

Hydrothermal Growth and Photoelectrochemistry of Highly Oriented, Crystalline Anatase TiO₂ Nanorods on Transparent Conducting Electrodes

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Supporting Information

During past few decades, titanium dioxide (TiO₂) has been extensively studied for use in photovoltaic devices, sensors, photocatalysis, and environmental applications. The unique utility of TiO₂ relative to other oxide semiconductors derives from its chemical stability, abundance and low cost, and electronic properties, which include favorable band edge potentials and charge carrier dynamics.¹ In several emerging applications, including heterojunction solar cells, a desirable architecture for TiO₂ is one that combines high surface area with fast and directional charge transport.² Vertically aligned, crystalline TiO₂ nanostructures meet these needs because they minimize the carrier trapping that is predominately associated with grain boundaries in nanocrystalline TiO₂ films.^{3–5} Recently, high quality single crystal rutile TiO₂ nanorod films have been made by hydrothermal and solvothermal reactions,^{4,6–9} and crystalline anatase TiO₂ nanotubes have been made by anodization of Ti^{10,11} and by template methods.¹² The photocatalytic activity of anatase nanocrystals has been shown to be crystal face-dependent.¹³ Motivated by the fact that the anatase phase of TiO₂ exhibits slower charge recombination rates and better transparency than rutile,¹⁴ much effort has been dedicated to fabricating single crystal anatase nanowire structures.¹⁵ However, the synthesis of high aspect ratio anatase single crystals has been challenging because of the strong tendency of the anatase phase to twin and form intergrowths by oriented attachment during crystal growth.¹⁶ Although there have been reports of the synthesis of crystalline anatase TiO₂ nanowires,^{17–21} defects induced by phase transformation processes, either from the precursor materials to TiO₂ or from amorphous to crystalline TiO₂, have been difficult to avoid. The applications of these materials have therefore been limited.

Earlier reports have shown that HCl promotes the hydrothermal growth of highly oriented rutile nanorods, presumably because of strong adsorption to the (110) crystal face.^{6,7} It has also been shown that SO₄²⁻ ions promote the growth of phase-pure anatase nanostructures.¹⁸ We hypothesized that mixed sulfate/chloride solutions, at concentrations

where both ions adsorb, could provide a route to highly oriented crystalline anatase TiO₂ nanorods. We report here the hydrothermal preparation of such nanorods films, which grow along the [001] direction, on transparent conductor substrates. Consistent with our hypothesis, we found that the growth of anatase, rutile, or a mixture of phases could be controlled by simply changing the pH and the ratio of [Cl⁻] to [SO₄²⁻] (Supporting Information Table S1). Figure 1 shows the XRD pattern and SEM and TEM images of TiO₂ nanorod films obtained at a H⁺ concentration of 6 M and a 14:1 molar ratio of [Cl⁻]/[SO₄²⁻]. Under these conditions, titania nanorods grow vertically on the fluorine-doped tin oxide on glass (FTO) substrate to a length of 1.8 μm and with nanowire diameters ranging between 30 and 150 nm from the top to the bottom, as shown in Figure 1a,b,d. The X-ray diffraction pattern shows only one peak at 2θ = 37.9° in Figure 1c, which can be assigned to the (004) peak of the anatase phase. This indicates highly oriented growth with respect to the plane of the substrate, along the [001] direction of the anatase unit cell. High resolution TEM images of an individual nanorod at different locations along the rod are shown in Figure 1e,g,i. These images show an interplanar spacing *d*₀₀₂ of 0.475 nm, in good agreement with the *d*-spacing of the anatase (002) planes, supporting the conclusion that the dominant (004) diffraction peak observed in XRD arises from the preferred [001] growth direction. The selected-area electron diffraction (SAED) pattern shown in Figure 1f,h,j illustrates the high quality and phase purity of the anatase TiO₂ rods. In contrast to the growth direction observed in the presence of SO₄²⁻ and Cl⁻ ions, anatase nanorods grow along the [100] direction in the presence of NH₄F.²² Anatase nanorods grown by oriented attachment of anatase nanoparticles on their {101} surfaces have also been observed.²³

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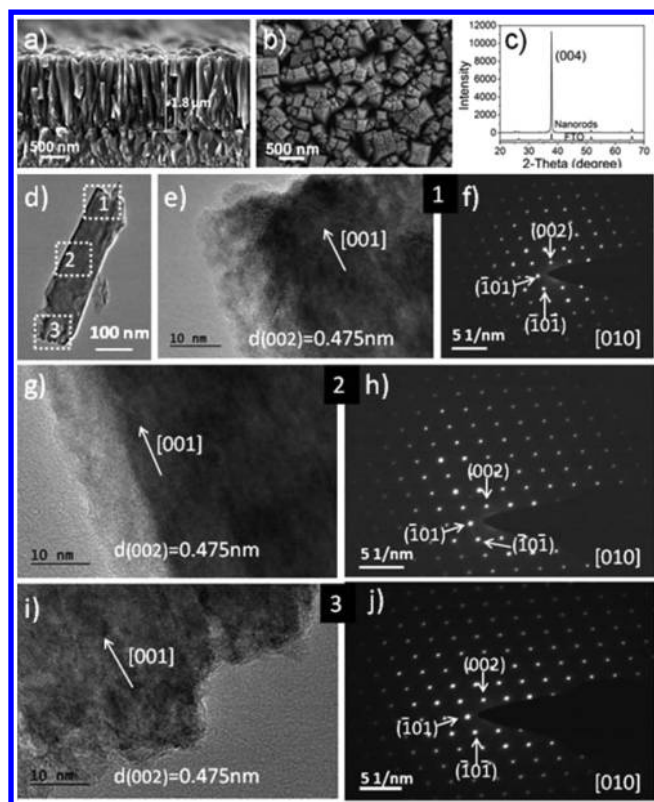


Figure 1. SEM images (cross sectional (a) and top view (b)), XRD pattern (c), TEM (d), and HRTEM images (e, g, i) and SAED patterns (f, h, j) at three locations along the TiO₂ nanorods.

Supporting Information Table S1 summarizes results on the crystal phase and morphology of TiO₂ films obtained under different growth conditions on FTO substrates, and corresponding characterization data are shown in Supporting Information Figures S1–S6. When the concentration of H⁺ was fixed at 4 M, oriented growth of the rutile phase of TiO₂ occurred along the [001] direction at high concentrations of Cl[−] ([Cl[−]]:[SO₄^{2−}] ≥ 7:1). This is consistent with earlier results on the growth of TiO₂ nanorods in aqueous HCl solutions, where Cl[−] was found to adsorb selectively onto the (110) crystal faces and promote anisotropic crystal growth along the [001] direction.^{6,7} When the ratio of [Cl[−]] to [SO₄^{2−}] was lowered to 6:1 or 5:1, a mixture of anatase and rutile phases was obtained. Surprisingly, phase pure anatase films with a [001] preferred growth direction were found when the ratio of [Cl[−]] to [SO₄^{2−}] was in the broad range of 5:1 to 1:1. This oriented growth disappeared when the ratio of [Cl[−]] to [SO₄^{2−}] was lower than 0.8:1, but the anatase phase was still obtained. At higher concentration of H⁺ (6 M), only anatase was obtained over the full range of the [Cl[−]] to [SO₄^{2−}] ratio tested, from 14:1 to 1:10. Under these conditions, oriented anatase films were found for [Cl[−]]:[SO₄^{2−}] ratios between 14:1 and 1:4. Most interestingly, highly oriented anatase nanorod films were formed at high [Cl[−]]:[SO₄^{2−}] ratios, between 14:1 and 12:1. It is interesting that the highly oriented growth of anatase crystals occurs only under these conditions, implying critical roles of the pH and absolute concentration of SO₄^{2−}. Additionally, the requirement for both Cl[−] and SO₄^{2−} in a certain ratio suggests that there is a synergistic effect of the two ions during crystal growth.

Figure 2a compares linear sweep voltammograms of samples with different TiO₂ phases and morphologies under AM 1.5G

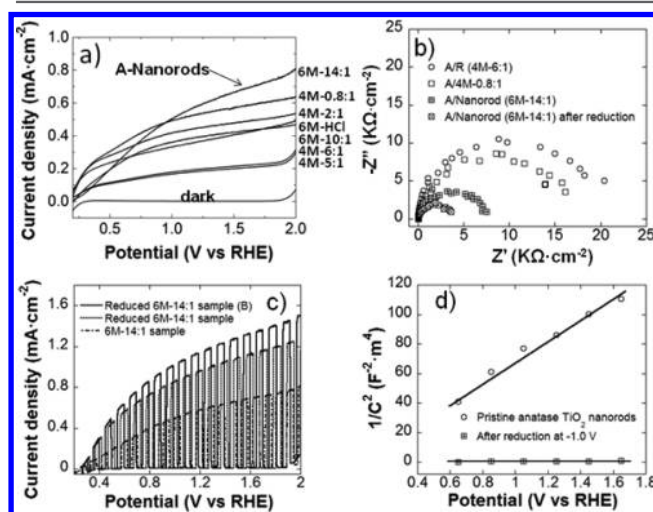


Figure 2. (a) Photocurrent density of samples prepared at different H⁺ concentrations and [Cl[−]]:[SO₄^{2−}] ratios, under AM 1.5G 100 mW·cm^{−2} light. (b) Electrochemical impedance spectra of the same samples under 380 nm monochromatic light, at a bias of 0.8 V vs SCE, in 1.0 M NaOH. (c) Photocurrent density of pristine anatase TiO₂ nanorod films and the same films after electrochemical reduction, measured under chopped AM 1.5 G, 100 mW·cm^{−2} light. The data for sample B were obtained by illuminating from the FTO side of the electrode. (d) Mott–Schottky plots of pristine anatase TiO₂ nanorod films and electrochemically reduced films; data were obtained in 1.0 M NaOH solution in the dark.

(100 mW·cm^{−2}) illumination in 1 M NaOH, using TiO₂ films grown on FTO as working electrodes, Pt foil as the counter electrode, and a saturated calomel electrode as the reference. Highly oriented anatase nanorod films (grown at 6 M H⁺, 14:1 anion ratio) showed the highest photocurrent density, 0.6 mA·cm^{−2}, at a potential of 1.25 V vs RHE, among the samples represented in Supporting Information Table S1. This value is already over half of the theoretical photocurrent of anatase TiO₂ films of the thickness shown in Figure 1a, which is 1.1 mA·cm^{−2} under AM 1.5 G illumination.²⁴ Consistent with their high photocurrent density, these nanorods also showed superior photogenerated charge transport behavior, as measured by impedance spectroscopy in Figure 2b. These data confirm the advantages of using crystalline one-dimensional TiO₂ nanorod films for photoelectrochemical conversion, which requires efficient charge transport and collection of carriers at the back electrode. The low photocurrent at low bias is probably due to the large diameter of nanorods as shown in Figure 1a,d, which leads to a long distance for holes to reach the solid-solution interface. It is noteworthy that the samples with mixtures of rutile and anatase phases (4 M, 6:1 and 5:1) exhibited the lowest photocurrent, as well as the highest charge transport resistance (as seen in Figure 2b), suggesting the deleterious effects of multiple grain boundaries between the rutile and anatase nanocrystals on the transport of carriers. This differs from the behavior of single junction core/shell structures, formed by coating rutile nanorods with anatase.²⁵ The pure rutile TiO₂ nanorod film grown in 6 M HCl aqueous solution gave a photocurrent of 0.32 mA·cm^{−2} at a bias of 1.25 V vs RHE, which is lower than that of pure anatase TiO₂ nanorods but higher than mixed phase TiO₂.

In order to further improve their performance, the TiO₂ nanorod films were electrochemically reduced at -1.0 V vs SCE for 30 min in 1.0 M Na₂SO₄. UV-vis spectra of nanorod films before and after reduction are shown in Supporting Information Figure S6. After this treatment, photocurrent densities as high as 1.0 mA·cm⁻² were observed at 1.25 V vs RHE, as shown in Figure 2c. When the samples were illuminated from the FTO side, the photocurrent was further increased by approximately 20%, reaching 1.2 mA·cm⁻² at 1.25 V vs RHE. The remarkable enhancement of the photocurrent in the reduced sample can be attributed to the self-doping of Ti³⁺ as evidenced by XPS spectra (Supporting Information Figure S8).²⁶ A lower charge transfer resistance of the doped nanorods is also evidenced by the smaller semicircle in electrochemical impedance spectra relative to that of pristine nanorods, Figure 2b. The presence of Na is probably due to the Na₂SO₄ electrolyte in which the electrochemical reduction was carried out. It is possible that Na⁺ exists as a charge-balancing cation, stabilizing Ti³⁺. The trace Si observed may be introduced during sample preparation and annealing (Supporting Information Figure S9). The short-circuit current of anatase TiO₂ nanorods before and after electrochemical reduction was measured to be about 0.08 mA·cm⁻² under zero bias (Supporting Information Figure S10). The small photocurrent under zero bias is expected because the conduction band edge potential of TiO₂ is positive of the hydrogen evolution potential.

The donor density of as-prepared anatase TiO₂ nanorods was calculated from the Mott-Schottky equation to be 4.35×10^{20} cm⁻³, which is comparable to that of polycrystalline TiO₂ nanotubes²⁴ but higher than that of rutile TiO₂ nanorods.²⁷ The donor density was 5.30×10^{22} cm⁻³ after reduction, an increase of 2 orders of magnitude. The increased photocurrent of the reduced TiO₂ nanorod films derives from the increased donor density, which shifts the Fermi level of TiO₂ and accelerates charge separation by increasing the band bending at the TiO₂-solution interface.²⁸ In contrast, a similar reduction treatment for polycrystalline TiO₂ nanotubes only induces a slight increase in donor density even though the nanotubes possess a smaller wall thickness. It is possible that the high density of crystal defects in the latter case results in more efficient trapping of charge and consequently a much lower density of free carriers at similar doping density.³ The inferior charge transfer characteristics of anatase films that were not oriented, relative to oriented nanorod films, was evident in the impedance spectra (Figure 2b), consistent with this hypothesis.

Moreover, the incident photon current efficiency (IPCE) of the reduced TiO₂ nanorod films was greatly enhanced over the entire UV range of the spectrum as shown in Supporting Information Figure S11. A maximum IPCE of 17% at 380 nm for pristine nanorods and 32% at 370 nm for reduced nanorods was measured. These values are comparable to IPCEs of pristine rutile TiO₂ nanorods and Sn-doped rutile,²⁹ respectively. Pure rutile TiO₂ nanorods grown in 6 M HCl give an IPCE value of 13% and a shift of the current cutoff edge to the long wavelength direction relative to anatase TiO₂ nanorods. This shift is consistent with the smaller band gap of rutile. The enhancement of IPCE values in the anatase case provides direct evidence of more efficient charge separation and transport of photogenerated carriers in electrochemically reduced TiO₂. Increased IPCE values in the UV region have also been observed with hydrogen-annealed rutile TiO₂ nanorods,²⁷ in which oxygen vacancies have been found. No

significant enhancement of the IPCE was found for reduced anatase TiO₂ nanorods in the visible part of the spectrum. Hence, the increase in photocurrent derives from more efficient use of UV light as a result of the increased donor density. This result demonstrates that electrochemical reduction is a facile and effective method for improving the photoelectrochemical performance of anatase TiO₂ nanorods, enabling one to avoid the often used high temperature process of hydrogen annealing.^{30,31}

In summary, a facile hydrothermal method was developed for growing highly oriented, crystalline anatase TiO₂ nanorods on transparent conducting substrates. The phase and morphology of the TiO₂ nanocrystals can be controlled by tuning the pH and molar ratio of [Cl⁻] to [SO₄²⁻]. The oriented growth of anatase TiO₂ nanorods requires the presence of both Cl⁻ and SO₄²⁻. By testing the photoelectrochemical performance of samples grown under different conditions, we found that oriented anatase nanorod films exhibited the highest photocurrent, which was a consequence of the low defect density of the nanocrystals in the films. A photocurrent density of 1.2 mA·cm⁻² at 1.25 V vs RHE was obtained by self-doping with Ti³⁺ via electrochemical reduction. IPCE measurements show that the enhancement of photocurrent is due to the improved photoactivity in the UV region, as a result of the increased concentration of free carriers. These anatase TiO₂ nanorod films could serve as important materials for photoelectrochemical and photovoltaic devices.

■ ASSOCIATED CONTENT

⑤ Supporting Information

Other details are given in Supporting Information. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.5b00782.

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Notes

The authors declare no competing financial interest.

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