Supplementary Material

Heterogeneous Photocatalysis with Inverse Titania Opals: Probing Structural and Photonic Effects

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Experimental Methods

Fabrication of as-prepared i-nc-TiO$_2$-o

Polystyrene spheres of 130, 150, 180 and 210 nm were used to obtain opal templates via evaporation-induced self-assembly.[1] The disordered samples consisted 0.5 fraction of 130 nm and 0.5 fraction of 190 nm spheres. The thickness of the templates was 20 - 25 layers. After necking the spheres at 60 °C for 1 hour, infiltration was carried out by placing the opal templates in ethanol solutions containing 0.4 – 0.7 vol% of titanium butoxide. The alkoxide precursor filled the voids and hydrolyzed there as ethanol was evaporated under low pressure. The composites were then incubated at a relative humidity of 80 % for 1 day, followed by calcination at 450 °C for 4 hours to produce anatase phase.

Increasing the Filling Fraction of TiO$_2$

The as-prepared i-nc-TiO$_2$-o films were immersed in a solution containing 0.015M (NH$_4$)$_2$TiF$_6$, 0.011M H$_3$BO$_3$ and 0.01M HCl at 65 °C. After half an hour (or the specified time), the films were removed from the solution, rinsed with water and dried.
The as-deposited TiO\textsubscript{2} was amorphous therefore a second calcination step to 450 °C for 4 hours was carried out to crystallize the additional TiO\textsubscript{2} to the anatase phase.

**Determination of the Mass of Films**

The mass of the films were measured using a microbalance (ATI/CAHN C-34 model) with 1.0 μg precision. The mass of the film on a glass substrate was measured first, followed by scraping off the film and reweighing the glass substrate. The difference corresponds to the mass of film of ~1x2 cm\textsuperscript{2} in dimension. The reported values were obtained from an average over two to three films with error from the standard deviation.

**Specific Surface Area from Dye Adsorption-Desorption**

For dye adsorption, each film was placed in 10-mL solution of 7 μM methylene blue at pH 8 in the dark. The absorbance of the films was measured and compared with monolayer coverage data for reference. To determine the absolute number of molecules of dye adsorbed, each film was immersed into 5 mL acidic water at pH 3 for 1 hour (in the absence of light) to desorb methylene blue. The absorbance of the solutions was then measured using a UV-Vis spectrophotometer and the concentration extrapolated from a calibration curve. Typical desorbed dye concentrations were in the range of 0.9 – 1 μM where linear interpolation according to Beer-Lambert’s law actually does not apply. So an exponential-like calibration curve was mapped out in this low concentration region for the determination of desorbed dye concentration. The reported values were obtained from an average over three runs with error from the standard deviation.

**Solution Photocatalysis**

White-light photodegradation of 7 μM methylene blue in water at pH 8 by i-nc-TiO\textsubscript{2}-o was carried out using a Xe lamp with a filter that cuts off λ < 300 nm. The
solution was in a large homemade rectangular cell (2x2x7 cm³) with the surface of the film and the front wall of the cell aligned perpendicular to the light beam. The solution was continuously stirred and samples were taken every 3 minutes where the absorbance at 660 nm measured. The rate constants were averaged over 2 – 5 runs from different samples with the standard deviation shown as error bars.
**Supplementary Figures**

**Figure S1.** Theoretical enhancement factor of i-nc-TiO$_2$-o in water as a function of the volume fraction of TiO$_2$ in the inverse opal framework, as calculated by SWA. The refractive index of anatase TiO$_2$ used for modeling was obtained from the optical analysis by Kim.$^2$
Figure S2. XPS spectra of F 1s (a) and Ti 2p (b) of inverse opal treated with TiF$_6^{2-}$ followed by calcination at 450 °C. No fluorine signal was detected in (a) while only one chemical environment of Ti 2p was detected in (b) just as in un-doped TiO$_2$. There is no evidence of F impurity on the surface of TiO$_2$ after calcination, in accordance with previous report in which the amount of F impurity was found to decrease with increasing calcination temperature.$^3$
**Figure S3.** XRD of bulk TiO$_2$ powder obtained from TiF$_6^{2-}$ reaction after calcination at 450 °C. Rietveld refinement suggests crystal size of 12 ± 3 nm. (The diffraction pattern of inverse opal film on glass showed anatase peaks but was not good enough for refinement due to low signal arising from the limited amount of material; therefore bulk TiO$_2$ powder was investigated.)
References

