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Synthesis and Self-Assembly of Photonic Materials from Nanocrystalline Titania Sheets

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Supporting Information

ABSTRACT: We describe the use of benzyl alcohols in a solvothermal/alcoholysis reaction to form nanocrystalline sheets of anatase titania. By tuning the reaction conditions, we adjust the size of the nanosheets. The type and density of benzyl groups that decorate the basal plane of the titania sheets control the self-assembly into layered structures. These layered materials can be grown from solid substrates to create iridescent thin films that reflect specific wavelengths of visible light.

This manuscript describes a biomimetic self-assembly approach to prepare photonic materials comprised of nanocrystals of anatase titania. Titania is an important semiconductor for many applications involving photoprocesses such as photovoltaics, photodegradation of pollutants, and photocatalytic H_2 production via water splitting.[1−4] Nanostructuring of titania is a proven method to optimize and tune these photochemical processes.[5−7] Furthermore, coupling nanostructuring with photonics further improves properties in applications involving photochemistry by concentrating the light wavelength.[8−13] In this study, we describe a method to utilize benzyl alcohols in a solvothermal/alcoholysis reaction with titanium tetrafluoride to form nanocrystalline sheets of anatase titania. By tuning the reaction time and stoichiometry, we tune the size of the sheets on the nanometer length scale. The type and density of benzyl groups that decorate the basal plane of the titania sheets control the self-assembly into layered structures. If titanium foil is included in the reaction mixture, the layered structure grows from the substrate to yield iridescent thin films that reflect specific wavelengths of visible light.

We base the synthetic strategy on previous studies that employ a variety of alcohols in combination with titania precursors to generate a wealth of new nanostructured titanium oxides.[14] In one of these previous studies, we found that the hydroxyl groups of glycerol are important in creating a hydrogen bond network that forms layered structures called "nanotechtons". Unfortunately, the materials that result from the glycerol synthesis lack crystallinity. In the study described here, we use the combination of benzyl alcohols and titanium tetrafluoride in a dual alcoholysis/solvothermal reaction sequence.[15] In a typical synthesis, TiF_4 (0.10 g, 0.81 mmol) is added to 40 mL of benzyl alcohol (molar ratio of TiF_4/benzyl alcohol, 1:500), followed by stirring until a homogeneous solution is obtained (~2 h). The solution is then transferred to a 50 mL Teflon-lined stainless steel autoclave for heating and kept at 160 °C for 24 h. After cooling, the white crystalline titania powder is collected by centrifugation and then washed thoroughly with ethanol. The band gap of the TiO_2 prepared in this way is ~3.3 eV.

Figure 1 shows scanning electron microscopy (SEM) and transmission electron microscopy (TEM) of the material from the above reaction. The TiO_2 nanosheets have a highly ordered layering with all the nanosheets oriented parallel to each other. The thickness of the nanoplates can be estimated from the micrograph of the edge of the stacks (Figure 1b) to be 15 ± 3 nm. The interlayer spacing between the nanoplates is less than 10 nm. A top view of the nanosheets in the TEM (Figure 1c) reveals that they are squares with an ~250 nm edge length. The selected area electron diffraction (SAED) pattern reveals that the nanoplates are crystalline with a diffraction pattern of single-crystal anatase along the [001] zone axis. The high

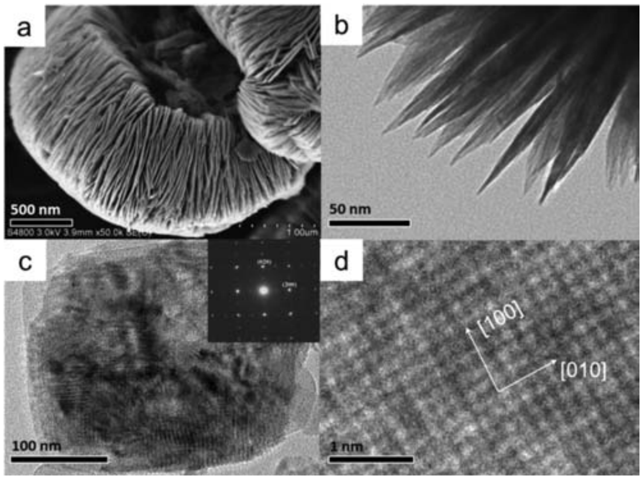

Figure 1. (a) SEM of layered structure obtained from the reaction of TiF_4 and benzyl alcohol. (b) TEM of the edge region of layered structure. (c) TEM of a thin section of the layered material. The inset is the small angle electron diffraction (SAED) of the nanoscale sheet of TiO_2. (d) HR-TEM image of a nanoscale sheet revealing the lattice planes of anatase TiO_2.

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resolution TEM image in Figure 1d reveals that the *d*-spacing is around 0.19 nm with an interfacial angle of 90° confirming that the plates expose the facets of the anatase crystal. Figure S1 displays the powder X-ray diffractogram of this material further confirming the anatase phase. The narrow (101) peak and broad (001) peak strongly suggest that the crystal growth is limited primarily to the [001] axis, leading to the dominant (001) facets. TEM analysis is consistent with this result, revealing that ~90% of the exposed facets in the plates to be the (001) facet.

The temperature was found to be important for the success of the reaction. At higher temperatures (>200 °C), larger crystalline structures result and the layered structure is absent. At lower temperatures (<130 °C), no product was obtained. In the optimal temperature range (~160 °C), the result is reproducible and the yield is 82 ± 5%.

The TEM images in Figure 2 reveal the effect of reaction time on the formation of these stacked nanostructures in the case of fixed reaction temperature and stoichiometry (see experimental details in the Supporting Information). First, we obtain irregularly shaped Ti-organic clusters lacking any stacked structures after reaction for 3 h (Figure 2a). The SAED pattern (inset of Figure 2a) reveals that these Ti-organic clusters are amorphous. After reaction for 5 h, these amorphous clusters transform into TiO_2 clusters with a measurable crystallinity (Figure 2b), which displays a stacked, lamellar structure in the HR-TEM (Figure 2f). The spacing between adjacent layers is ~1.3 nm. Increasing the reaction time to 8 h allows the TiO_2 clusters to grow along the stacking axis to form layered TiO_2 nanocrystals (Figure 2c). When the reaction time is further increased from 8 to 12 h (Figure 2d), the particle size increases from ca. 100 nm (length) and 30 nm (thickness) to 300 nm (length) and 100 nm (thickness), respectively. After reaction for 18 h, we find that the width of the nanosheets (~300 nm) was similar to that obtained after 12 h, but the height of the stacked structure increases to more than 1 μm (Figure 2e).

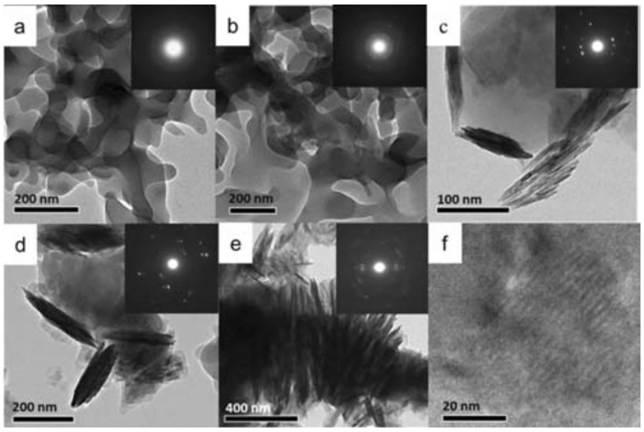

Figure 2. TEM and SAED (insets) of self-assembling TiO_2 sheets after solvothermal for (a) 3.0, (b) 5.0, (c) 8.0, (d) 12, and (e) 18 h. (f) HR-TEM image after reaction for 5 h. The self-assembly process forms a layered structure.

Figure S2 reveals the effect of stoichiometry and concentration on the stacked nanosheets formation. Relatively low amounts of TiF_4 (molar ratio of TiF_4/benzyl alcohol, 1:4800) yield only small TiO_2 nanoplates (50 nm) that aggregate irregularly. We hypothesize that there is not a high enough concentration of nanosheets and that they are not large enough to form the stacks. Moreover, the large excess of unreacted benzyl alcohol may block the assembly. When we increase the ratio of TiF_4 to benzyl alcohol from 1:1200 to 1:600, the edge length of nanosheets gradually increases from 150 to 300 nm. As the amount of the TiF_4 increases, the parallel arrangement of these nanosheets becomes more and more regular. However, at very high ratios of TiF_4 (molar ratio of TiF_4/benzyl alcohol, 1:240), neither the layered structure nor the crystalline TiO_2 nanosheets form. We reason that the relatively high TiF_4 ratios provide an excess of HF formed in situ that etches the (001) crystal face of TiO_2. The ratio of TiF_4 to benzyl alcohol needs to be in the range of 1:2400 to 1:300 to obtain the stacked crystalline nanosheets.

Figure 3 contains a model of how the nanosheets self-assemble. We hypothesize that the nanosheets form with benzyl groups on their surface and that the nanosheets then stack (and are held together) through π-stacking between benzyl groups in neighboring sheets. On the (001) crystal face, the distance between the adjacent unsaturated Ti atoms is about 0.4 nm. This distance is consistent with that of π−π stacking between benzene rings. The distance between two layers from the model is 0.92 nm, which is smaller than the distance (1.3 nm) measured from the HRTEM image (Figure 2f). The difference may be due to the strong chemical bond holding the adjacent layers closer. Those benzyl groups, bonded on the surface of the (001) facet, connect the TiO_2 nanosheets with each other to form the layered structure. Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA) provide support for this structure. TGA (Figure S3) reveals a high content of organic species (ca. 78% by weight) is present in the initially obtained TiO_2 precursors. After a prolonged reaction, the organic Ti species gradually decreases, together with the formation of crystalline TiO_2. FTIR (Figure S4) confirms the existence of aromatic rings from the vibration at 1489 cm^{-1}. The broad vibrations at 3010 and 2893 cm^{-1} are attributed to the strong interaction of the aromatic rings on TiO_2 surface.[16] Physisorbed benzyl alcohol on the surface of commercial P-25 TiO_2 lacks the vibration at 3010 and 2893 cm^{-1}.

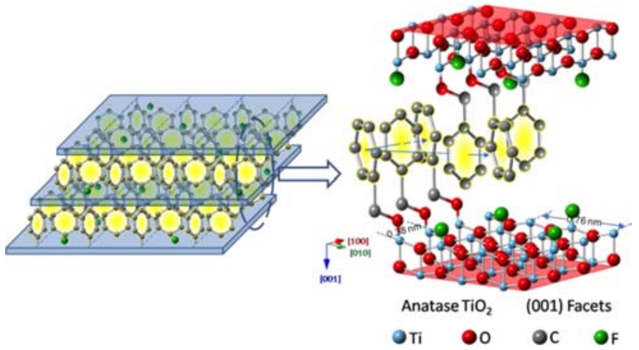

Figure 3. Schematic representation of the layered structure with TiO_2 nanosheets held together through π-stacking between the layers.

We performed several experiments to further test the π-stacking hypothesis. Pentafluorobenzyl alcohol does not effectively π-stack, and when used in these reactions, we found no nanosheet or stacked structure. When we used a 1:1 ratio of pentafluorobenzyl alcohol to benzyl alcohol in the reaction, we found that the well organized stacked structure returns (Figure S5). The π-stacking interaction between the mixture of benzyl alcohol and pentafluorobenzyl alcohol is stronger than that of benzyl alcohol on its own. The distance between each nanoplate is smaller (5 ± 2 nm) by about half compared to the case of the samples from benzyl alcohol. To further test for π-stacking, we test benzyl alcohols with halogens in the para-position. Only *p*-fluorobenzyl alcohol forms a layered structure (Figure S6). Both *p*-chlorobenzyl alcohol and *p*-bromobenzyl alcohol fail to yield the layered structure due to their larger size compared to a fluorine or hydrogen atom. It is important to note that the *p*-chlorobenzyl and *p*-bromobenzyl alcohols still form nanosheets but they do not stack. Aliphatic alcohols such as cyclohexanemethanol and *tert*-butanol do not form the stacked nanosheet structure. Using butanol as an alcohol source, only nanoparticles could be obtained. Finally, the surface bonded benzyl alcohol will limit the growth of the Ti species along the [001] zone and will contribute to the nanosheet structure formation.

The nanoscale stacked sheets in Figure 1 are reminiscent of structures formed in natural systems such as nacre and butterfly wings that consist of nanosheets that are regularly organized to form a photonic structure.[9,17,18] To test whether these structures would mimic this behavior, we insert titanium foil in the reaction mixture. The X-ray diffractogram from a film on titanium foil (Figure S7) reveals that the films are also anatase phase. The stacked structures form oriented thin films on the surface of the titanium substrate (Figure 4a). The films are colored to the naked eye. The color depends on the conditions of the reaction. Figure 4c contains an optical micrograph of a green film that is 190 ± 10 nm thick (Figure 4b). Figure 4d shows the diffuse reflectance UV–vis spectrum of the film on titanium. The spectrum contains strong bands at ~400 and ~640 nm due to this stacked crystalline structure. As a point of comparison, TiO_2 films (thickness, 190 ± 10 nm) on Ti foil from the Sol–gel method have a dark color and low visible light absorption (Figure S8).

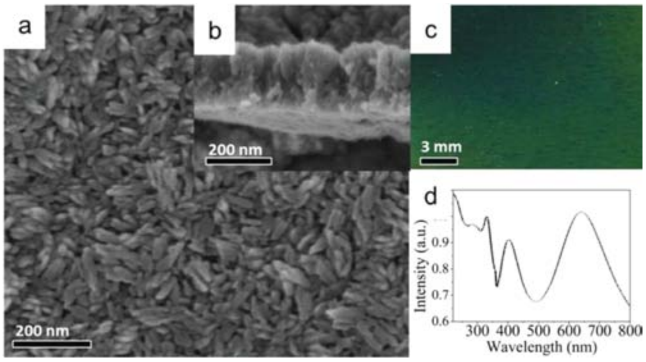

Figure 4. (a) Top view SEM and (b) cross-sectional SEM of stacked TiO_2 sheets on Ti foil. (c) Optical micrograph. (d) UV–vis diffuse reflectance spectra of green TiO_2 film grown on Ti foil.

This study reveals an intricate hierarchy of reactivity and self-assembly to make a new type of photonic materials formed from a hybrid organic/nanocrystalline titania. At the shortest length scale in the hierarchy, the combination of benzyl alcohol and titanium fluoride creates an organic-rich titanium precursor. As this precursor reacts, sheets of anatase TiO_2 form on the nanoscale. On the surface of these nanosheets are groups that encourage self-assembly at yet a larger length scale. Directing the self-assembly of these materials from surfaces creates photonic materials that mimic systems found in nature. These new materials should have immediate application in photochemical processes such as photovoltaics and photocatalysis that involve titania. Moreover, by tuning the wavelength of the photonic band gap, it may be possible to create environmentally friendly, reflective coatings.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Methods for sample preparation, characterization, and Figures S1–S7. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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