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Letters

Porous "Coral-like" TiO₂ Structures Produced by Templating Polymer Gels

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A new synthetic approach to generate highly porous semiconductor networks that could be used for catalytic and solar cell applications is reported. Titanium dioxide networks were produced using a polymer gel templating procedure, resulting in a coral-like structure with a wall thickness of about 100−150 nm and pore sizes ranging from 100 nm to micrometers in diameter. Calcination results in the production of either the anatase or rutile crystal phases without carbon contamination from the starting polymer materials, with the individual titanium dioxide particles contacting neighbors, thereby forming a continuous network. The results obtained are of importance to various fields of research as the open "coral-like" network structure of the titanium dioxide allows high access of the titanium dioxide surface to the reaction medium.

Introduction

Titanium dioxide nanoparticles have many applications in the chemical,[1] medical,[2] biological,[3] environmental,[1,4] and solar energy fields.[5] The use of titanium dioxide in photocatalysis processes is dependent on the absorption characteristics of TiO₂, which allow it to absorb photons of UV light, producing an electron−hole pair that can react with surrounding materials.[1,4b,6] Its durability and stability[7] during such reactions make it an ideal material for any application where the material is to be used continuously without frequent replacement. In the majority of its applications, accessibility to the surface and the crystal phase of the TiO₂ are of prime importance.[8] The surface of the material is, for example, where the semiconductor is in contact with the reaction solution or where gases can adsorb from the air in a photocatalytic air purifier. The different crystal phases of TiO₂ (the most commonly used being anatase or rutile) determine its efficiency in different applications. Therefore, the production of an open, highly

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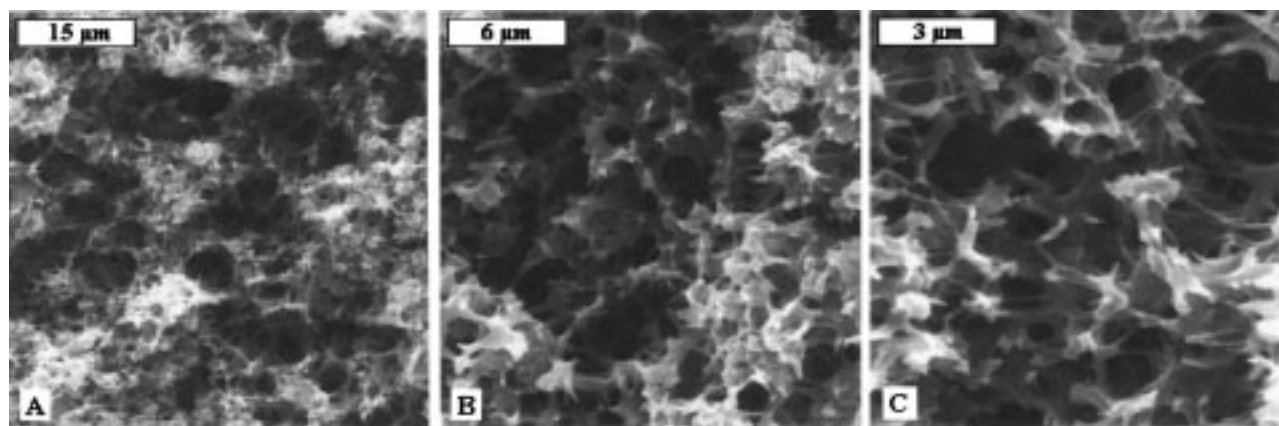
Figure 1. SEM images of the acrylamide/glycidyl methacrylate polymer gel template. The gel was dried overnight in the drying oven at 60 °C after being removed from a 2-propanol solution. Magnification increases from (A) to (C).

porous titanium dioxide network in either crystal phase is significant due to the fact that (i) the high surface area allows maximum contact between the network and reaction media, (ii) the continuity of the network prevents traps or dead spots from depleting its efficiency, and (iii) the anatase or rutile phase of the crystal can be chosen depending on its end application.

Some of the latest methods used for the production of porous titanium dioxide structures involve sol—gel processes[9,10] and templating of aluminum oxides[11,12] (commonly used in templating procedures of polymers, metals, or ceramics). For example, Hoyer[11] has used a two-step process, including electrodeposition, to replicate alumina and produce nanotubes of TiO_2. Martin et al.[12] use a sol—gel method to template (i.e., negatype structure) alumina, synthesizing both nanotubes and nanofibrils. The novel method used in this Letter to produce "coral-like" TiO_2 is similar to the templating of the alumina except that it involves the molding of an easily formed polymer gel template that is conveniently removed during the calcination process. The advantage of using polymer gels for templating titanium dioxide is that the gels allow not only control of the final pore size but also of the overall network structure.

Experimental Section

All chemicals were obtained from Aldrich except for Brij 58 (main component eicosaethylene glycol hexadecyl ether), which was purchased from Fluka Chemika.

Polymer Gel Formation. Aqueous solutions containing surfactant (Brij 58), monomers (acrylamide and glycidyl methacrylate, used in a 1:1 weight ratio), cross-linker (ethylene glycol), and initiator (potassium persulfate) were heated to 55 °C for 5 h. (Weight ratio of water:Brij 58:monomer:cross linker was 8:1:2:0.4.) The resulting gel was cut into pieces of ca. $1 \times 1 \times 0.3$ cm[3] and cleaned using Soxhlet extraction in ethanol (which resulted in slight shrinkage of the gel), followed by gentle agitation in deionized water until the conductivity of the rinsing water equaled that of deionized water.

Titanium Dioxide Templating. Titanium(IV) isopropoxide (99.999%), which hydrolyzes rapidly on contact with water, was used as the titanium precursor. Hence a solvent exchange process for the gels, now cut to $1 \times 0.3 \times 0.3$ cm[3], was carried out, slowly increasing the 2-propanol-to-water ratio until the gels were in high purity 2-propanol (99.5%). Again, slight shrinkage of the gel occurred on transfer from an aqueous to alcohol solution. The

gels were then transferred into titanium(IV) isopropoxide and gently agitated for at least 6 h; hydrolysis occurred when these gels were placed into a solution of 2-propanol and water (50:50 by vol). During the precursor incorporation and the hydrolysis steps there was no observable change in gel size. Again, the gels were gently agitated for at least 6 h and then placed into a drying oven at 60 °C overnight. To produce the anatase structure, the dried gels containing the amorphous TiO_2 were heated to 450 °C (ramped at 15 K min^{-1}) under N_2. The gels were then left at this temperature under O_2 for 6 h. The resulting crystal phase could be altered by controlling the maximum temperature during the calcination process: when heating to 990 °C, the rutile phase resulted. After cooling to room temperature, the samples were analyzed using electron microscopy, X-ray scattering, and N_2 sorption measurements.

Characterization. A Zeiss DSM 940 A scanning electron microscope was used to examine the morphology of the polymer and TiO_2 structures. Thin slices, ~50 nm in width, of the TiO_2 samples were prepared using a Leica ultracut UCT ultramicrotome. These slices were placed onto copper grids for analysis on a Phillips CM12 high-resolution transmission electron microscope operating at 120 kV (equipped with an EDAX 9800 analyzer) to obtain information on the individual TiO_2 particles and their crystal phases. The specific surface areas of the samples were obtained using the Micromeritics Gemini II 2375 surface area analyzer.

Results and Discussion

The macroporous polymer gels were prepared using a method similar to that described by Antonietti et al.[13] Figure 1 shows scanning electron microscopy (SEM) images of the acrylamide/glycidyl methacrylate polymer gel used for the templating discussed in this paper. It can be seen at lower magnification (Figure 1A) that the gel is homogeneous and porous, and at a higher magnifications (Figure 1B,C) thin fibers connecting the thicker, flat portions of the gel are observed. After incorporation of the titanium precursor into the polymer gel, followed by hydrolysis and calcination, the "coral-like" titanium dioxide network is produced. The network retains the template shape, although the overall size shrinks slightly during heating. The sample does not fracture to a powder during the calcining step; force applied with tweezers or a blade is required to break the network into smaller pieces. The SEM images of the network are shown in Figure 2 and can be compared to the original polymer gel. The TiO_2 network is also homogeneous and porous, and at higher magnification hollow sections or tubes resulting from the removal of the thin polymer fibers are seen. The

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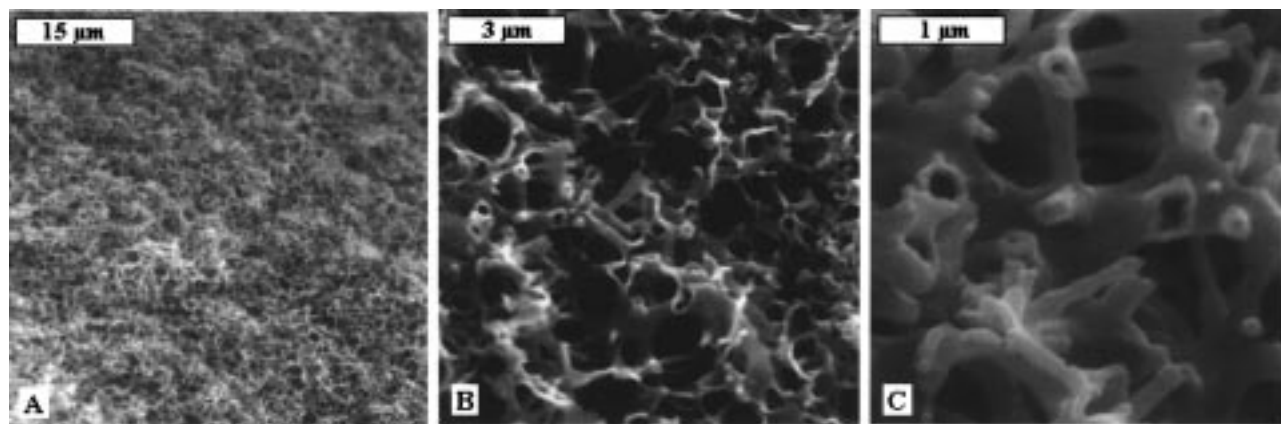
Figure 2. SEM images of the "coral-like" titanium dioxide network produced after the removal of the polymer gel template. Magnification increases from (A) to (C).
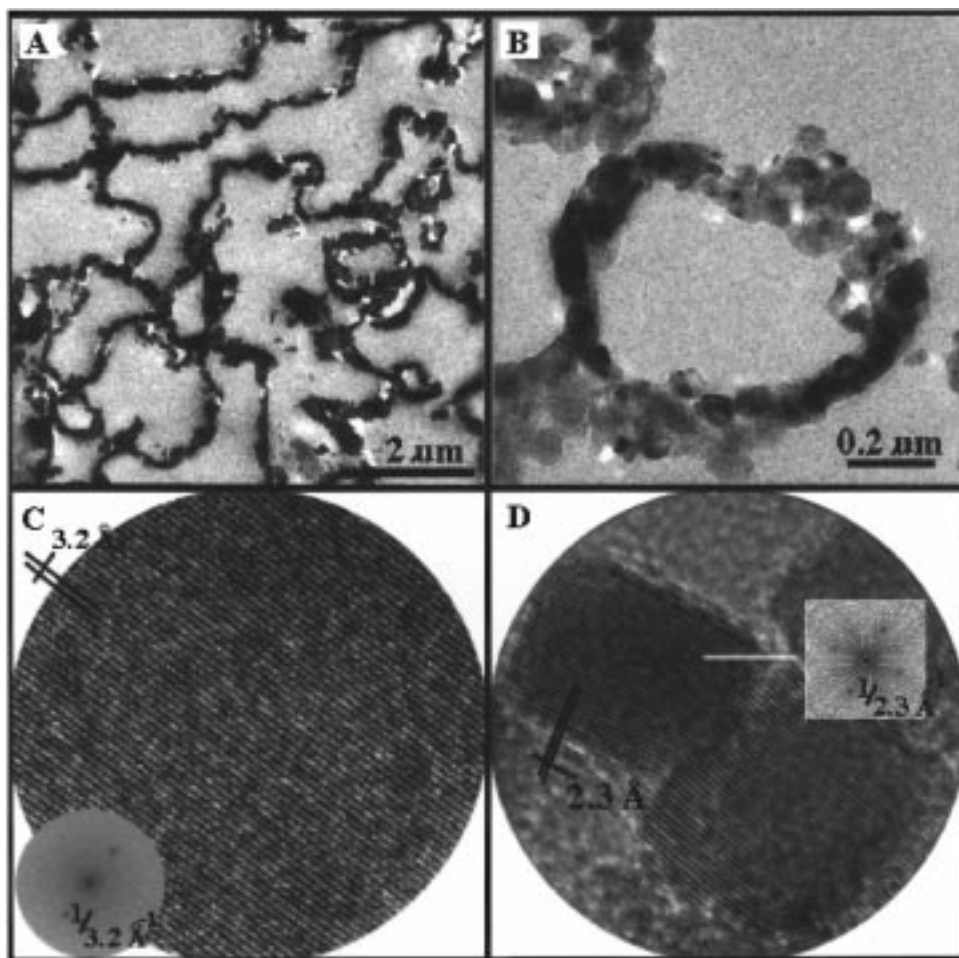

Figure 3. HRTEM images of an ultramicrotomed sample of the titanium dioxide network: (A) continuous connection of the TiO_2 particles; (B) higher magnification; (C and D) lattice plane images of rutile and anatase crystals, respectively, obtained from two different porous TiO_2 networks. Insets show corresponding diffraction patterns.

remaining TiO_2 structure is seen to be a direct plating of the original polymer gel.

High-resolution transmission electron microscopy (HRTEM) images of an ultramicrotomed sample of the titanium dioxide network (Figure 3) show TiO_2 particles ranging from 50 to 150 nm in diameter. The particles are connected in continuous "ribbons" throughout. This contact is essential for the formation of the stable solid network, making it a material that can be easily handled. In Figure 3C the individual particles of this sample can be seen to be in the rutile crystal phase (calcining temperature 990 °C). Similar networks of TiO_2 in the

anatase phase can also be produced by heating the sample to 450 °C, the individual particles in the anatase crystal phase can be seen in Figure 3D. The hydrolyzed sample before calcination was amorphous. Wide-angle X-ray anaylsis confirmed the crystal phase obtained from HRTEM. Carbon was not detected during energy-dispersive X-ray anaylsis of the calcinated sample, indicating complete removal of the organic material.

From TGA experiments the polymer gel starts pyrolyzing at 240 °C and is completely pyrolyzed by 450 °C; 29.5% (by mass) solid remains after heating the amorphous TiO_2 within the polymer gel to 450 °C. The volume porosity

of the polymer gel is measured to be 75%, which is comparable to the theoretical porosity of 79%. The accessible porosity of the TiO_2 network, measured by water uptake, is 89%, which is slightly less than that calculated for an ideal system. The surface area of the network (which had been evacuated for 16 h at 100 °C) was measured by the adsorption (and desorption) of N_2 molecules at 77 K. The BET (Brunauer−Emmett−Teller) surface area obtained for the TiO_2 network (shown in Figure 2) was 9.3 $m^2 g^{-1}$. The surface area of the polymer gel was 9.8 $m^2 g^{-1}$.

The production of coral-like TiO_2 networks is a result that lends itself to enhance many TiO_2 applications. The polymer template is an entity that can be modified in shape and size by the use of different surfactants, different surfactant-to-water ratios, different monomers and different combinations of monomer and surfactant; therefore, the final TiO_2 network could be produced to tailor-fit numerous systems. Of particular importance are flow-through systems, where the TiO_2 network can be fixed and gas or liquid can easily permeate the structure, such as in liquid solar energy cells[14] or photocatalytic air purification applications.[15]

In summary, the polymer gel templating procedure has been shown to provide a means for the production of porous semiconductor networks. The direct plating by TiO_2 has been observed with the acrylamide/glycidyl methacrylate polymer gel. The fact that both the rutile and anatase crystal phases can be produced increases the areas of application for these porous TiO_2 networks. Work is underway to template mesoporous polymer gels to produce smaller scale TiO_2 "coral-structured" networks. This would enhance the overall efficiency of the network due to an increase in the accessible surface area and therefore contact with the reaction media. The incorporation of nanometer-sized metal colloids, such as platinum, into the polymer gel and subsequently into the porous TiO_2 network is also being investigated, as the metal induces substantial modifications of the oxide's semiconductor properties.

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