Sandwich-Structured TiO₂ Inverse Opal Circulates Slow Photons for Tremendous Improvement in Solar Energy Conversion Efficiency

Ehsan Eftekhari, ^a Pierre Broisson, ^{a,b} Nikhil A, ^a Zhiqing Wu, ^a Ivan S Cole, ^c Xiaomin Li, ^{a,d} Dongyuan Zhao, ^{d,e} and Qin Li *^a

- ^{a.} Queensland Micro- and Nanotechnology Centre & School of Engineering, Griffith University, Nathan, QLD 4111, Australia
- ^{b.} Ecole Nationale Supérieure de Chimie de Rennes, 11 Allée de Beaulieu, 35708 Rennes, France
- ^{c.} Centre of Enabling Capability, School of Engineering, RMIT, VIC 3000, Australia
- ^{d.} Department of Chemistry, Fudan University, Shanghai, 200433, P.R. China
- e. Department of Chemical Engineering, Monash University, Clayton, VIC, Australia

*Corresponding Author: <u>qin.li@griffith.edu.au</u>

Address: Queensland Micro- and Nanotechnology Centre & School of Engineering, Griffith University, Nathan, QLD 4111, Australia. Telephone: (61)(07)37357514

Supplementary Figures:



Fig. S1 The absorbance spectrum of TiO_2 is shown as a black line. The red line indicates the electronic absorption band of TiO_2 .



Fig. S2 Schematic of fabrication procedure of sandwich-structured TiO_2 inverse opal with corresponding cross-sectional SEM images, the scale bars are 1 μ m.

EDX elemental mapping images (Fig. S3) unambiguously demonstrated the homogeneous spatial distribution of Ti (pink) and O (green). As shown in Fig. S3 (b) and S3 (c), TiO₂ nanocrystals had the analogous distribution with the large diameter distribution along the inverse opal structure. The crystalline phases of inverse opal and nc-TiO₂ and S-IO-TiO₂ films were further confirmed by typical XRD patterns as shown in Fig. S3 (d). Characteristic peaks 2

corresponding to anatase TiO₂, i.e. (101), (004), (200), (105), (211), (204), (116), (220) and (107), reflections could be found at $2\theta = 25.2^{\circ}$, 37.8° , 48.02° , 54.0° , 55.0° , 62.3° , 68.9° , 70.3° and 74.9° , respectively, analysed (JCPDS card no. 21-1272).¹⁻³ Upon calcination at 450 °C for 4 h, anatase phase was obtained, other peaks apart from the normal TiO₂ anatase phase were not observed verify the pure anatase phase in all inverse opal films and nc-TiO₂.



Fig. S3 (a) BSE-EDX elemental mapping of sandwich-structured inverse opal S-IO-TiO₂. **(b)** The corresponding EDX elemental mapping images of titanium (pink) and **(c)** oxygen (green) in the selected area. **(d)** A powder X-ray diffraction pattern of nc-TiO₂, monolithic and sandwich-structured inverse opal films indicate anatase.

It is important to note that same amount of TiO_2 were infiltrated in all opal films as well as the nc-TiO₂ film then calcinated at 450 °C for 4 hr. The nc-TiO₂ particles were formed and determined to be 5–20 nm by SEM image (Fig. S4). SEM image of the nc-TiO₂ particles indicates that the TiO₂ particles were anatase. TEM characterization of S-IO-TiO₂ confirms that TiO₂ is crystalline with an interplanar d-spacing of 0.352 nm corresponding to the (101) plane as shown in Fig. S3 (d).^{4, 5}



Fig. S4 (a) SEM image of TiO_2 nanocrystals (nc- TiO_2) and **(b)** high magnification SEM image of TiO_2 anatase nanocrystal with (101) and (001) crystal plains. Scale bars are 10 nm. **(c)** Transmission electron microscopy images of sandwich-structured inverse opal and **(d)** The HRTEM image confirms the single crystalline phase of TiO_2 with an interplanar spacing of 0.352 nm.

To understand and explore the effect of inverse opal configuration on slow photon circulation, it is useful to analyse the photonic band structure for all inverse opal films. The photonic band diagrams of close-packed TiO₂ inverse opals with water filling the voids show a pseudo stopband at the L point of the irreducible Brillouin zone along the Γ L (111) direction because the air–anatase dielectric contrast is too low (Fig. S5).^{6, 7}



Fig. 5 (a) *I–V* curves of the inverse opal films and nc-TiO₂ films under UV-visible light illumination.



Fig. S6 Photonic band diagrams of (a) Monolithic, (b) heterostructure and (c) sandwich-structured inverse opal films.

The important feature of the photonic crystal's band structure is edges of the stopband in which the group velocity of the light becomes anomalously small. On the red edge of the stop band, the slow photon is localized in the high dielectric part while on the blue edge these photons are localized in the low dielectric part. The group velocity is defined by the slope at these points indicate a series of photons of a null or a low group velocity.⁸ These photons are usually called "slow photons". The value of 0.021, 0.017 and 0.014 was obtained for monolithic, heterostructure and sandwich-structured, respectively (Fig. S6).



Fig. S7 Detail of the band structure along the Γ -L direction in the reciprocal space, that is, the [111] direction in real space. The distance of stopband is indicated a black arrow, the reduced group velocity for slow photons is also indicated schematically by approximate slopes at the edges of the stopband for (a) monolithic (b) heterostructure and (c) sandwich-structured inverse opals.

To further investigate experimental spectral observations and explore slow photon circulation, tomography of the field intensity is useful. Since the light propagation is not observable in experiments, simulation is the tool to resort to. The slow photon circulation was observed in Fig. S7a as the cross section plane showed that the intensity was predominantly concentrated in the middle of S-IO-TiO₂. The field spread on top and bottom films as well as a middle film but is predominantly confined in the middle part of S-IO-TiO₂, while in M-IO-TiO₂ and H-IO-TiO₂ light propagates along whole structure.



Fig. S8 Map of field intensity for (a) sandwich-structured (b) heterostructure and (c) monolithic inverse opal films.

To confirm that the observed photocatalytic efficiency change is indeed due to the photonic effect, the lattice parameter in Equation 1 is varied. A series of M-IO-TiO₂ films have been made with stopband maxima positioned at 300 nm, 340 nm (stopband red edge overlapping with TiO₂ excitation energy), 380 nm, 430 nm (stopband blue edge overlapping with TiO₂ excitation energy), and 480 nm. They were all tested for photo-degrading RhB under normal direction irritation of the Xenon lamp. As shown in Fig. S8, when the stopband peak coincides with the TiO₂ excitation energy as in the case of M-IO-380, there is no light coupling effect, similar to M-IO-300 and M-IO- 480.



Fig. S9 Photodegradation efficiency of RhB independence of stopband position of monolithic inverse opal films with different lattice diameter.

References

- 1. T. Wang, X. Yan, S. Zhao, B. Lin, C. Xue, G. Yang, S. Ding, B. Yang, C. Ma, G. Yang and G. Yang, *Journal of Materials Chemistry A*, 2014, **2**, 15611-15619.
- 2. T. K. Rahul and N. Sandhyarani, *Nanoscale*, 2015, **7**, 18259-18270.
- 3. C. Xue, X. Xu, G. Yang and S. Ding, *RSC Advances*, 2015, **5**, 102228-102237.
- 4. J. Jin, S.-Z. Huang, J. Liu, Y. Li, D.-S. Chen, H.-E. Wang, Y. Yu, L.-H. Chen and B.-L. Su, *Journal of Materials Chemistry A*, 2014, **2**, 9699-9708.
- 5. L. Song, L. Li, X. Gao, J. Zhao, T. Lu and Z. Liu, *Journal of Materials Chemistry A*, 2015, **3**, 6862-6872.
- 6. O. Deparis, S. R. Mouchet and B. L. Su, *Physical Chemistry Chemical Physics*, 2015, **17**, 30525-30532.
- 7. F. Sordello, V. Maurino and C. Minero, *Journal of Materials Chemistry*, 2011, **21**, 19144-19152.
- 8. M. Curti, J. Schneider, D. W. Bahnemann and C. B. Mendive, *The Journal of Physical Chemistry Letters*, 2015, **6**, 3903-3910.