

Direct Growth of TiO₂ Nanosheet Arrays on Carbon Fibers for Highly Efficient Photocatalytic Degradation of Methyl Orange

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Owing to its low cost, high chemical inertness, and environmental applications (high catalytic activity for the removal of pollutants in water and air), titanium dioxide (TiO₂) has been intensively investigated in photocatalysis.^[1] The photocatalytic efficiency of TiO₂ is affected not only by surface atomic structure, but also by the size, shape, crystallinity, and degree of exposure of reactive crystal facets.^[2,3] Recently, surface scientists have demonstrated that the order of the average surface energies of anatase TiO₂ is 0.90 J m⁻² for {001}, >0.53 J m⁻² for {100}, >0.44 J m⁻² for {101}.^[2,4] Because highly reactive facets are expected to effectively enhance surface properties, enormous effort has been devoted to the synthesis of {001} facet-dominated single-crystal anatase TiO₂ and the application of it to photocatalysis.^[3,5,6] However, the work in most of the mentioned publications is based on powdered TiO₂ nanosheets (NSs) or granular supported TiO₂ NSs, which are difficult to recycle from aqueous solution after photocatalytic reactions and will cause secondary pollution.^[6,7] To solve this problem, an ideal way is to grow these NSs on certain substrates in the form of an ordered film without agglomeration.

Here we introduce carbon fibers (CFs) as a substrate for growing TiO₂ NSs. Compared to the traditional stiff substrate, CFs are flexible, conductive, and stable in corrosive conditions, and they can supply a large surface area, which is critical for nanostructure-based photovoltaic technology. They also have good heat and fatigue resistance. Moreover, the synergistic effect of TiO₂ and C will greatly retard the recombination of photoinduced electrons and holes, which could significantly enhance photocatalytic performance.^[8,9] Although this material shows potential for applications in photocatalysis, a method of effective growth of single-crystalline TiO₂ NSs on CFs is still an issue.^[6,7,10] In this communication, we introduce a facile

solvothermal synthetic route to prepare ordered and uniform, single-crystalline TiO₂ NSs on CFs. Between about 40% and 92% of the facets were high-energy {001} facets, depending on the concentration of fluorine ions. In comparison with TiO₂ NSs grown on a planar substrate, the TiO₂ NS/CF hybrid structure exhibited 3.38-fold improved photocatalytic degradation of methyl orange (MO) and showed excellent stability under ultraviolet-visible (UV-vis) light irradiation.

Figure 1 shows a schematic representation of the growth process of a NS film grown on the CFs by hydrothermal treatment at 453 K for 5 h in a solution containing fluorine ions. Figure 2A shows the corresponding scanning electron microscopy (SEM) image. It can be seen more clearly in Figure 2B that the CF substrates are uniformly and compactly covered by a large number of NSs. All of the NSs were tetragonal in shape with a thickness of 40–65 nm and side length of 500–800 nm. The percentage of {001} facets in TiO₂ NSs was calculated to lie between 40% and 92%, depending on the concentration of fluorine ions.

Figure 2C shows a high-resolution transmission electron microscopy (HR-TEM) image of a tetragonal NS, the lattice spacings of the two set of lattices marked in the image are both 0.19 nm and oriented perpendicular to each other, corresponding to {200} and {020} atomic planes. The corresponding selected-area electron diffraction (SAED) pattern (indexed as the [001])

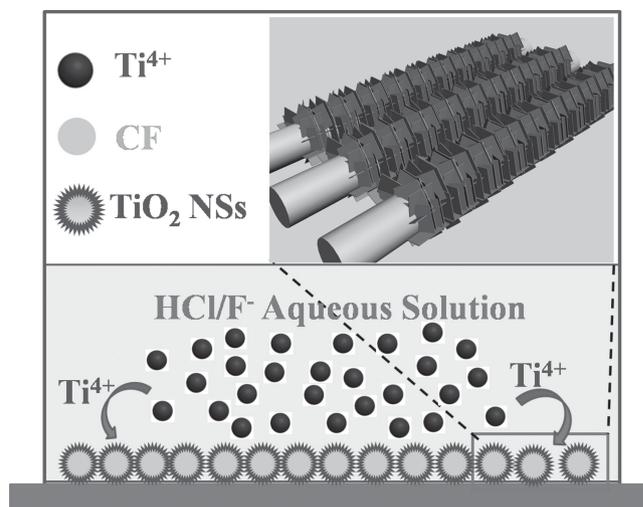


Figure 1. Schematic representation of the growth of TiO₂ NS arrays on CFs by the hydrothermal method.

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DOI: 10.1002/adma.201201075

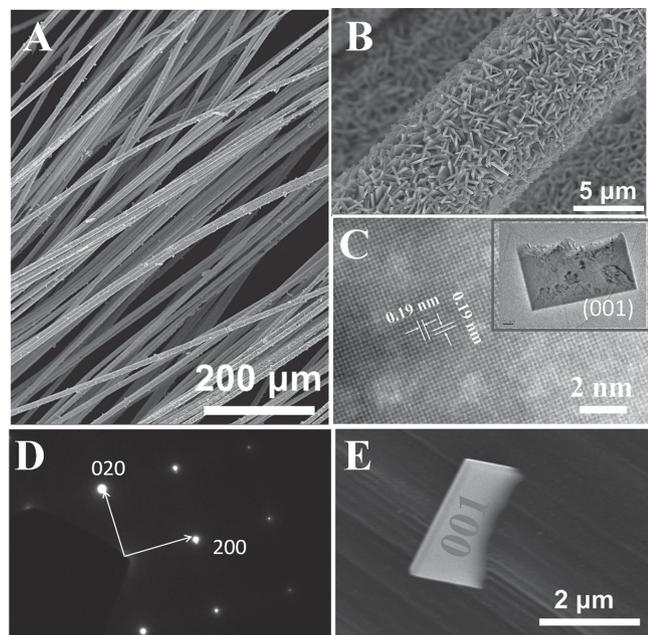


Figure 2. A,B) SEM top-view images at different magnifications of uniform and dense arrays of TiO₂ NSs grown on carbon fibers at 453 K for 4 h. C) HR-TEM image of a TiO₂ NS grown on a carbon fiber. Inset: Low-magnification image. D) SAED pattern of the same TiO₂ NS. E) A single TiO₂ NS grown on a CF. The (001) facet is labeled.

zone axis diffraction) shown in Figure 2D displays the single-crystalline nature and indicates that the top and bottom facets of the NSs are (001) planes. Figure S1A (Supporting information) displays the X-ray diffraction (XRD) pattern of the TiO₂ NSs on the CF substrate. All of the diffraction peaks of the tetragonal NSs agree well with the tetragonal anatase phase of TiO₂, indicating that the as-synthesized product was pure anatase TiO₂.

Figure 2E shows a single TiO₂ NS grown on a CF. The facet labeled in the image is the (001) facet and the isosceles trapezoidal sidewalls are (101) surfaces, indicating that the growth direction of the NS is perpendicular to the [001] axis, which could be beneficial to expose both sides of the (001) facets. The TEM image of a typical NS shown in the inset of Figure 2C shows a partially fractured NS, which indicates that the NS was merged about half-way into the CF and further proves the growth habit of NSs on CFs.

The photoactivity of the CF/TiO₂ samples was evaluated by degradation of MO. As a comparison, TiO₂ NSs were also grown on a fluorine-doped tin oxide (FTO) substrate under the same conditions. The XRD pattern and morphology of the TiO₂ NSs grown on the FTO substrate are shown in Figures S1B and S2 (Supporting Information), indicating that the film on FTO is uniform, dense, and single crystalline. The irradiation areas for CFs/TiO₂ and FTO/TiO₂ samples were kept the same. **Figure 3A** shows time profiles of C_t/C_0 under UV irradiation, where C_t is the concentration of MO at irradiation time t and C_0 the concentration at absorption equilibrium of the photocatalyst before irradiation. After 50 min irradiation, it was found that the as-prepared TiO₂ NSs on CFs exhibited much higher degradation

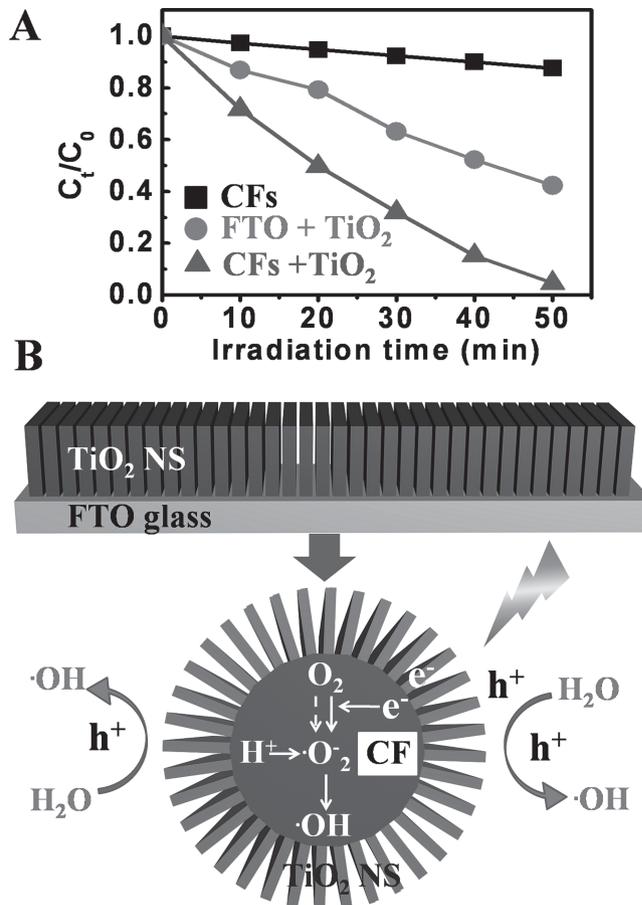


Figure 3. A) Comparison of the photocatalytic degradation rates of MO for TiO₂ NSs on carbon fibers (triangles), TiO₂ NSs on a FTO substrate (circles), and pure carbon fiber (squares). B) Schematic representation of the same amount of TiO₂ NSs grown on FTO-glass and CF substrates with same surface area.

efficiency than those on the FTO glass substrate. The rate constant of dye degradation of TiO₂ NSs on CFs and FTO glass are 0.0584 min⁻¹ and 0.0173 min⁻¹, respectively. The improvement could be caused by the following: First, CFs have a larger surface area to support the TiO₂ NSs than the FTO substrates. Second, the high-energy facets of TiO₂ NSs constitute both the side faces, therefore, an ideal morphology for NSs to achieve better photoactivity is to have all the reactive facets being exposed to reagent in a radial distribution rather than one side being covered up on a planar substrate. From the schematic diagram of FTO/NS and CF/NS hybrid structures shown in Figure 3B, it is easy to understand that CFs with micrometer-scale cylindrical structure are better able to expose all the reactive facets of the NSs when supporting the same amount of TiO₂ NSs. Third, suggested by previous work,^[8] the electron transfer between TiO₂ and C will greatly retard the recombination of photoinduced charge carriers and prolong electron lifetime, which may be an important cause of the better photoactivity of TiO₂ NS/CF hybrid samples. In addition, CFs are much more stable than a FTO glass substrate in a hydrothermal solution containing fluoride ions; it is impossible to grow a high percentage of exposed

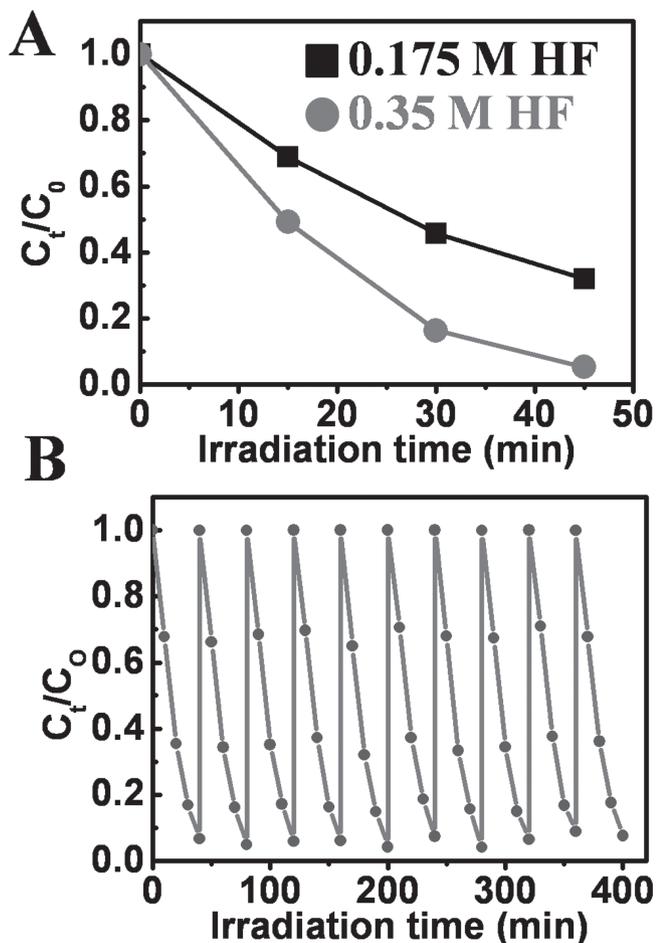


Figure 4. A) Comparison of photocatalytic degradation rates of MO for TiO₂ NSs on carbon fibers synthesized by adding 0.175 M HF (squares) or 0.35 M HF (circles) to a hydrothermal solution. B) Cycling degradation curve of TiO₂ NS arrays on carbon fibers.

(001) facet TiO₂ NSs on FTO by increasing the concentration of fluorine ions.

The concentration of fluorine ions plays a key role in the degradation efficiency of CF/TiO₂ NS hybrid structures by controlling the percentage of exposed (001) surface. We carried out control experiments by introducing different amounts of fluorine ions. **Figure 4A** shows a comparison of photocatalytic degradation rates of MO for TiO₂ NSs on CFs synthesized by adding either 0.175 M HF or 0.35 M HF. After 45 min irradiation with UV light, MO was almost decomposed by the TiO₂ NSs in the solution containing 0.35 M HF, which exhibited much higher degradation efficiency than the TiO₂ NSs in the solution containing 0.175 M HF. According to first-principles calculations, fluorine ions can markedly reduce the surface energy of the (001) surface to a level lower than that of {101} surfaces.^[2] Decreasing the concentration of fluorine ions could result in a decreased percentage of exposed (001) surface (from 92% to 40%). When the concentration of fluorine ions was too low, the obtained NSs were very thick and a continuous film was formed because of the lateral growth of the NSs, as shown

in Figures S3A and S3B (Supporting Information). The dense film will greatly decrease the exposed area of (001) surface and thus decrease the photoactivity of the hybrid materials.

Figure 4B shows the cyclic performance of the TiO₂ NS/CF hybrid structure. Before the photocatalytic properties were measured, the hybrid structure was treated with 0.1 M NaOH to remove the adsorbed fluorine ions.^[3,11] The photodegradation of MO was monitored for ten cycles (each cycle lasts 40 min). After each cycle, TiO₂ NSs/CF was washed and dried thoroughly, and then fresh MO solution was added. The photodegradation rate remained constant over ten consecutive cycles, indicating that as-prepared photocatalyst is stable under UV-light irradiation.

In conclusion, we prepared micrometer- and nanometer-sized anatase TiO₂ sheets, mainly dominated by (001) facets, on CFs using a facile hydrothermal synthetic route. The percentage of (001) facets in TiO₂ NSs was calculated to vary between about 40% and 92%. The morphologies, structural properties, and photocatalytic activities of the resultant TiO₂ NS/CF hybrid structure were investigated. In comparison with TiO₂ NSs grown on a planar substrate, the TiO₂ NSs/CFs hybrid structure exhibited a 3.38-fold improvement in photocatalytic degradation of MO under UV light irradiation. Combining the advantages of TiO₂ NSs and CFs, the hybrid structure can be applied in many fields, such as water splitting, organic solar cells, and lithium ion batteries. Furthermore, the three-dimensional (3D) TiO₂ NS/CF hybrid structure can capture light from all directions, thus showing potential for application in places with high albedo (high fraction of reflected radiation).

Experimental Section

Material Preparation: A schematic illustration of the growth of NSs on the CFs is given in Figure 1. In a typical synthesis process, tetrabutyl titanate, Ti(OBu)₄, (0.6–1.5 mL) was slowly dropped into HCl (18 mL, 5 M) solution. After the solution had been stirred for 30 min, hydrofluoric acid (0.1–0.5 mL, 47%) was added to the mixed solution. After another 5 min stirring, the solution was transferred into a polytetrafluoroethylene (Teflon)-lined stainless-steel autoclave with a total volume of 25 mL. The CFs were then immersed in the solution. The hydrothermal synthesis was conducted at 423–463 K for 2–18 h in an electric oven. The autoclave was cooled to room temperature with flowing water for 10 min after the growth process. Next, the CFs were ultrasonically cleaned for 3 min in a 2:1 (v/v) mixture of 2-propanol (isopropyl alcohol) and water. Before the photocatalytic properties were measured, all the hybrid structures were treated with NaOH (0.1 M) to remove the adsorbed fluorine ions.

Characterization and Measurements: The morphology and microstructure of the TiO₂ nanostructures were examined by SEM, using a LEO 1530 scanning electron microscope (Zeiss, Germany), and by TEM, using a JEOL 4000EX transmission electron microscope. For TEM samples, TiO₂ NSs were detached from the substrate by ultrasonic treatment in ethanol and all of the TEM samples were created by depositing a drop of diluted suspension on a carbon-coated copper grid. Phase identification of TiO₂ was conducted by XRD using a PANalytical X'Pert PRO diffractometer. The photocatalytic activity was evaluated using MO aqueous solution (initial concentration 5 mg L⁻¹). A 300 W xenon lamp was employed as the UV light source. The distance between the sample and lamp was 10 cm. Prior to irradiation, all the samples were immersed in the MO solution and kept in the dark for the whole night to ensure that an adsorption/desorption equilibrium was established. In order to be able to compare the photocatalysts, the irradiation areas for all the samples were kept the same. The absorbance changes of MO were monitored by measuring the maximal absorption at

wavelength $\lambda = 508$ nm using a UV-vis spectrophotometer (Unico 2100, Dayton, NJ). All the experiments were performed with continuous air bubbling. In the durability test of the catalyst for the photodegradation of MO under UV light, ten consecutive cycles were tested. The samples were washed thoroughly with water and dried after each cycle.

Supporting Information

XRD patterns of TiO₂ NSs on CFs and FTO glass, SEM images of TiO₂ NSs grown on FTO glass, and SEM images of TiO₂ NSs on CFs with different concentrations of fluorine ions are provided in the Supporting Information, which is available from the Wiley Online Library or from the author.

Acknowledgements

The authors are grateful for the support of NSF and BES DOE. W.X.G. thanks the Chinese Scholars Council for support, and C.J.L. gratefully acknowledges financial support from the National Basic Research Program of China (2012CB932900).

Received: March 15, 2012

Revised: May 25, 2012

Published online:

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