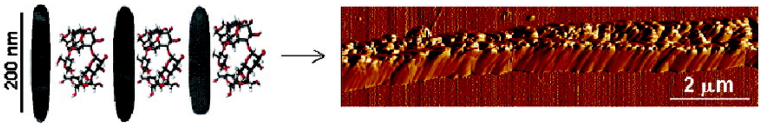
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

Self-Assembly of Photoactive TiO–Cyclodextrin Wires

Jun Feng, Alex Miedaner, Phil Ahrenkiel, Michael E. Himmel, Calvin Curtis, and David Ginley

J. Am. Chem. Soc., **2005**, 127 (43), 14968-14969• DOI: 10.1021/ja054448h • Publication Date (Web): 05 October 2005



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
COMMUNICATIONS

Self-Assembly of Photoactive TiO_2−Cyclodextrin Wires

Jun Feng,[†] Alex Miedaner,[‡] Phil Ahrenkiel,[‡] Michael E. Himmel,*,[†] Calvin Curtis,[‡] and David Ginley[‡]

National Bioenergy and Basic Science Centers, National Renewable Energy Laboratory, Golden, Colorado 80401

Received July 5, 2005; E-mail: mike_himmel@nrel.gov

New molecular devices based on nanometer scale assemblies that display flexibility, stable electronics, and rapid response and long lifetime under photoinduced current are needed for microelectronics applications. Assembly processes studied with respect to the chemical and structural transformation and reconstruction of semiconductor surfaces by water and other oxygen-rich molecules, such as ZnS[1] and TiO_2[2,3] nanoparticles, have been a topic of considerable recent interest. The association of water molecules with such surfaces displays a reversible characteristic, and this property implies that the oxygen atom in water does not interact through a coordinate covalent bond. Our recent ab initio calculations demonstrate that the energy advantage for water molecules to directly interact with a ZnS surface is very small. However, if one considers the case of a molecule containing multiple hydroxyl groups, the interaction becomes stronger and generates coordinate covalent bonds with the surface atoms. This mechanism has been proposed for the interaction between ZnS with cyclodextrins.[4] In this communication, we report that cyclodextrins (CDs) appear to irreversibly coat the surface of anatase TiO_2 particles and produce ultralong wires. For this purpose, CD molecules may play the role of linker molecules, with hydroxyl groups protruding from both faces. These interactions appear to result in a kind of self-assembly of the TiO_2 particles, resulting in super long TiO_2−dextrin wires generated irreversibly (Figure 1). X-ray diffraction (XRD) shows that the wires maintain the expected structural signature for the TiO_2 particles, and FTIR confirms their relevant chemical content. The well-formed wires are mechanically flexible, behaving like ropes in water. They may even be straightened linearly using tweezers under a microscope (Figure 1 inset). Preliminary photocurrent and electronic measurements show the rapid response of photoexcitation of isolated TiO_2−dextrin wires and constant electric resistance.

Approximately 1 mg of anatase TiO_2 nanorods, made by a hydrothermal process from sodium titanate[5] and 5 mg of cyclodextrin, was mixed with 1 mL of distilled water. The mixture was sonicated for 5 min and then transferred to a temperature-controlled (25 °C) quartz tube illuminated by UV light. Within one to two weeks, hairlike wires were observable in the suspension. They were separated from the suspension using tweezers and thoroughly washed with water. The wires were stored in a hydrated condition. These wires were surprisingly long and extend to as much as 9 mm in length (Figure 1). Three cyclodextrins, α, β, and γ, were used, and all induced wire formation. Some pH effects were observed. Solutions of pH 5 to 7 were the best for wire formation, and higher pH incubations (pH 7 to 9) produced only wires of poor quality.

Under UV light, TiO_2 surfaces generate electron−hole (e^-/h^+) pairs that can be separated and move toward different sites. The holes are thought to cause interactions with surface molecules. It was recently revealed that alcohols and polyhydroxyl compounds[6,7] can scavenge holes efficiently. This scavenging ability increases with the number and spatial distribution of the hydroxyl groups per molecule,[8] which suggests that the photoexcited TiO_2 surface has a tendency to associate strongly with available hydroxyls.

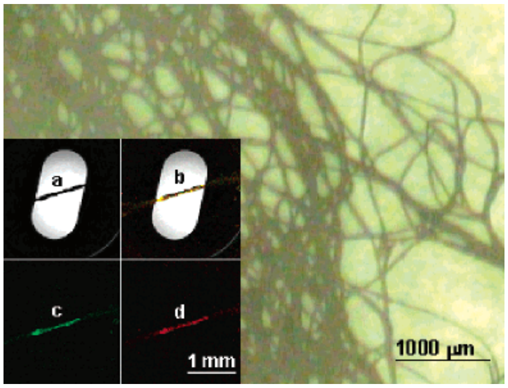


Figure 1. TiO_2 wires induced by β-cylodextrin complexation displayed under light microscopy. The inset shows the confocal images of a straightened wire on a TEM grid (using tweezers under the light microscope). (a) Regular light image. (b) Multilight image. (c) Fluorescence image with 488-nm illumination. (d) Fluorescence image with 534-nm illumination.

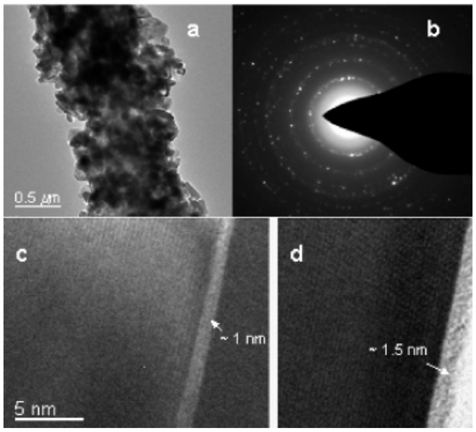


Figure 2. TEM images of (a) the TiO_2−dextrin wire bundle, (b) the electron diffraction of the wire bundle, (c) the interdextrin layer between the two TiO_2 particles, and (d) the dextrin layer on the particle surface.

The susceptibility to manipulation (Figure 1 inset) and stability in water (over one year) suggest the potential utility of these wires. This property may be explained by the gross structure of the wires. Transmission electron microscopy (TEM) revealed that on the TiO_2 rod surface and within the interface of two particles, there is an amorphous layer of molecules (Figure 2). The “carbohydrate” layer between the rods is about 1 nm in thickness, which is very close to the cyclodextrin height profile. We believe this random block particle composite structure is the reason the TiO_2−dextrin wires possess the mechanical properties observed.

Chemical adsorption of the hydroxyls on photoexcited TiO_2 surfaces has been shown to result in crystal coordinate bonds

---

[†] National Bioenergy Center.
[‡] Basic Science Center.

10.1021/ja054448h CCC: $30.25 © 2005 American Chemical Society

between oxygen and with titanium,[6] which suggests that multiple Ti−O−R bonds are formed during the reaction of cyclodextrins and the TiO_2 surface. We know that the surfaces of photoexcited TiO_2 particles generate electron−hole (e^-/h^+) pairs that result in radical formation on the TiO_2 surface ($Ti^{IV}-O^•$) and in solution (OH_{ads}). The reaction of $Ti^{IV}-O^•$ with HO−R generates $OH^•$ species that may combine with an electron and a proton to produce a water molecule. Furthermore, the surface modification of anatase with sugar molecules and other polyols was found to result in the coordinated bonding of these hydroxylated functionalities to titanium atoms in a way that resulted in two of the oxygen atoms being octahedrally coordinated to a single titanium atom.[8,9] Reports from other workers demonstrated that the interaction between hydroxyl compounds and the photoexcited TiO_2 nanoparticles resulted in the oxidation of the hydroxyl ligands.[10] In this view, the electron−hole (e^-/h^+) pairs generated by photoexcitation would be separated and the charge trapping time could be much longer than the time of hole scavenging by the hydroxyl compounds.[8] Thus, when the hydroxyls of cyclodextrin molecules take the place of the "holes" on the anatase surface, the coordinate bonds between oxygen atoms and titanium atoms are formed.

In XRD experiments, the peaks close to 25, 38, and 48 θ demonstrate that these wires consist of pure anatase TiO_2. From the FTIR of the TiO_2−dextrin wires, bands appearing at 2880 and 2930 cm^{-1} are consistent with the principal carbohydrate stretching vibrations of $-CH_2-$ and −CH. Also observed was a band at 806 cm^{-1} that could result from an O−C−C−O relative ring vibration. The presence of an O−C−C−O ring with the titanium atom reflects the nature of the association of the oxygen atoms in cyclodextrins with a titanium atom, as well as the carbon bridge between the two hydroxyls of the cyclodextrin.

Electronic measurement of the TiO_2−dextrin wires showed that the wire resistance has a good linear relationship with the length of the wire. Also, the resistance of the wires stays constant with voltage change. For example, a 390-μm length of wire maintains constant resistance with voltage change from 4 to 10 V, or 500-Ohm μm^{-1}.

From the inset of Figure 1, we see the photoluminescence emission of the wires. Using a UV lamp (254/366 nm, model UVSL-58) and an electrochemical analyzer with $I-t$ function (CHI 650), we measured the photoactivity of single TiO_2−dextrin wire. The photocurrent of a wire bundle at a potential of 10 mV is about 410 pA and appears stable within 1000 s. Also important was the observation that the photo current responds quickly during the light on/off cycles.

The FTIR and XRD data shown above suggest that cyclodextrins accommodate into the titanium octahedral complex. Although the assembly process itself is not yet known, a plausible explanation lies in simple entropic control of the cyclodextrin−TiO_2 complexes in water. For example, the cyclodextrins have two hydrophilic edges and a hydrophobic lumen, and the TiO_2 surface is normally hydrophobic, yet hydrophilic when photoinduced. Therefore, the assembly process observed may be induced by surface energetics alone.

Although larger wire bundles were observed, single wires have remarkably consistent diameters (∼400−800 nm; Figure 3). The distinct energy facets of the titanium crystals[11] combined with the lowest-energy principle may explain control of wire formation. The photoactive and mechanically stable TiO_2 wires described here may provide new strategies for producing semiconductor devices at the nanometer scale. Potential applications are ultrasmall light-induced electronic junctions, switches, and sensors.

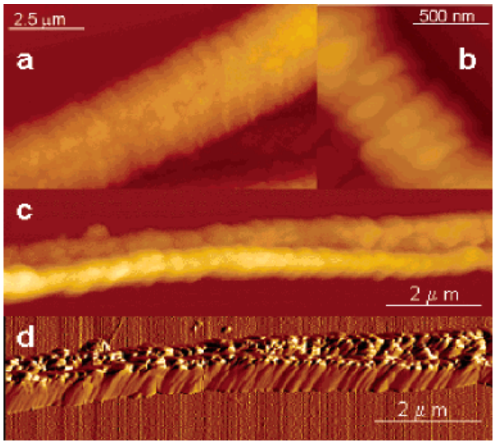


Figure 3. Topographic AFM images of (a) TiO_2−dextrin wire bundle, (b) surface structural features of the association of TiO_2 particles, (c) two strands of the TiO_2−dextrin wires, and (d) illumination mode image of the image in (c).

Acknowledgment. This work was funded by the DOE Solar Photochemisry Program funded by OS/BES, Division of Chemical Sciences, Geosciences, Biosciences under Contract No. DE-AC36-99GO10337.

Supporting Information Available: XRD, FTIR measurements, electronic and photocurrent measurements, and the wire height profile measurement of the TiO_2−dextrin wires. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Meyer, B.; Marx, D.; Dulub, O.; Diebold, U.; Kunat, M.; Langenberg, D.; Woll, C. *Angew. Chem., Int. Ed.* **2004**, *43*, 6642−6645. (b) Zhang, H. Z.; Gilbert, B.; Huang, F.; Banfield, J. F. *Nature* **2003**, *424*, 1025−1029.
(2) (a) Seki, K.; Tachiya, M. *J. Phys. Chem. B* **2004**, *108*, 4806−4810. (b) Wang, R.; Hashimoto, K.; Fujishima, A.; Chikuni, M.; Kojima, E.; Kitamura, A.; Shimohigoshi, M.; Watanabe, T. *Adv. Mater.* **1998**, *10*, 135−138.
(3) Miyauchi, M.; Kieda, N.; Hishita, S.; Mitsuhashi, T.; Nakajima, A.; Watanabe, T.; Hashimoto, K. *Surf. Sci.* **2002**, *511*, 401−407.
(4) Feng, J.; Ding, S. Y.; Tucker, M. P.; Himmel, M. E.; Kim, Y. H.; Zhang, S. B.; Keyes, B. M.; Rumbles, G. *Appl. Phys. Lett.* **2005**, *86*, 033108.
(5) Chen, Q.; Zhou, W.; Du, G.; Peng, L. M. *Adv. Mater.* **2002**, *14*, 1208−1211.
(6) (a) Yamakata, A.; Ishibashi, T.; Onishi, H. *J. Phys. Chem. B* **2002**, *106*, 9122−9125. (b) Yoshihara, T.; Katoh, R.; Furube, A.; Tamaki, Y.; Murai, M.; Hara, K.; Murata, S.; Arakawa, H.; Tachiya, M. *J. Phys. Chem. B* **2004**, *108*, 3817−3823.
(7) (a) Bahnemann, D.; Henglein, A.; Spanhel, L. *Faraday Discuss. Chem. Soc.* **1984**, *78*, 151−163. (b) Bahnemann, D.; Henglein, A.; Spanhel, L. *J. Phys. Chem.* **1984**, *88*, 709−711.
(8) Shkrob, I. A.; Sauer, M. C.; Gosztola, D. *J. Phys. Chem. B* **2004**, *108*, 12512−12517.
(9) Rajh, T.; Chen, L. X.; Lukas, K.; Liu, T.; Thurnauer, M. C.; Tiede, D. M. *J. Phys. Chem. B* **2002**, *106*, 10543−10552.
(10) (a) Goldstein, S.; Czapski, G.; Rabani, J. *J. Phys. Chem.* **1994**, *98*, 6586−6591. (b) Tachikawa, T.; Tojo, S.; Fujitsuka, M.; Majima, T. *J. Phys. Chem. B* **2004**, *108*, 5859−5866.
(11) Diebold, U. *Surf. Sci. Rep.* **2003**, *48*, 53−229.

JA054448H