

Fig. 4. a) Optical micrograph of PS impact specimen fracture surface. b) SEM of PS impact specimen fracture surface. c) Optical micrograph of PS/0.5 wt.-% DRC impact specimen fracture surface. d) SEM of PS/0.5 wt.-% DRC impact specimen fracture surface. e) Optical micrograph of PS/1.0 wt.-% DRC impact specimen fracture surface. f) SEM of PS/1.0 wt.-% DRC impact specimen fracture surface.

is difficult to draw specific conclusions about the mechanism by which DRC modifies PS fracture mechanics, the features of DRC/PS samples are compatible with observations of greater molecular orientation, and suggest the scaffold formed by self assembling molecules may increase viscous flow, multiplanar subcritical defect formation, and crack deflection.

Experimental

Styrene (Aldrich) inhibited with 10–15 ppm 4-*tert*-butylcatechol was added to glass vials containing premeasured amounts of DRC. Sealed vials were ultrasonicated for two minutes and then heated via heat gun with gentle shaking. When DRC had gone into solution, samples were heated for an additional minute to promote supramolecular assembly. After 10 min of ambient cooling to allow for dissipation of excess heat, vials were transferred to a 100 °C oven for polymerization, where a nitrogen atmosphere was maintained to prevent oxidation. After 72 h, caps were removed and vials containing solid polymer were returned to the oven under vacuum to promote evaporation of residual monomer. One day after removal of caps, vials were broken and solid polymer cylinders were returned to the oven under vacuum where they were heated for an additional 24 h before cooling to room temperature.

Portions of all samples were dissolved in tetrahydrofuran and injected into a Waters 2690 gel-permeation chromatography (GPC) unit for molecular weight analysis. Fractions were monitored by a Waters 2410 refractive index detector and calibrated to PS standards. The following molecular weight averages were obtained for each group of polymers: PS: $M_w = 543\,000 \pm 84\,000$, PDI = 2.7 ± 0.2 ; PS/0.5 % DRC: $M_w = 561\,000 \pm 78\,000$, PDI = 2.6 ± 0.2 ; PS/1 % DRC: $M_w = 513\,000 \pm 87\,000$, PDI = 2.7 ± 0.2 .

To prepare Charpy samples, solid polystyrene cylinders were machined into tensile specimens with gauge dimensions $0.25'' \times 0.25'' \times 0.4''$ (1 inch ~ 2.5 cm) by a Bridgeport milling machine connected to a South Western Industries Proto-Track MX2 numerical controller. To promote molecular orientation without cracking, specimens were drawn in uniaxial tension at 4.0 mm min^{-1} with an

MTS Sintech testing machine equipped with a heating chamber set at 108 °C (slightly higher than T_g for PS). At 200 % strain, drawing was stopped and samples were quenched with a water mist and removed from the chamber to preserve orientation. Gauge sections of drawn tensile samples were machined into Charpy impact specimens with dimensions $3.15 \times 3.15 \times 17.5 \text{ mm}$ ($\pm 0.05 \text{ mm}$) and 1 mm deep notches aligned normal to the direction of drawing.

Birefringence measurements were made with a Cary 500 UV-vis spectrophotometer on gauge sections of tensile specimens drawn to 200 % and 1000 % strain at 108 °C. Crossed plastic polarizers (Edmund) were placed on either side of samples so light could not be transmitted through optically isotropic material. Samples were oriented with their axes of drawing at 45° to the polarizer/analyzer pair. The spectrometer was operated in double beam mode while percent transmission was recorded from 400 to 700 nm. Using the method described by Devon and Rogers [13], transmission minima were numbered by order of appearance from 400 nm to 700 nm, and plotted as the ordinate against $1/\lambda$ to provide a linearly fitted curve with slope $1/(L\Delta n)$, where L denotes sample thickness and Δn denotes birefringence.

Optical emission specimens were prepared by adding DR1 dye (Aldrich) to DRC-styrene solutions before gelation. Gels containing DRC and DR1 were polymerized and drawn to 200 % strain at 108 °C. Samples were excited with a linearly polarized, Q-switched Nd:YAG laser (355 nm, 10 Hz, 35 ps) incident normal to their surfaces. Axes of drawing were parallel to the laser polarization direction (i.e., electric field). Forward emissions were collected and recorded by CCD. A polarizer was used to selectively filter parallel (I_{\parallel}) and perpendicular (I_{\perp}) emission components.

SEM samples were mounted on aluminum stubs with double-sided carbon tape and coated in 6 nm gold. Images were collected with a Hitachi 4500 SEM. Error bars in Figures 1 and 2 represent t distribution confidence intervals at 90 %.

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Eggshell Membrane Templating of Hierarchically Ordered Macroporous Networks Composed of TiO₂ Tubes**

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Recently, much effort has been devoted to the synthesis of hierarchically ordered macroporous materials with bimodal porosity because they combine the accessible diffusion path-

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ways of macroporous networks with the high surface area, selectivity, and catalytic or ion-exchange properties of the smaller pore systems.^[1–8] To date, the bimodal porous materials, which are of potential importance in various fields including catalysis and separation techniques, have been prepared usually by employing dual templates with appropriate reaction solutions or nanoparticle building blocks. It is noteworthy that in addition to synthetic templates such as polymer latex particles^[3,5,6] and polyurethane foams,^[8] some biological matrices, including organized bacterial threads,^[1,2] wood cellular structures,^[7] and starch gels,^[4] have been used as templates for the fabrication of macroporous networks constituting bimodal porosity. Interestingly, ordered macroporous structures have also been successfully produced by templating both organic matrix isolated from cuttlebone^[9] and inorganic skeletal plates of echinoids,^[10] which are among the considerable efforts made to develop environmentally benign routes to synthetic materials with sophisticated structural ordering analogous to biominerals. In this paper, we describe a biomimetic strategy for the fabrication of hierarchically ordered macroporous networks composed of TiO₂ tubes comprising anatase nanocrystals by using the intact organic membrane isolated from eggshells as a single template.

Titanium dioxide is well known for its utilization in diverse applications such as photocatalysis and photovoltaics; accordingly, the synthesis of macroporous TiO₂ networks^[6,11–14] and hollow TiO₂ fibers^[15,16] has attracted increasing interest. In particular, sol-gel coating^[17] has been shown to be a simple and versatile method for the preparation of such structured TiO₂ materials. For example, macroporous “coral-like” TiO₂ networks were fabricated by sol-gel coating of polymer gels^[12,13] and cellulose acetate membranes,^[14] whereas TiO₂ tubes were produced by sol-gel coating of electrospun polymer fibers.^[15] However, to the best of our knowledge, the synthesis of hierarchical macroporous networks composed of TiO₂ tubes has not been reported.

In the current work, the sol-gel coating procedure has been applied for the TiO₂ coating of organic eggshell membrane consisting of interwoven shell membrane fibers. It is known that avian eggshells are formed by layered organization of calcified shell and organic eggshell membranes containing collagen types I, V, and X, and glycosaminoglycans.^[18] Eggshell membranes, which are stable in aqueous and alcoholic media and undergo pyrolysis on heating, consist of the outer shell membrane, inner shell membrane, and limiting membrane surrounding the egg white.^[19] The outer shell membrane, which can be easily isolated from eggshells, was used as a removable template for the synthesis of hierarchically ordered macroporous TiO₂ in this work. Facile sol-gel procedures, which are built on the soaking method previously used for the TiO₂ coating of polymer gels^[12,13] and membranes,^[14] were used for templating the eggshell membrane. The sol-gel coating procedure was readily carried out by the hydrolysis of tetra-*n*-butyl titanium (TBT) in neutral solutions^[14] or in acidic solutions involving acetyl acetone (acac).^[20] The eggshell template was removed upon subsequent heat treatment at 500 °C.

Figure 1 shows a typical scanning electron microscopy (SEM) image of the eggshell membrane used as the template in this work. It reveals that the membrane is a macroporous network composed of interwoven and coalescing shell membrane fibers ranging in diameter from 0.5 to 1.5 μm. The pres-

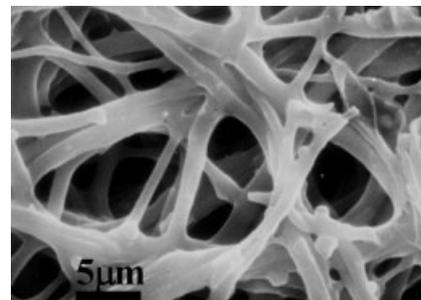


Fig. 1. SEM image of the eggshell membrane template.

ence of macropores with pore sizes of about 5 μm is evident. The eggshell membrane contains amines, amides, and carboxylic surface functional groups that may interact with the titanium precursor, anchoring the precursor molecules to the membrane fiber surface where titania coating can occur. SEM images of a porous TiO₂ network obtained from sol-gel coating of the eggshell membrane under neutral conditions are shown in Figure 2. As shown in Figure 2a, the obtained porous TiO₂ network is composed of interwoven and coales-

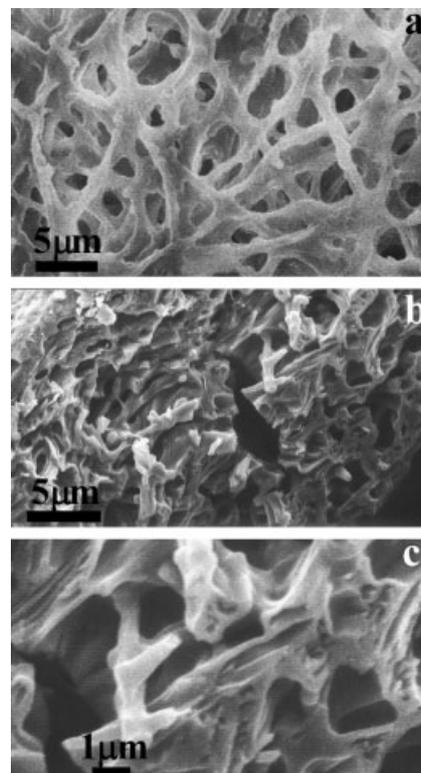


Fig. 2. SEM images of the TiO₂ network templated by the eggshell membrane using the neutral hydrolysis method: a) overview of the surface, b) overview of the cross section, and c) higher magnification of the cross section showing the broken hollow tubes.

cing TiO₂ fibers ranging in diameter mainly from 0.3 to 1.2 μm, slightly smaller than the diameters of the membrane fibers. On the other hand, the pore sizes of the macropores are significantly decreased (typically 1.5 μm), indicating a considerable shrinkage during template removal. A SEM image of the cross section of the TiO₂ network shown in Figure 2b suggests that the product is actually a thin film with a thickness of about 25 μm. An enlarged image shown in Figure 2c clearly shows the hollow nature of the TiO₂ fibers constituting the network, suggesting that the macroporous network is composed of TiO₂ tubes, resulting in a hierarchically ordered macroporous material. It can be observed that the wall thickness of the TiO₂ tubes is usually less than 200 nm.

Transmission electron microscopy (TEM) images evidenced the presence of hollow TiO₂ fibers or TiO₂ tubes. Figure 3a shows a relatively wide TiO₂ tube with a diameter of about

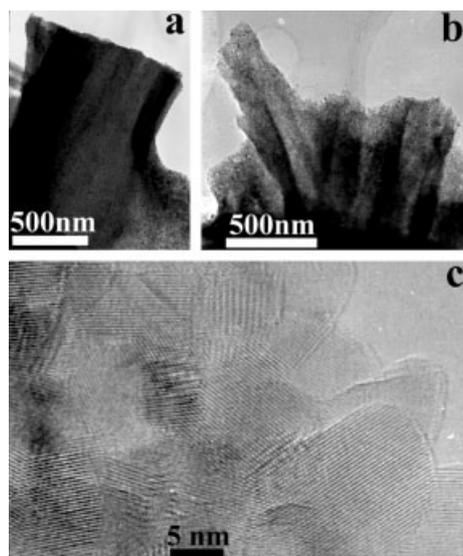


Fig. 3. TEM (a,b) and HRTEM (c) images of the TiO₂ network templated by the eggshell membrane using the neutral hydrolysis method.

1 μm and a wall thickness of about 160 nm, whereas Figure 3b shows three thin TiO₂ tubes with diameters of ~0.3 μm and wall thicknesses of ~120 nm. Closer TEM observations also showed that the TiO₂ tubes comprised nanoparticles ranging in diameter from 5 to 15 nm. A typical high-resolution TEM (HRTEM) image of the tube walls (Fig. 3c) revealed the presence of many nanocrystals showing clear anatase lattice fringes, indicating that the TiO₂ tubes consisted of anatase nanocrystals. The related X-ray diffraction (XRD) pattern confirmed that anatase was the only crystal phase present in the product. An average crystallite size of about 10 nm was estimated according to the line width analysis of the anatase (101) diffraction peak based on the Scherrer formula, which is in good agreement with the TEM and HRTEM observations.

Thermogravimetric analysis (TGA) experiments on the organic membrane/inorganic hybrid before calcination suggested that the eggshell membrane started pyrolyzing at 270 °C and was completely pyrolyzed by 500 °C, leaving 23.6 % (by mass) inorganic solid. Since titania involved in the

organic membrane/inorganic hybrid resulting from sol-gel coating was amorphous, it can be deduced that the crystallization of amorphous titania to anatase nanocrystals occurred during the calcination accompanying the membrane pyrolysis. The specific surface area of the final TiO₂ network was measured to be 62 m²g⁻¹ and the Brunauer–Emmett–Teller (BET) average pore size was estimated to be 8.2 nm, indicating the presence of mesopores within the tube walls comprising TiO₂ nanocrystals. The surface area value is rather high and comparable to macroporous TiO₂ material obtained by sol-gel coating of polymer gels^[13] and membranes.^[14] The combination of high surface area and high porosity of macroporous TiO₂ networks is expected to enhance the wide and ever-growing range of applications of titania.^[13] Moreover, the unique hierarchical characteristic of the current macroporous network composed of TiO₂ tubes comprising anatase nanocrystals may endow it with unusual photocatalytic and photovoltaic properties that would be of potential importance in many applications. Apparently, the unique network structure of eggshell membranes composed of biomacromolecular fibers provides a novel template for the biomimetic templating of the hierarchical macroporous TiO₂ networks, which also demonstrates the advantage of using this biological structure.

A porous TiO₂ network was also produced by sol-gel coating of the eggshell membrane under highly acidic conditions (pH 1) where a chelator, acetyl acetone, was present. Similarly, the obtained TiO₂ network is composed of interwoven hollow TiO₂ fibers ranging in diameter mainly from 0.4 to 1.4 μm (Fig. 4). However, the pore sizes of the macropores (typically 4 μm) are much larger than that for the TiO₂ network ob-

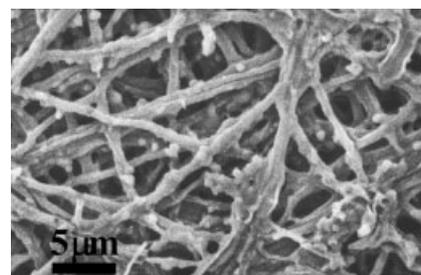


Fig. 4. SEM image of the TiO₂ network templated by the eggshell membrane using the acidic hydrolysis method.

tained under neutral conditions, indicating that there was just a slight shrinkage during template removal and crystallization of titania. The acidic hydrolysis conditions, as well as the slow hydrolysis process of the precursor due to the complexation of acetyl acetone with TBT, could lead to a more homogeneous TiO₂ coating of the membrane fibers, resulting in a relatively tough network that can largely withstand the shrinkage during template removal and crystallization of titania upon calcination.

In summary, the eggshell membrane templating procedure has been shown to provide a facile, biomimetic method for the synthesis of hierarchically ordered TiO₂ material: It has a macroscopic morphology of a thin film with a thickness of

about 25 μm ; the film exhibits a microstructure of macroporous networks composed of interwoven TiO_2 tubes with diameters of less than 1.4 μm ; the tube walls consist of anatase nanocrystals around 10 nm in diameter. The unique hierarchical structure together with the high surface area and substantial porosity makes this material attractive for a number of applications. Work is underway to test the catalytic and photovoltaic properties of this material. The templated synthesis of similar macroporous networks composed of other oxide materials such as ZrO_2 and SiO_2 using the eggshell membrane is also in progress.

Experimental

Separation of Eggshell Membrane: Commercial eggs were gently broken and emptied via the blunt end. The eggshells were washed with water and then the inner shell membrane and the limiting membrane were manually removed. The remaining eggshell was rinsed in 1 M HCl to dissolve the CaCO_3 shell, leaving the organic outer shell membrane. After the outer shell membrane was washed with water thoroughly, a solvent exchange process for the membrane was carried out by slowly increasing the ratio of 2-propanol to water until the membrane was in high-purity 2-propanol (99.7%), similar to the case of polymer gels [12]. Then the dehydrated eggshell membrane was used as a template for the TiO_2 coating.

Titanium Dioxide Templating: Two simple procedures were used for the TiO_2 coating of the eggshell membrane. In the first method, the neutral hydrolysis method, the eggshell membrane was simply dipped into a closed vessel containing a 10 vol.-% solution of tetra-*n*-butyl titanium (TBT) in 2-propanol for 1 h. The membrane filled with the precursor TBT was then transferred to 2-propanol/water (50:50 v/v) for 1 h where hydrolysis and condensation reactions occurred. After removal from this solution, the membrane/inorganic hybrid was dried in air at room temperature. The yellow hybrid material was then heated to 500 °C in an oven in air to burn off the organics and crystallize titania. In the second method, the acidic hydrolysis method, the eggshell membrane was dipped into a solution containing 2 g of TBT, 0.35 g of acetyl acetone (acac), and 19 g of 2-propanol whilst stirring for 2 h. Subsequently, a dilute HCl solution was added into the solution to control a low pH (about 1.0). The molar ratios of the ingredients were as follows: TBT/acac/ H_2O /2-propanol = 1:0.5:1:36. After stirring for another 3 h, the resultant membrane/inorganic hybrid was removed and treated in a manner identical to the first method.

Characterization: SEM measurements were performed with an Amray 1910FE microscope. TEM and HRTEM investigations were conducted on a JEM-200CX microscope and a Hitachi H-9000HAR microscope, respectively. Powder XRD patterns were recorded on a Rigaku Dmax-2000 diffractometer with $\text{Cu K}\alpha$ radiation. TGA was carried out on a LCT-1 type thermoanalyzer in air. The specific surface area and average pore size were obtained from BET analysis after nitrogen sorption using a Micromeritics ASAP 2010 system.

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Synthesis and Micropatterning of Semiconducting Polypyrrole Nanofilms by a Two-Step Deposition/Polymerization Process**

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With the discovery of novel electrical and optical properties in conjugated polymers, it has become desirable to use these polymers as active layers in light-emitting diodes (LEDs), field-effect transistors, photovoltaic cells, and sensors in the form of thin films.^[1,2] Compared with inorganic semiconductors, polymeric semiconductor materials have the advantages of being flexible, inexpensive, and their properties can be tailored by modifying the molecular structure.^[1] Typically, conjugated polymers must be modified either by adding flexible side groups to the polymer backbone, or by copolymerization to render the conjugated polymer sufficiently soluble so that solution-based techniques can be used to process the materials into thin films. There is currently very active research to develop conjugated polymers with good processability while retaining the desired electrical or optical properties.^[3,4] An alternate strategy, however, is to deposit conjugated polymers in-situ on the desired substrate by vacuum deposition. Vacuum deposition of inorganic thin films has played a vital role in the semiconductor and coating industries. Various vacuum deposition processes have been developed to grow high quality metal, semiconductor, or ceramic films. On the other hand, the study of vacuum deposition of organic materials, especially polymers, is a continuously developing field. The objective of this research is to investigate the possibility of preparing conjugated polymers (without the necessity of side group

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