured on a Shimadzu UV-2550 spectrophotometer, Japan). Insets in Figure 2 are the digital photographs of the $\text{TiO}_2/\text{glass}$ substrate as well as the bare glass, where the under image (the image corresponds to the symbol of our lab) can be easily seen through the substrates. No obvious difference was found between the two substrates, indicating the excellent transparency of the TiO_2 product.

In comparison to other semiconductor photocatalysts, TiO_2 is a suitable material described as high-performance

FIGURE 3: (a, b, and c) peak values of absorption spectra of MB (664 nm), MO (554 nm), RhB (460 nm), respectively. (d) changes of the organic dye concentrations with reaction time during photocatalytic process.

photocatalysts because of its biological and chemical inertness, cost-effectiveness, environmental friendliness, availability, and long-term stability against photo- and chemical-corrosion [19–21]. With regular shapes and excellent optical transparency, the as-obtained highly ordered TiO_2 macropore arrays may be used as interesting transparent photocatalyst to fit some special applications. Photocatalytic properties of the highly ordered TiO_2 macropore arrays were studied by photodegradation of organic dyes, such as methylene blue (MB), methyl orange (MO), and rhodamine B (RhB). All the organic dyes were dissolved in water with ratio of $15\ \mu\text{L} : 15\ \text{mL}$. The TiO_2 product was first immersed in the organic dye solution for 60 minutes to reach an adsorption

equilibrium, before being irradiated by 365 nm UV light ($50\ \text{mW}/\text{cm}^2$). After every 30 minutes of UV light exposure, $400\ \mu\text{L}$ of the testing organic dyes solution was subjected to UV-spectrophotometer. The concentration of organic dye solution was determined by the peak values from the UV-Vis absorption spectrum.

Figures 3(a), 3(b), and 3(c) show the spectra changes of main peaks originated from MB (664 nm), MO (554 nm), and RhB (460 nm) with the irradiation time, respectively. Under UV light illumination, the peaks of three organic dyes obviously decrease revealing good photocatalytic properties of the fabricated $\text{TiO}_2/\text{glass}$. Furthermore, to quantify photocatalytic abilities of the as-synthesized $\text{TiO}_2/\text{glass}$,

the changes of the organic dye concentrations with reaction time were recorded and shown in Figure 3(d). Clearly, TiO₂/glass showed not only higher adsorption ability but also higher photodecomposition ability to MB solution than to other dyes solutions at room temperature. During the dark reaction, about 20% of MB dyes were adsorbed. And about 93.6% of MB dyes were decomposed after 3 h irradiated by UV light. While for MO and RhB dyes, the adsorption effects in the presence of TiO₂/glass were poor, and the concentrations of MO and RhB solutions decreased to 87.2% and 82.3% under exposure to UV light for 3 h, respectively, which were lower than that of MB solution.

As described above, the current glass-clamping method shows great superiority in fabricating transparent 2D ordered arrays on glass substrate. We found that such a simple method may also be extended to other substrates. As an example, we successfully synthesized 2D TiO₂ ordered arrays on aluminium substrate, as can be seen in Figure S3.

4. Conclusion

In conclusion, we have developed a simple glass-clamping method to fabricate 2D TiO₂ ordered arrays on a large scale by using hexagonally arranged PS monolayer as the sacrificial mask. The as-obtained 2D TiO₂ ordered arrays show great uniformity and regularity with an excellent transparency of about 92%. The as-obtained 2D TiO₂ ordered arrays were used as high performance transparent photocatalysts for the photodegradation of organic dyes, such as MB, MO, and RhB. Considering the high transmittance, the 2D TiO₂ arrays might be utilized as self-cleaning glass, transparent optoelectronic devices, and other applications. Moreover, we have applied this simple method on the fabrication of 2D TiO₂ ordered arrays on other substrates, which widely expands its potential applications.

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