**Supporting Information** 

## Synergetic Enhancement of Photocatalytic Activity with Photonic Crystal Film as Catalyst Support

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## **Experimental Section**

**Materials:** Trimethylolpropane ethoxylate triacrylate (ETPTA, average Mn=428) Hexadecyltrimethylammonium bromide (CTAB, 96%), triblock copolymer Pluronic F127, Poly (ethyleneimine) (PEI, Mw=6000, 50 wt% in H<sub>2</sub>O), cyanamide (50 wt% in H<sub>2</sub>O) and triethaolamine were purchased from Sigma-Aldrich. Tetraethylorthosilicate (TEOS, 98%), aqueous ammonia (NH<sub>3</sub>·H<sub>2</sub>O, 28%), ethanol (99.7%), hydrochloric acid (HCl, 37%) and hydrofluoric acid (HF, 40%) were obtained from Sinopharm Chemicals. Rhodamine B (RhB, 96%) was purchased from Amethyst Chemicals.

Synthesis of SiO<sub>2</sub> nanotubes through etching of mesoporous SiO<sub>2</sub> nanorods: Mesoporous SiO<sub>2</sub> nanorods were synthesized by using CTAB and F127 as binary templates in basic aqueous solutions at room temperature. In a typical process, F127 (0.738g), CTAB (1.8g) and NH<sub>3</sub>·H<sub>2</sub>O (28wt%, 6mL) were dissolved in water (174mL) to form a colorless and transparent solution. Then TEOS (6mL) was injected into the above solution under stirring for 2h at room temperature to obtain mesoporous SiO<sub>2</sub> nanorods. The products were refluxed in the mixture of HCl (6mL) and ethanol (120mL) at 75°C for 1h to remove the surfactant molecules. Finally, the washed SiO<sub>2</sub> nanorods were dispersed in water as a stock solution with concentration of 25mg/ml.

The stock solution of washed  $SiO_2$  nanorods (60 mL) was mixed with an aqueous solution of PEI (1200 mL, 5mg/mL) at room temperature. Then, the mixture was heated to 90°C and maintained for

2h to produce  $SiO_2$  nanotubes. After being washed and dried, the  $SiO_2$  nanotubes were calcined at 550°C for 4h to remove PEI adsorbed on the surface of  $SiO_2$ .

Synthesis of mesoporous g-C<sub>3</sub>N<sub>4</sub> nanorods (meso-C<sub>3</sub>N<sub>4</sub> NR): The as-made SiO<sub>2</sub> nanotubes powder was mixed with cyanamide solution (30 mL, 50 wt%) and stirred for 10 min to produce cyanamide loaded SiO<sub>2</sub> nanotubes. Then the product was centrifuged and dried in vacuum. The above process was repeated for two times to fully fill the nanotubes with cyanamide. The cyanamide/SiO<sub>2</sub> composites were calcined at 550°C in N<sub>2</sub> for 4h to produce g-C<sub>3</sub>N<sub>4</sub>/SiO<sub>2</sub> nanorods. After the removal of SiO<sub>2</sub> by HF (80mL, 10 wt%), pure meso-C<sub>3</sub>N<sub>4</sub> nanorods could be obtained finally.

**Synthesis of SiO<sub>2</sub>/ETPTA photonic crystal (PC) film:** Monodisperse silica particles were first synthesized by a modified Stöber method. The particles (0.3 mL) are well dispersed in ethanol by sonication and then mixed with ETPTA (0.7 mL) containing photo initiator, 2-hydroxy-2-methylpropiophenone (5%) to form a homogeneous dispersion. The mixture is heated to 90 °C for 2 hours to evaporate the ethanol content, which produces a liquid SiO<sub>2</sub>/ETPTA precursor (~ 1 mL) in centrifuge tube. Before being cooled down to room temperature, the liquid precursor is added to the center of a petri-dish with diameter of 9 cm and then spun by a spin coater. The speed of spin coating is set to be 1500 rpm and a thin liquid film is obtained after the precursor being spun for 45 seconds. Finally, the liquid precursor spreading in the Petri-dish is placed in vacuumed desiccator and cured by UV light (365 nm, 4.8 mW/cm<sup>2</sup>) for several minutes to produce a photonic crystal film with strong reflection and narrow band gap. The reflection intensity of the PC film with same wavelength can be controlled by adding 3%, 5% and 10% of photo initiator during the synthesis, which leads to the production of PC film with intensity of 90%, 48% and 13%, respectively.

Synthesis of PC film supported meso-C<sub>3</sub>N<sub>4</sub> photocatalyst: Mesoporous C<sub>3</sub>N<sub>4</sub> nanorods are loaded onto the SiO<sub>2</sub>/ETPTA photonic crystal film to form a supported photocatalyst. Typically, meso-C<sub>3</sub>N<sub>4</sub> (5 mg) powders are dispersed in ethanol (0.5 mL), which is spread automatically all over the PC film. Before being used in photocatalytic reaction, the meso-C<sub>3</sub>N<sub>4</sub> loaded PC film is heated to 60 °C for several minutes to strengthen the adhesion between catalysts and supporting film.

**Characterization:** The spin-coating was performed by a Laurell WS-650MZ spinner. Scanning electron microscope (SEM) images were operated by a Hitachi S-4800 scanning electron microscopy.

UV-Vis diffuse reflectance spectrum (DRS) was performed on Shimadzu UV-2700. The optical microscope images were taken on an Olympus BXFM reflection-type microscope operated in dark-field mode. The reflection spectra were measured using an Ocean Optics Maya 2000 Pro spectrometer coupled to a six-around-one reflection/back scattering probe, where both the incident and reflective angles are fixed at 0°. The light source for the photo catalysis was a 300 W Xe arc lamp equipped with a cutoff filter of 420 nm, which provide a simulated sun light in the visible range.

**Photocatalytic degradation of RhB:** The concentration and total volume of the dye solution were fixed at 4 ppm and 25 mL. Before degradation, the suspensions were magnetically stirred in dark for 30 min to ensure the balanced adsorption and desorption of dyes on the catalyst surface. After initiating the photocatalytic degradation with illumination of 300W Xe lamp, a small amount of solution (1 mL) was sampled out at proper time and centrifuged to remove the catalyst. Finally the solution was analyzed by a UV-Vis spectrometer to obtain a relative concentration of dye.

**Photocatalytic H<sub>2</sub> production:** For the test of dispersed photocatalyst, meso-C<sub>3</sub>N<sub>4</sub> powders were dispersed in an aqueous solution (50 mL) containing triethanolamine (10 vol%) and 3 wt% H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O (respect to Pt) was added to produce Pt nanoparticles as cocatalyst. Pt nanoparticles were produced *in-situ* on photocatalysts through irradiation of UV-VIS light for 2 hours. The reaction solution was evacuated several times to remove H<sub>2</sub> completely prior to irradiation. For the test of immobilized photocatalyst, the reaction condition is the same as described above. Then the solution was irradiated under the visible light only ( $\lambda \ge 420$  nm) using a 300W Xe-lamp with a UV cutoff filter. The temperature of the reaction solution was maintained at room temperature by a flow of cooling water during the reaction. The evolved gases were sampled out every 30 min. The gases carried by Ar were analyzed by gas chromatograph equipped with a thermal conductive detector (TCD) and a 5Å molecular sieve column.



**SI Figure 1.** Reflection spectrum measured in the inner (I), middle (M) and outer (O) region of the SiO<sub>2</sub>/ETPTA photonic crystal film. As shown in the left scheme, 4 points are tested in each group and their reflection spectra are very close.



**SI Figure 2.** Digital photos of (a)  $SiO_2/ETPTA$  photonic crystal film and (b) meso- $C_3N_4$  loaded PC film. (c) SEM image and (d) UV–Vis diffuse reflectance spectrum of meso- $C_3N_4$  nanorods photocatalyst.



SI Figure 3. Reflection spectrum of  $SiO_2/ETPTA$  photonic crystal film with and without the loading of meso- $C_3N_4$  nanorods.



**SI Figure 4.** Comparison of photodegration efficiency when the catalysts are supported by pure ETPTA film (dash line) and SiO2/ETPTA photonic crystal film (solid line). The catalysts dosage is set to be 0, 1, 5 and 15 mg, respectively.



SI Figure 5. Comparison of photocatalytic activity for immobilized and dispersed meso- $C_3N_4$  in 5 successive 60min degradation of RhB.



SI Figure 6. Comparison of the catalytic activity for H<sub>2</sub> production between meso-C<sub>3</sub>N<sub>4</sub> photocatalysts loaded on ETPTA film and SiO2/ETPTA PC film. For the test, 5 mg of catalyst loaded on PC film is immersed in 50 mL of aqueous solution containing triethanolamine (10 vol%). The system is sealed and vacuumed by rotary pump. The reaction temperature is kept at about 5 °C by a flow of cooling water during the reaction. The water splitting is performed under the illumination of a 300W Xe-lamp with a UV cutoff filter ( $\lambda \ge 420$  nm).