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The effect of photonic band gap on the photo-catalytic activity of nc-TiO_2/SnO_2 photonic crystal composite membranes

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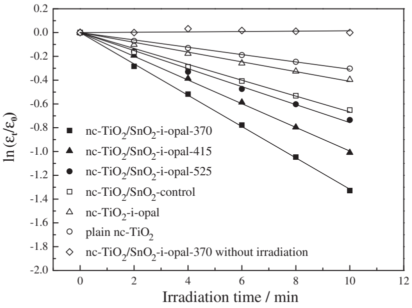
HIGHLIGHTS

- nc-TiO_2/SnO_2 photonic crystal composite membranes were fabricated.
- The photocatalytic activity of the composite membranes was greatly enhanced.
- The nc-TiO_2 harvests slow photons produced by the SnO_2 photonic crystal layer.
- The closer the PBG to the EBG of TiO_2, the greater the catalytic activity.

GRAPHICAL ABSTRACT



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ABSTRACT

nc-TiO_2/SnO_2 photonic crystal composite membranes were prepared by depositing nanocrystalline TiO_2 layers on top of inverse opal SnO_2 photonic crystals films. The photonic band gap of the SnO_2 photonic crystals layer was tuned by changing the particles size of polystyrene microspheres. Photons trapped in the SnO_2 photonic crystal layer are more effectively absorbed by TiO_2 at the TiO_2/SnO_2 interface creating photoelectrons that assist in oxidation reactions. It was shown that the closer the photonic band gap of the phonic crystals layers matches the electronic band gap of TiO_2 catalyst layer, the higher the photocatalytic activity of the composite membranes. The photo-activity of TiO_2 can be enhanced by the synergistic effect of photonic crystal light localization at the SnO_2/TiO_2 interface.

1. Introduction

Titanium oxide (TiO_2) has been the most useful photocatalytic catalyst in environmental cleanup, solar cells and photolysis of water, owing to its good photocatalytic performance, high chemical stability, low toxicity, availability and low price [1–3]. The photocatalytic activity of TiO_2 is limited by the small portion of the solar spectrum absorbed by TiO_2 owing to its large electronic band gap (EBG) (Eg = 3.2 eV). Various strategies have been adopted for improving the energy harvesting efficiency of TiO_2. They can be classified as morphological modifications, which increase surface area and porosity of the TiO_2 layer [4–6], chemical modifications, which incorporate additional components in the TiO_2 to enhance the absorptivity of light or reduce the EBG for photoexcitation [7–9], and combination of morphological modification and chemical modification [10,11].

Monodispersed nanoparticles [12] and one dimensional titania nanostructures (nanowires, nanorods, nanotubes, nanobelts, and the like) [13–15] have been used as TiO_2 photocatalysts that attempt to minimize the exciton diffusion distance to the particle surface and increase catalyst surface area. Mesoporous thin films

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of TiO_2 have been prepared with controlled porosity and pore size which show enhanced activity for photodecomposition of organic dyes [16,17].

TiO_2 can be doped with impurities in order to reduce its EBG energy [18–22]. Photosensitive dyes may be added to absorb photons of lower energies and produce electrons and then transfer the electrons to TiO_2 [23–25]. However, increasing the wavelength response range sometimes decreases the photocatalytic efficiency of TiO_2, because the photoelectrons are at a lower redox potential. Additionally exciton recombination is catalyzed by structural defects traps in the doped TiO_2 [2,23].

Recently Mallouk and co-workers [26,27] reported that when an inverse opal nano-crystalline TiO_2 was used as the anode of a dye-sensitized solar cell (DSSC), the short circuit photo-current of the DSSC was increased by 26%. Dye (Ruthenium 535 bis-TBA) was adsorbed on the internal surfaces of the TiO_2 inverse opal. The center of photonic band gap (PBG) of the inverse opal was 610 nm ($E_{gap} = 2$ eV), matching the absorbance edge of the dye. The increased photo-current was attributed to light-trapping within the inverse opal nano-crystalline TiO_2 and therefore the enhanced light absorption by the dye in the photonic crystal. Subsequently, Mihi and Míguez provided insight into the origin of this enhancement through theoretical calculations [28]: the inverse opal acting as a dielectric mirror which increased the effective path length of light through nc-TiO_2 layer, resulting in greater absorption of light by the dye at those wavelengths. Very recently, Mihi et al. prepared silica inverse opal films and then transferred the preformed three-dimensional photonic crystals onto DSSCs; the power efficiency of the solar cell with photonic crystal was 39% better than a reference cell [29]. O'Brien et al. reported that the photoconductivity in a thin semiconductor (a-Si:H) film can be enhanced by depositing a silica opal photonic crystal onto the backside of this film. They obtained 130% enhancement of photoconductivity in the film by designing the film thickness and the PBG [30].

Ozin and co-workers showed that a TiO_2 inverse opal photonic crystal with a PBG close to the EBG of TiO_2 (387 nm) could enhance photocatalysis. They adsorbed methylene blue into photonic crystals and showed that the rate of photodegradation was significantly enhanced. They suggested that the photonic crystal slowed down the phase velocity of light, creating "slow-photons" that were more effectively absorbed by the TiO_2 nanocrystals [31,32]. This report by Ozin and co-workers appears to be the first paper specifically focusing on photocatalytic activity enhancement by photonic crystals. In 2008, Ozin and co-workers reported that the photocatalytic activity of TiO_2 was further increased through adding Pt onto the TiO_2 inverse opal photonic crystals [33].

Photonic crystals contain regularly repeating regions of high and low dielectric constant. Photons propagate through this structure – or not – depending on their wavelength. Disallowed bands of wavelengths are called photonic band gaps (PBG). A photonic crystal traps light by internal reflection at the wavelength of the PBG. The light trapping gives the appearance of reduced photon velocity or slow photons in the photonic crystal. Ozin's group showed that slow photons enhanced light absorption and hence the photo activity of TiO_2. Ozin's group used the TiO_2 as both the catalyst and the photonic crystal.

Recently our group demonstrated that the light trapping and catalysis functions could be separated. We created optical crystals of inverse opal SnO_2 to trap light. A catalyst layer of TiO_2 was deposited on the surface of the photonic crystal. The evanescent waves from internal reflection in the SnO_2 penetrated the thin TiO_2 layer creating excitons in the TiO_2 that catalyzed the oxidation of methyl orange in solution [34].

SnO_2 has a larger EBG ($E_{gap,SnO2} = 3.8$ eV) than TiO_2 and is almost transparent in the EBG of TiO_2 ($E_{gap,TiO2} = 3.2$ eV). SnO_2 is also chemically stable and inexpensive making it a near ideal material of choice for the photonic layer. In our previous study the PBG of the SnO_2 inverse opal was designed to be ~350 nm (3.55 eV), to be transparent to the EBG of SnO_2, but absorbed by TiO_2.

We report here the photocatalytic efficiency of TiO_2/SnO_2 photocatalyst/photonic crystal structures with different PBGs. Rates of photodegradation of Rhodamine B (RB) over different kind membranes, such as nc-TiO_2/SnO_2-porous membrane, nc-TiO_2/SnO_2-dense membrane, TiO_2 inverse opal membrane and plain nc-TiO_2 membrane, were compared. The best catalytic performance was obtained with TiO_2/SnO_2 photocatalyst/photonic crystal membranes where the PBG was intermediate to the EBG of TiO_2. Experiments showed that inverse opal SnO_2 with a PBG less than the EBG of TiO_2 generated enhance photocatalysis resulting from higher order reflections in the photonic crystal.

2. Experimental methods

2.1. Preparation of SnO_2 inverse opal layer through liquid phase deposition (LPD)

20 g SnF_2 was dissolved in 100 ml DI water; ~15 ml 30 wt% H_2O_2 was added into the solution to precipitate $SnO_2{\cdot}1.65H_2O$. $SnO_2{\cdot}1.65H_2O$ was rinsed 3–4 times with 50 ml deionized water, and dried at room temperature. The $SnO_2{\cdot}1.65H_2O$ was converted to a SnF_4-HF solution by adding 11.813 g of $SnO_2{\cdot}1.65H_2O$ into 52 g 40% hydrofluoric acid. Finally, a SnO_2 LPD solution was obtained by adding 39.8 ml 0.307 mol/L H_3BO_3 solution to 1 g (~1 ml) of the SnF_4-HF solution.

H_3BO_3 added in the LPD solution acts as an F^- scavenger. SnO_2 is formed through the ligand-exchange hydrolysis of metalofluoro complexes and the H_3BO_3 reacts with the F^- ions forming BF_4, shifting the hydrolysis equilibrium to form SnO_2, as shown in reactions 1 and 2.

$$H_3BO_3 + 4HF \Longleftrightarrow BF_4^- + H_3O^+ + 2H_2O \tag{1}$$

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

SnO_2 inverse opal films were fabricated through filling the voids of thin film polystyrene (PS) microsphere opals with SnO_2 by the LPD method [34]. Monodispersed PS particles were prepared by emulsion polymerization [35]. PS opals were prepared by room temperature floating self-assembly (RTFSA) developed in our lab [36,37]: Clean quartz substrates were dipped into a PS suspension of water–ethanol–PS particles and slowly removed. After the solvents evaporated, a face-centered-cubic (FCC) 3D-ordered PS opal film of ~4 μm thickness remained on the quartz substrates.

$SnCl_2$ was adsorbed on the PS opal films to act as a nucleating agent for SnO_2 deposition. $SnCl_2$-ethanol solution was prepared by dissolving 6.6768 g $SnCl_2{\cdot}2H_2O$ in 30 ml absolute ethanol. The quartz substrates with PS opal layers was dipped into the $SnCl_2$-ethanol solution and dried at 30 °C oven for 1 h. The substrates were immersed into the LPD solution at 30 °C for 10 h, precipitating SnO_2 and filling the voids of the PS opal layer. The PS opal + SnO_2 was rinsed with DI water and dried at room temperature. Finally, the SnO_2-filled PS opal structures supported on the quartz substrates were calcined in air at 450 °C for 2 h removing the PS and densifying the SnO_2. A disordered macroporous SnO_2 film (designated as SnO_2-control) was fabricated in the same way as the SnO_2 inverse opal layer, substituting a polydispersed mixture of PS microspheres for the monodispersed suspension of PS used to make the opals. The UV–Vis transmittance spectra of the prepared SnO_2 inverse opal membranes and the disordered porous SnO_2 membrane were recorded on a UV/Vis spectrophotometer of UV-2100PC (Unico Co., Shanghai, China) using the UV–Vis