

# Electronic Supplementary Information

## Bio-inspired double-layer structure artificial microreactor with highly efficient light harvesting for photocatalysts

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### Experimental Section

**Pretreatment:** Before the fixation procedure, the fresh aquatic plant samples were rinsed with deionized water carefully several times to remove the surface adsorbed plankton. Afterwards, the leaves were treated with 2.5% glutaraldehyde/phosphate buffered saline (PBS; pH = 7.2) solution at 4 °C for one day for the fixation of cells and tissues. The fixed samples were rinsed in the same buffer solution and dehydrated in a graded ethanol series (10%, 20%, 30%, 50%, and 70%, respectively). For SEM observation, the fixed samples were further critical point dried with CO<sub>2</sub> and then sputter-coated with thin layer of gold. For viewing of leaves cross sectional anatomy, fully dehydrated samples were frozen in liquid nitrogen and fractured manually using tweezers.

**Synthesis of TiO<sub>2</sub> precursor sol:** In a typical synthesis, 20 g of TBT was dissolved in 20 g of ethyl alcohol with stirring for 1 hour. Then 2.12 g of acetic acid, 4.06 g of hydrochloric acid and 7 g of ethyl alcohol were mixed homogenously and followed with adding dropwise into the above solution and stirred for another 3 hours. The obtained

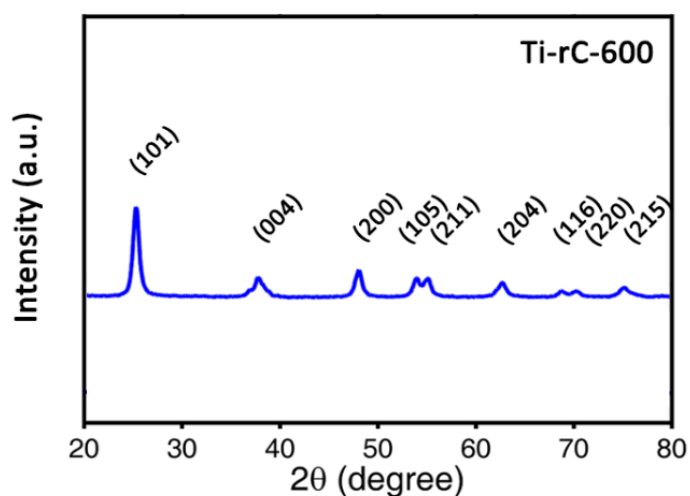
yellow transparent solution was allowed to undergo hydrolysis reaction at room temperature overnight.

**Synthesis of TiO<sub>2</sub> replica of aquatic plant leaves:** The pre-fixed leaves are immersed in dilute HCl aqueous solution for 2 hours at room temperature to remove the Mg<sup>2+</sup> in the chlorophyll molecules. The treated samples are immersed in above as-synthesized TiO<sub>2</sub> precursor sol under vacuum for one day. The sol-infiltrated leaves samples were then left dry at room temperature. The samples were then placed in muffle oven at 40, 60, 80 °C successively and tempered for two hours at each temperature, respectively. Then the samples were programmed heating to the desired temperatures at a heating rate of 1°C min<sup>-1</sup> and tempered at the temperatures for 4 hours.

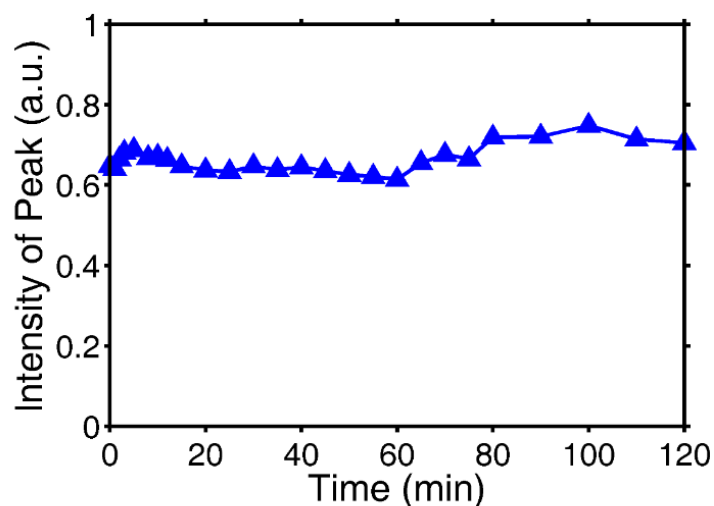
**Simulation:** The demonstration schemes for FDTD simulation were achieved based on the structures of the leaves. The index of the leaves cells were set to 1.6. The index for the TiO<sub>2</sub> replicas of the leaves cells were set to 2.5. The background index was set to 1.333 due to the surrounding medium was water. The simulations were performed on the software of Lumerical Solutions.

**Characterization:** Small pieces of fixed leaves were embedded in the tissue freezing medium (Leica Instruments Company) at -25 °C. Cross sections of 10 µm thickness were prepared using a cryomicrotome (Leica CM3050-Cryostat, Leica Instruments Company) at -20 °C, and collected on Poly (L-lysine)-coated slides. The fluorescence microscopy was carried out using a Laser-Scan-Microscopy (FV1000-IX81, Olympus). Chlorophyll fluorescence was excited by 488 nm laser. The microscale morphologies of the leaves morphologies were observed using three-dimensional MicroXCT-200 (Xradia Inc. Concord) at 40 times magnification. Computed tomography (CT) facilitates viewing an object in 3D perspective. The transmission X-ray imaging of the specimen was performed using an X-ray at 90 kV, 8 W. TEM images were obtained on a JEOL JEM-2010 transmission electron microscope operating at 200 kV. Samples obtained by scratching the films from the substrate for TEM measurements were dispersed in ethanol. Carbon coated copper grids were used as the sample holder.

**Photocatalytic characterization:** The photocatalytic activity for Methylene blue degradation was measured as follows: 100 mg of the synthesized TiO<sub>2</sub> replica sample of the leaves was dispersed in 100 ml of 10<sup>-5</sup> mol L<sup>-1</sup> Methylene blue aqueous solution. The suspended solution was placed in dark environment for 2 hours to reach the adsorption-desorption equilibrium. The samples were irradiated by a black light (15 W, peak wavelength: 365 nm) from a distance of 5 cm for certain minutes. The solution was sampled every certain minute and centrifuged to separate the TiO<sub>2</sub> sample. The liquid supernatant was collected and tested in Ocean Optics fiber spectrometer to measure the absorption spectra. The photodegradation experiments for each sample were performed 3 times independently and the photodegradation rate constants were averaged over 3 times. The rate of degradation was assumed to obey pseudo-first-order kinetics. The degradation rate constant,  $k$  (min<sup>-1</sup>), was obtained via least square fitting according to the equation,  $A = A_0 e^{-kt}$ , where  $A$  was the intensity of characteristic absorption peak of MB after degradation for a time of  $t$  (min),  $A_0$  was the initial intensity.<sup>1,2</sup>



**Fig. S1** XRD characterization of Ti-rC-600.



**Fig. S2** Reaction kinetics of Methylene blue (MB) photodegraded by Ti-rC-600 under irradiation of solar simulator equipped with 420 nm cut off filters.

**Table S1.** Parameters derived from N<sub>2</sub> adsorption-desorption isotherm and its photocatalytic performance

Sample	S <sub>BET</sub> <sup>a</sup> / (m <sup>2</sup> /g)	V <sup>b</sup> / (cm <sup>3</sup> /g)	D <sub>BJH</sub> <sup>c</sup> / (nm)	Crystal size/ (nm)	Rate constants/ (min <sup>-1</sup> )
TiO <sub>2</sub> -rC-600	38.4	0.069	8.8	15.0	0.0964
TiO <sub>2</sub> -rV-600	59.7	0.084	5.8	9.9	0.0745
P25	54	-	-	15-25	0.0884
nc-TiO <sub>2</sub>	58.5	0.132	6.4	15.1	0.0133

<sup>a</sup> BET surface area calculated from the linear part of the BET plot ( $P/P^0=0.1-0.2$ ). <sup>b</sup> Total pore volume, taken from the volume of N<sub>2</sub> adsorbed at ( $P/P^0=0.977$ ). <sup>c</sup> Average pore diameter, estimated using the adsorption branch of the isotherm and the Barrett-Joyner-Halenda (BJH) formula.

## Reference:

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