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Enhanced Photocatalytic Performance of Nanocrystalline TiO_2 Membrane by Both Slow Photons and Stop-band Reflection of Photonic Crystals

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An nc-TiO_2/SnO_2 inverse opal composite membrane was fabricated, the photo-activity of which was significantly enhanced by utilizing both slow photons and stop-band reflection of the photonic crystal layer. The materials of the photonic crystal layer must be transparent in the area of adsorption edge of the nc-TiO_2, so that SnO_2, having much greater electronic band gap than TiO_2, was used for the materials of the photonic crystal layer. The photonic band-gap of the SnO_2 photonic crystal was designed at the semiconductor band gap of TiO_2 to harvest slow photons in the interface between the SnO_2 layer and the TiO_2 layer. The two layer structure makes it possible to couple the stop-band reflectivity of the photonic layer to the photocatalyst. Composite membranes can improve solar energy harvesting and substantially improve photocatalysts for photolysis and photochemical degradation of environmental pollutants. *AIChE J*, 58: 568–572, 2012
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Introduction

Titanium oxide (TiO_2) is widely used as a photocatalyst for environmental cleanup and photolysis of water. As a photocatalysts, it is chemically stable in reactive environments, is nontoxic and is available at low cost.[1,2] However, the solar energy harvesting efficiency of TiO_2 is low. Its moderate electronic band-gap ($Eg = 3.2eV$) limits the useful range of the solar spectrum that can excite TiO_2 to a few percent. The lifetimes of the photo-excited states are short, and are frequently quenched before reaching the surface where reactants are adsorbed. Despite its shortcomings TiO_2 has been the photocatalyst of choice for scientific studies since the discovery of photocatalytic splitting of water on TiO_2 e1ectrodes in 1972.[3] Extensive efforts have attempted to enhance the photocatalytic efficiency of TiO_2 by chemists, physicists, and chemical engineers; success has been limited, and there are few commercial applications of photocatalysis. We seek to improve the efficiency of TiO_2 photocatalysts by increasing light absorption in thin films of nanocrystalline thin films.

Energy harvesting efficiency by TiO_2 may be enhanced by either reducing the band-gap to more favorably match the solar spectrum, or by increasing the transport of excitons to the surface for chemical reaction.[4,5] Solar absorption may be enhanced by decreasing the band-gap to access a larger portion of the solar spectrum. TiO_2 can be doped with impurities to reduce the band gap energy,[6,7] or dyes may be added to absorb photons at lower energies.[1,8] However, increasing the wavelength response range sometimes decreases the photocatalytic efficiency of TiO_2 because of the lower redox potential of electrons and holes created by photoexcitation. The most effective approach to improve photocatalytic activity of TiO_2 is to enhance absorption of thin films without chemical compositional changes.

Thin films are necessary to permit electrons and holes to migrate to the interface between the TiO_2 and reactant before quenching. Unfortunately, the absorptivity of TiO_2 is small and light passes through thin films of TiO_2 with only a small fraction of the sub-band-gap light absorbed. If the light could be trapped in thin TiO_2 films until it is absorbed, energy harvesting would be enhanced.

Recently, Mallouk and coworkers[9,10] reported a 26% increase of the short current photocurrent of a dye-sensitized solar cell (DSSC) constructed of a bilayer structure of a thick nanocrystalline TiO_2 (nc-TiO_2) layer on top of a TiO_2 inverse opal. The photonic stop band of the inverse opal was 610 nm, close to the absorbance edge of the dye used in the DSSC. They attributed the increased current to light absorption by the dye. Subsequent theoretical calculations by Mihi and Míguez[11] indicated that the increased efficiency could be explained by the inverse opal acting as a dielectric mirror, which increased the effective pathlength of light through nc-TiO_2 layer, permitting greater absorption.

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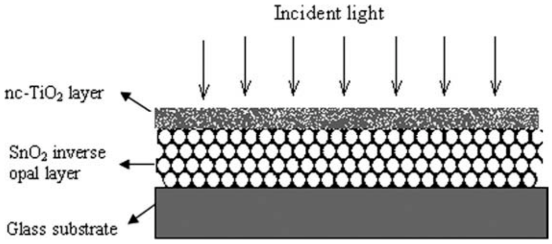

Figure 1. The structure of the composite photocatalytic membrane.

Ozin and coworkers demonstrated the use of TiO_2 photonic crystals to improve photocatalytic activity. They fashioned the photonic crystal to have a photonic band-gap close to the electronic band-gap of TiO_2. The photonic crystal slowed down the phase velocity of light, creating ‘‘slow-photons’’ that are more effectively absorbed by the TiO_2 nanocrystals.[12,13] They absorbed methylene blue into their photonic crystals and showed that photodegradation was enhanced by matching the photonic crystal band-gap to the electronic band-gap of TiO_2. This report by Ozin and coworkers appears to be the first article specifically addressing photocatalytic activity enhancement by photonic crystals.

Photonic crystals have a periodic dielectric contrast at the length scale of the wavelength of light. Bragg diffraction forbids light with certain wavelength to propagate through the material. This gives rise to stop-band reflection, and the range of energies that is reflected back depends on the periodicity and dielectric contrast of the photonic crystal. At the frequency edges of these photonic stop bands, photons propagate with strongly reduced group velocity in the periodic photonic structures, giving rise to ‘‘slow photons’’ that have a long-effective path length through the photonic crystal. These slow photons can be observed in disfigurement of the periodic photonic structures at energies just above and below the photonic stop band[14]

Ozin and coworkers used the slow photons of the photonic band gap to amplify the photoactivity of TiO_2 within the photonic crystal, but the reflected light of stop-band reflection was not used. To use both the slow photons of the photonic band gap and the band gap reflection, we constructed a composite photocatalytic membrane by coupling a SnO_2 photonic crystal layer to a nc-TiO_2 catalyst membrane. The photonic band gap of the SnO_2 layer was designed to match the electronic stop band of TiO_2 semiconductor. The structure of the composite membrane is shown in Figure 1. By separating the functionality of the photonic crystal and the photocatalyst, it also permits greater flexibility in choosing materials for the two.

When sunlight hits on the nc-TiO_2 layer, a fraction of the light with shorter wavelengths than the electronic stop band of TiO_2 is absorbed creating electron hole pairs that migrate to the surface of the nc-TiO_2 catalyst membrane. Light with wavelengths longer than the electronic stop band of TiO_2 passes through the nc-TiO_2 layer. Normally, only a small fraction of the short wavelength light is absorbed in the thin TiO_2 film. By using a photonic crystal as a dielectric mirror, it is possible to increase the light path through the thin TiO_2 layer and enhance the absorption of light.

The material in the photonic crystal should be transparent to light at energies above the electronic stop band of the TiO_2 to minimize light attenuation within the photonic crystal. It should also have a high dielectric contrast at higher energies to reflect the light at energies above TiO_2’s band gap. The photonic crystal layer acts as a dielectric mirror for the slow photons. Light is absorbed by evanescent waves upon reflection at the interface between the photonic crystal and TiO_2. The slow photons in the photonic crystal create a long effective path length for the evanescent waves so most of the light capable of exciting TiO_2 does so.

The photonic crystal is a multiple internal reflection crystal with an absorbing film coating one surface of the crystal. Light is absorbed by the nc-TiO_2 layer. There is no alteration of the band gap of the TiO_2 so the redox potential of electrons and holes is retained. The photocatalytic activity of the composite photocatalyst-photonic crystal membrane should be not only higher than that of a plain nc-TiO_2 membrane, but also higher than that of TiO_2 fashioned as inverse opals as reported by Ozin and coworkers,[12,13] because the composite membrane proposed in this article can use both slow photons and stop-band reflection produced by photonic crystals.

We chose tin oxide (SnO_2) for the photonic crystal, because SnO_2 has a larger electronic band gap ($Eg = 3.8$ eV) than TiO_2 and is almost transparent in the electronic stop band of TiO_2. SnO_2 is also chemically stable and inexpensive making it a near ideal material of choice for the photonic layer. As it is difficult to prepare monodispersed SnO_2 spheres, the photon crystals were constructed as SnO_2 inverse opal structure.

Experimental

Preparation of SnO_2 liquid-phase deposition (LPD) solution

SnF_2 was dissolved into DI water. Drop-wise addition of H_2O_2 resulted in precipitation of $SnO_2{\cdot}nH_2O$. The precipitate was washed with DI water repeatedly, dried at room temperature, and then dissolved into 40% hydrofluoric acid. The SnO_2 LPD solution was prepared by pouring 1.5mol/L H_3BO_3 solution into the SnF_4-HF solution at the final concentrations of the 0.025 mol/L SnF_4-HF and 0.2 mol/L H_3BO_3. The H_3BO_3 was used as an F^{-1} scavenger.

SnO_2 was formed through the ligand-exchange hydrolysis of metalfluoro complexes. Boric acid is added to the stannum-fluoro complex solution to react with the F^{-1} ions forming BF_4, shifting the hydrolysis equilibrium to form SnO_2, as follows.

$$H_3BO_3 + 4HF \Leftrightarrow BF_4^- + H_3O^+ + 2H_2O$$

$$SnF_x^{(x-4)-} + nH_2O \Leftrightarrow SnO_2 + xF^- + 2nH^+$$

Preparation of SnO_2 inverse opal layer

Quartz substrates were immersed vertically into a dispersion solution of monodispersed polystyrene (PS) particles, which were prepared through emulsion polymerization method.[15] The dispersion solution of PS with the quartz substrates was maintained at 50°C to slowly evaporate water and a PS opal layers were deposited on the quartz substrates. The quartz substrates with PS opal layers were immersed vertically into the SnO_2 LPD solution at 30°C and the SnO_2 precipitated and filled into voids of the PS opal layer. After maintaining in the solution for about 10 h, the quartz substrates with PS opal/SnO_2 were removed from the SnO_2 LPD solution, washed with DI water, and dried at room temperature. The SnO_2 inverse opal layer was obtained by calcination of the quartz substrates in air at 450°C for 2 h.

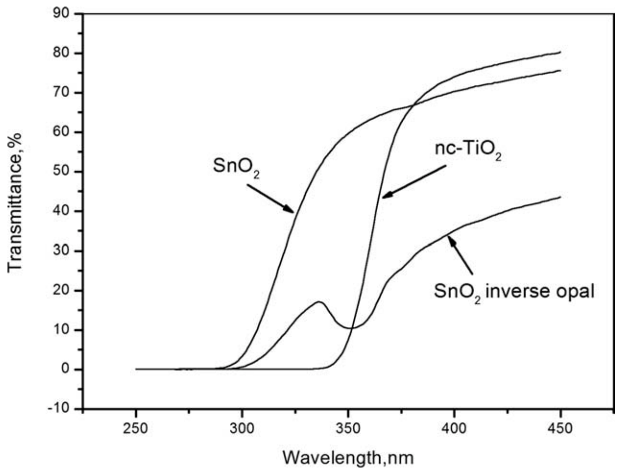

Figure 2. The UV-vis transmittance spectra of nc-TiO_2 and SnO_2 and SnO_2 inverse opal membranes.

Preparation of nc-TiO_2/SnO_2 inverse opal composite membranes

The nc-TiO_2 was prepared through sol-gel method. A 40-mL of mixture of titanium isopropoxide and iso-propylenol (25:15 volume) was added into 150-mL dilute aqueous solution of HNO_3, and TiO_2 gel was precipitated from the reaction mixture by the hydrolysis of the titanium isopropoxide. The solution containing the TiO_2 precipitate was heated to 80°C and kept at 80°C for 8 h, then transferred into an autoclave, heated to 220°C and hydro-treated for 12 h. An nc-TiO_2 dispersion was obtained by cooling down the TiO_2 dispersion. Before spin coating the dispersions, they were sonicated for 10 min. The nc-TiO_2 was coated onto the SnO_2 inverse opal membrane through spin-coating, and the thickness of the nc-TiO_2 layer was controlled by spin speed rate and the solid content of the nc-TiO_2 sol solution. The nc-TiO_2/SnO_2 inverse opal composite membranes were obtained through calcining the membranes at 450°C for 2 h.

Photodegradation performance test

The photodegradation of methyl orange (MO) was used as the probe reaction to test the photocatalytic activity of the membranes. The concentration of the MO was 10 mg/L. A photocatalyst membrane of 25 × 10 mm was fixed in the center of a 1 mm × 1 mm × 4.5 cm quartz ultraviolet (UV) cell and 3-mL MO solution was put into the UV cell. The UV cell was then placed into a light tight box and irradiated by a 150W Xe lamp; the intensity at the UV cell was 3.5 mW/cm^2. The concentration change of the MO was followed through recording the UV-Vis spectra of the MO solution at different time down the reaction using a UV-vis spectrometer. The reaction conditions were the same for all experiments.

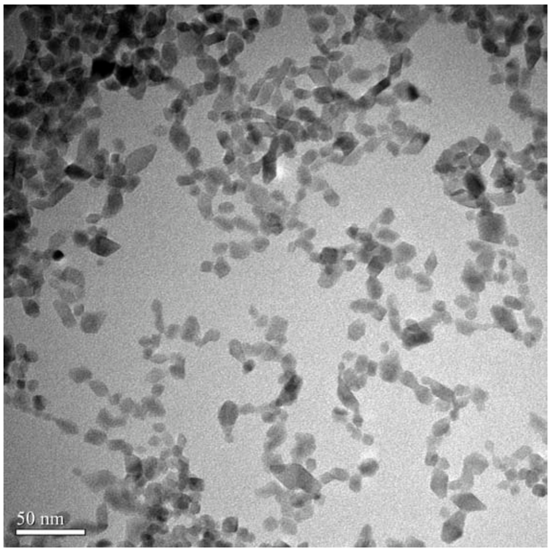

Figure 3. The TEM of the prepared nc-TiO_2 particles.

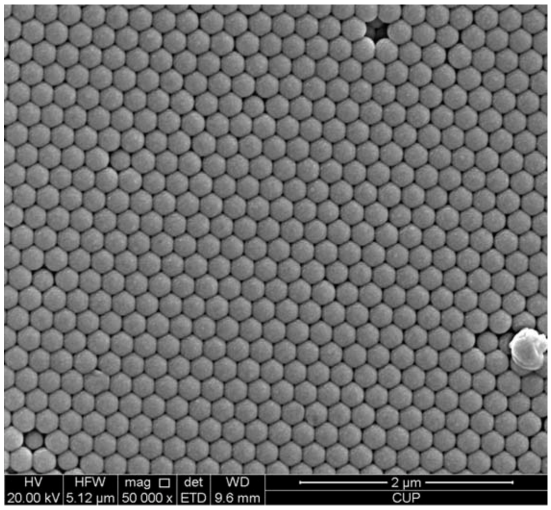

Figure 4. The SEM of the top view of the PS opal layer deposited on a quartz substrate.

Results and Discussions

The UV-vis absorption spectrum SnO_2 and TiO_2 layers are shown in Figure 2; light between 300 and 350 nm is able to propagate through the SnO_2 photonic crystal creating slow photons that can be absorbed by TiO_2. The thin film of TiO_2 was from nanocrystalline anatase particles. X-ray diffraction (XRD) of the nc-TiO_2 particles indicates that the prepared TiO_2 particles were anatase. The transmission electron microscopy (TEM) of the nc-TiO_2 particles as shown in Figure 3 shows that these particles were of 5∼20 nm.

SEM images of the prepared PS opal layer and the prepared SnO_2 inverse opal membrane, as shown in Figures 4 and 5 respectively, reveal that the PS spheres were highly ordered packed as the opal layer and the its replica-- SnO_2 inverse opal membrane, prepared by filling SnO_2 into the PS opal and then removing PS spheres, inherited the ordered structure of the PS opal.

An SEM image of the cross-section of the prepared nc-TiO_2/SnO_2 inverse opal composite membrane is shown in Figure 6, indicating that the thicknesses of the SnO_2 photonic layer and the nc-TiO_2 layer are ∼1.2 and ∼0.55 um, respectively.

The photonic band gap of the SnO_2 inverse opal was obtained at normal incidence to compare to the electronic band gap of TiO_2. A sample of the SnO_2/opal PS membrane was calcined at 450°C before coating the nc-TiO_2 to obtain a SnO_2 inverse opal. The UV-Vis transmittance spectrum of the SnO_2 photonic crystal is compared with the UV-vis absorption spectra of TiO_2 and SnO_2 in Figure 2. The

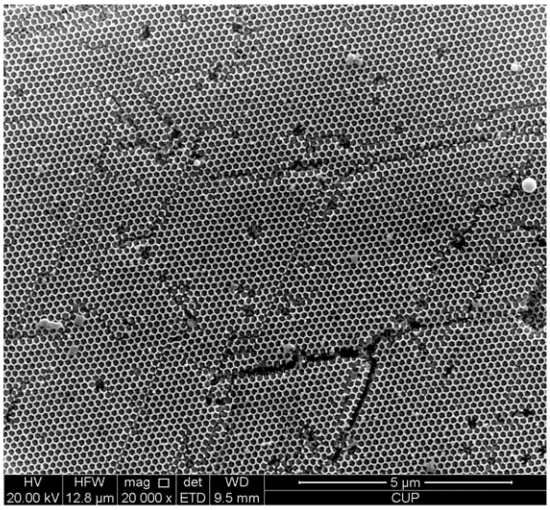

Figure 5. The SEM of the top view of the SnO_2 inverse opal composite membrane.

photonic band gap is evident at 335∼370 nm, overlapping with the electronic band gap of the anatase TiO_2.

Photocatalytic activity of the membranes was tested using decomposition of methyl orange (MO) in water solution as the probe reaction. The MO-containing solution was contained in a UV-cell, in which a TiO_2 photocatalyst substrate was suspended. The UV cell was irradiated by a Xe lamp and in a light tight box. The UV cell was removed periodically and the UV-vis spectrum recorded to determine the MO concentration. The photocatalytic decomposition of the MO follows first-order decay rate law. The decay rate constant was obtained from the logarithmic plot of the relative concentration of the MO as a function of time. It was previously reported that the SnO_2 added into the TiO_2 as a doping agent can increase the photoactivity of the TiO_2,[16,17] because the conduction band of SnO2 is lower than that of the TiO2, the former acts as a sink for the photo-generated electrons thereby making charge separation more efficient and improving the photocatalytic activity. To elucidate the photoactivity produced by the slow photons, the photocatalytic activity of an nc-TiO_2 membrane supported on quartz and an nc-TiO_2 membrane supported on a dense SnO_2 layer were compared with the nc-TiO_2 layer supported on the SnO_2 photonic crystal. For convenience, the composite membrane of nc-TiO2/ SnO_2 inverse opal, the membrane of nc-TiO_2 layer supported on a dense SnO_2 layer and the membrane of nc-TiO_2 layer supported on quartz are designated as nc-TiO_2/SnO_2-i-opal-352, nc-TiO_2/dense-SnO_2 and plain nc-TiO_2, respectively. Figure 7 shows the logarithmic plot of the concentration of the MO as a function of time for variety of membranes. The photocatalytic activity of these membranes is in the order of nc-TiO_2/SnO_2-i-opal-352 > nc-TiO_2/dense-SnO_2> plain nc-TiO_2; the decay rate constants of MO on these membranes are 0.109 h^{-1}, 0.0787 h^{-1}, and 0.0557 h^{-1}, respectively. The increased decomposition rate indicates greater absorption of the incident radiation. The greater photocatalytic activity of the nc-TiO_2/dense-SnO_2 membrane compared to a plain nc-TiO_2 membrane is the result of the SnO_2 acting as a sink for the photo-generated electrons thereby making charge separation more efficient. The light absorption is further enhanced by employing a SnO_2 photonic crystal with "slow photons."

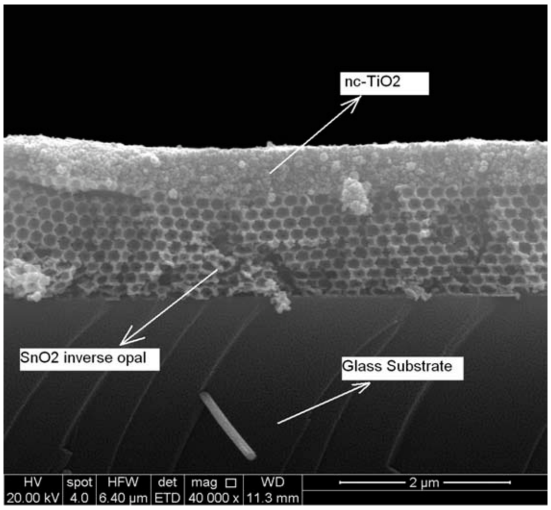

Figure 6. The SEM of the cross-section of the nc-TiO_2/ SnO_2 inverse opal composite membrane.

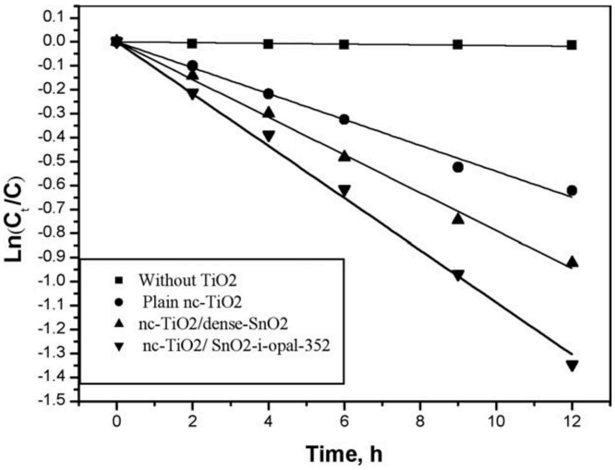

Figure 7. Photocatalytic degradation kinetic curves of MO.

(Reaction condition: 20°C, 3 mL 10 ppm MO in 1 cm × 1 cm × 4.5 cm UV cell, 3.5 mW/cm^2 radiation of Xe lamp, and 1 cm × 2.5 cm area of the photocatalyst).

The reason why the photoactivity of the nc-TiO_2/SnO_2-i-opal-352 composite membrane is higher than nc-TiO_2/dense-SnO_2 membrane is that the former makes use of the slow photons at the stop band reflection produced by the SnO_2 photonic crystal layer. The slow photons are produced at the interface between the nc-TiO_2 layer and the SnO_2 photonic crystal layer enhancing absorption and the photoactivity of the nc-TiO_2 layer.

The key difference in light energy utilization between Ozin's membranes and our composite membranes is that more photons near the external surface of the composite membrane are utilized. The composite structure we introduced also exploits both slow photons and stop band reflection, while the TiO_2 inverse opal membranes reported by Ozin and coworkers used only slow photons and the stop band reflection energy was wasted. Furthermore, Ozin used the internal surface area of the TiO_2 inverse opal and all their reactant was adsorbed on the TiO2 surface before irradiation. They had a stoichiometric reaction. In contrast, our membranes had sustained catalytic cycles, the MO adsorbed from solution, reacted, products desorbed and the catalytic site was restored.

The coupling of photonic crystals with photocatalysts can offer a variety of novel fabrication possibilities.

Conclusions

We fabricated an nc-TiO_2/SnO_2 inverse opal composite membrane, the photoactivity of which was significantly enhanced by utilizing both slow photons and stop-band reflection of the photonic crystal layer. The materials of the photonic crystal layer must be transparent in the area of adsorption edge of the nc-TiO_2, so that SnO_2, having much greater electronic band gap than TiO_2, was used for the materials of the photonic crystal layer. The photonic bandgap of the SnO_2 photonic crystal was designed at the semiconductor band gap of TiO_2 to harvest slow photons in the interface between the SnO_2 layer and the TiO_2 layer. The two-layer structure makes it possible to couple the stop-band reflectivity of the photonic layer to the photocatalyst. Composite membranes can improve solar energy harvesting and substantially improve photocatalysts for photolysis and photochemical degradation of environmental pollutants.

Acknowledgments

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