Electronic Supplementary Information (ESI)

Light-Induced Formation of Porous TiO_2 with Superior Electron-Storing Capacity

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Experimental Section

Synthesis of TG. The TG precursor was prepared by following the procedures reported previously.[1] Typically, titanium n-butoxide (5 mL) was added to ethylene glycol (50 mL) and heated at 160 °C for 2 hours under vigorous stirring to form the TG compound. After cooling down to room temperature, the white TG precipitate was washed several times with ethanol and dried naturally at room temperature.

Light-induced formation of porous TiO_2. Irradiation of TG under UV-light was performed in a water-cooled quartz cylindrical cell which was illuminated from an internal light source with about 1 cm optical path length. The UV light source was a 400 W high-pressure mercury lamp (main output 313 nm) and the irradiation intensity of the UV-light was about 9.1×10^4 $\mu W/cm^{-2}$. The TG precursor (2.0 g) was dispersed in water (400 mL) and then subject to the UV light irradiation. During the irradiation process, gaseous N_2 was bubbled through the solution. After the UV-irradiation, the color of the solid sample turned from white (TG) to intense blue (porous TiO_2), and about 0.95 g of TiO_2 was finally obtained. At given irradiation intervals, the solid product was separated from the mixture and dried in vacuum for further characterization.

Measurement of electron-storing capacity. Quantitative measurement of electron accumulation in the as-prepared porous TiO_2 was performed through titration using $K_2Cr_2O_7$ (1.6×10^{-2} $molL^{-1}$) as an electron acceptor. By determining the amount of the reduced $K_2Cr_2O_7$, the amount of electron accumulation was calculated according to the following equation: $Cr_2O_7^{2-} + 6e^- + 7H_2O \rightarrow 2Cr^{3+} + 14OH^-$. For comparison, the as-prepared porous TiO_2 material was calcined at 400 °C and 500 °C for 2 h, and the corresponding samples were designated TiO_2(400) and TiO_2(500), respectively. The electron-storing properties of TiO_2(400), TiO_2(500) and the commercial TiO_2 P25 were measured under UV-light irradiation in the presence of ethanol.

Stability of the as-prepared porous TiO_2 for light-induced electron storage. The excellent stability of as-prepared porous TiO_2 for light-induced electron storage was demonstrated by a cycling experiment. In a typical cycle, a certain amount of air-exposed porous TiO_2 (6 g), which does not contain any stored electrons because of electron scavenging by the O_2 in air,[2] was irradiated by UV-light under N_2 protection in the presence of ethanol. At given irradiation intervals, the amount of electron accumulation in porous TiO_2 was determined through titration using $K_2Cr_2O_7$ as an electron acceptor. It was noted that the ethanol molecules in the system functioned as a hole scavenger (just as the ethylene groups in the TG precursor did), and the photogenerated holes in the porous TiO_2 abstracted hydrogen atoms from ethanol which was subsequently oxidized to aldehyde. Indeed, in the liquid phase of the reaction system, aldehyde was detected by gas chromatography. In addition, the stored electrons in the porous TiO_2, once generated, are very stable even in the absence of a hole scavenger (ethanol). This was confirmed by the observation that the stored electrons remained for long-term storage (over six months) after complete removal of the organic species from the porous TiO_2 system (Fig. S6).

Reduction of aromatic nitro compounds. TiO_2 (2 g) with stored electrons (1.4 mmol electrons/g TiO_2) was mixed with an aqueous solution of nitrobenzene (or other aromatic nitro compound) (20 mL, 2.5 $molL^{-1}$) at room temperature under N_2 protection. At given stirring time intervals, an aqueous solution (1 mL) was collected and filtered though a Millipore filter to remove the suspended TiO_2 particles for analysis by gas chromatography. For comparison, water as a solvent was replaced by chloroform ($CHCl_3$) and cyclohexane for the reduction reaction.

General characterization. The powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/Max 2550 X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å). The scanning electron microscopic (SEM) images were taken on a JEOL JSM 6700F electron microscope, whereas the TEM image was obtained on a JEOL JSM-3010 TEM microscope. The UV/vis diffuse reflectance spectra were recorded on a Perkin-Elmer Lambda 20 UV/vis spectrometer, and the absorbance spectra were obtained from the reflectance spectra by means of Kubelka-Munk transformation. The FT-IR spectra were acquired on a Bruker IFS 66v/S FTIR spectrometer. The nitrogen adsorption and desorption isotherms were measured using a Micromeritics ASAP 2020M system, whereas the electron paramagnetic resonance (EPR) spectra were recorded on a JES-FA 200 ESR spectrometer. The surface photocurrent spectroscopy was performed on a home-made surface photocurrent spectrometer.[3] A superconducting quantum interference device magnetometer (Quantum Design, MPMS-XL) was used for the magnetic property measurements. The analysis of the organic species present in the UV-irradiation reaction system was performed on a Shimadzu GC-2014C gas chromatograph.

[1] X. X. Zou, G. D. Li, M. Y. Guo, X. H. Li, D. P. Liu, J. Su, J. S. Chen, *Chem. Eur. J.*, 2008, 14, 11123.

[2] O. Kameneva, A. I. Kuznestov, L. A. Smirnova, L. Rozes, C. Sanchez, A. Alexandrov, N. Bityurin, K. Chhor, A. Kanaev, *J. Mater. Chem.*, 2005, 15, 3380; P. D. Cozzoli, M. L. Curri, A. Agostiano, *Chem. Commun.*, 2005, 3186.

[3] T. S. Wu, K. X. Wang, L. Y. Zou, X. H. Li, P. Wang, D. J. Wang, J. S. Chen, *J. Phys. Chem. C*, 2009, 113, 9114.

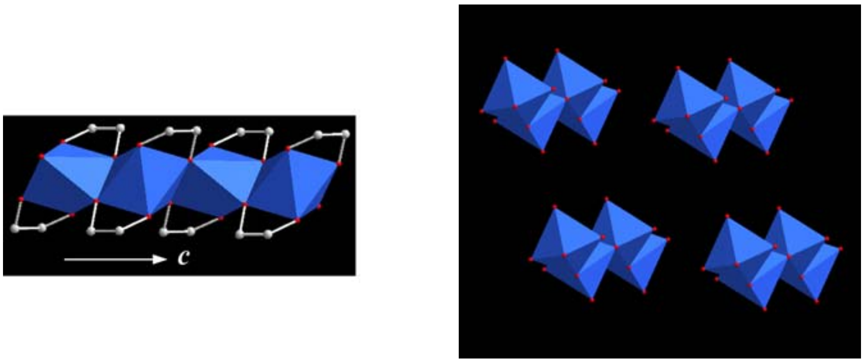

Figure S1. Polyhedral view of the 1D chain of TG along the *c* axis (left); and a periodic array assembled by the 1D chains in TG (right). The O and C atoms are represented by red and white balls, respectively, whereas the TiO_6 unit forms an octahedron (blue) with the O atoms at the vertices.

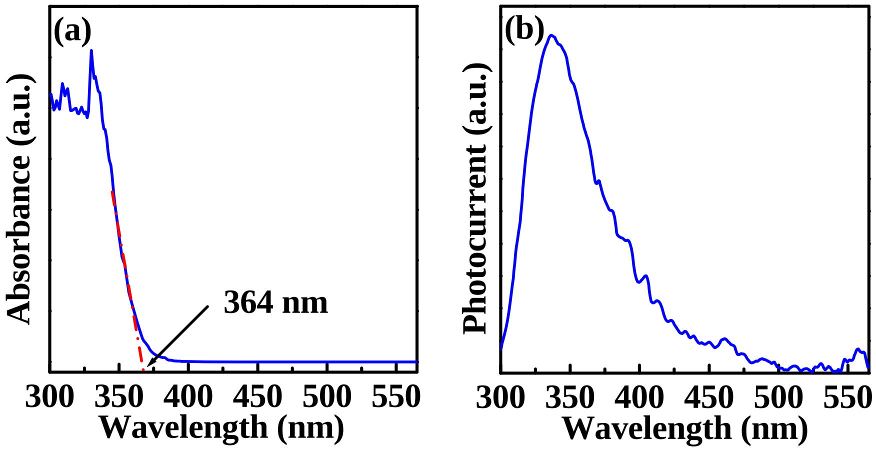

Figure S2. (a)The UV/vis absorption spectrum of the TG compound obtained from the diffuse reflectance one through Kubelka-Munk transformation; and (b) the surface photocurrent spectrum of TG.

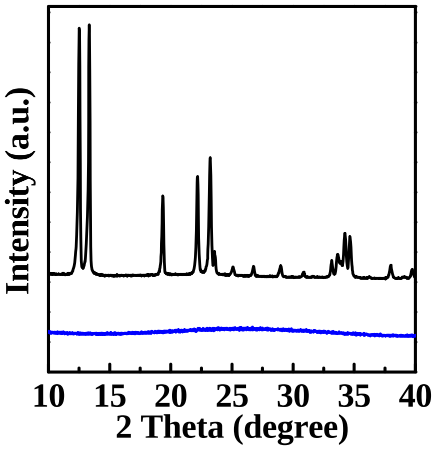

Figure S3. Powder X-ray diffraction patterns of TG before (black line) and after (blue line) UV-light irradiation.

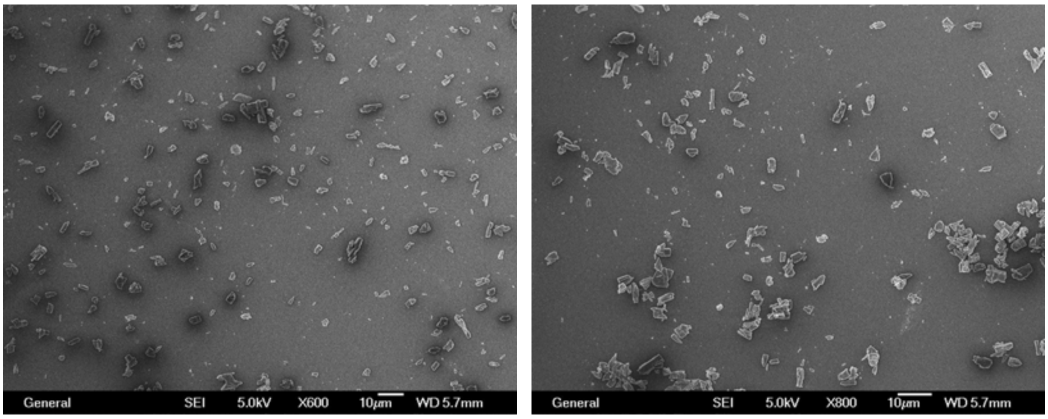

Figure S4. SEM images of TG before (left) and after (right) UV-light irradiation.

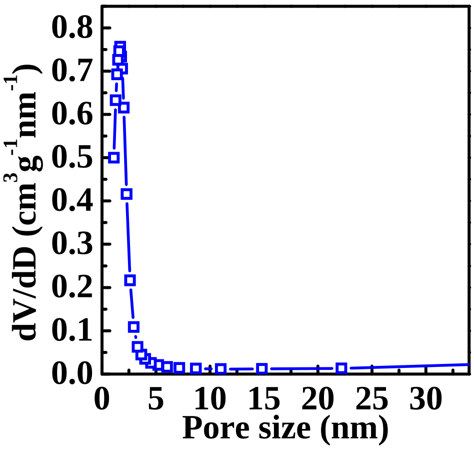

Figure S5. The BJH pore-size distribution for the as-formed porous TiO_2.

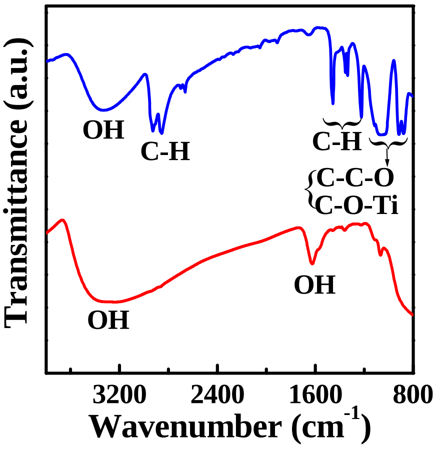

Figure S6. The FT-IR spectra of TG before (blue line) and after (red line) UV-light irradiation.

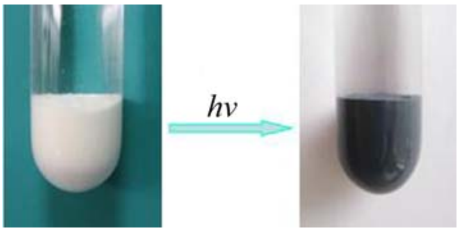

Figure S7. Photographs of the TG precursor and the as-prepared porous TiO_2 with stored electrons.

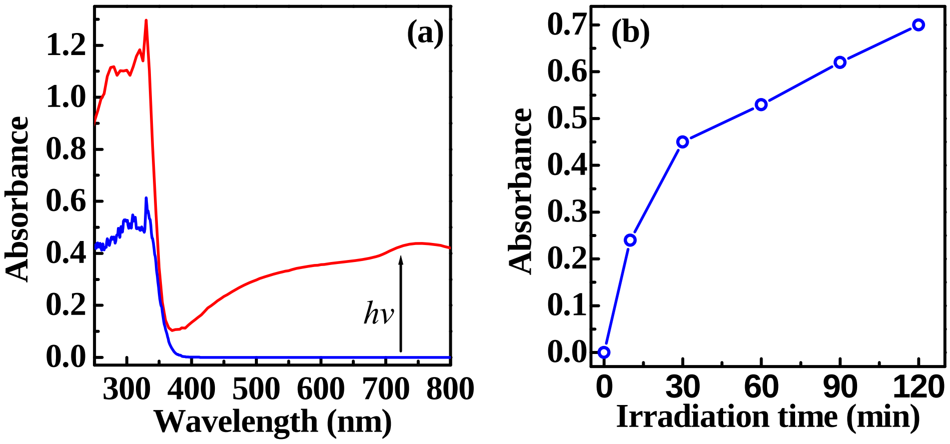

Figure S8. (a) The UV/vis absorption spectra of TG before and after irradiation for 30 minutes; (b) the UV/vis absorbance intensity at 750 nm as a function of irradiation time for the TG material.

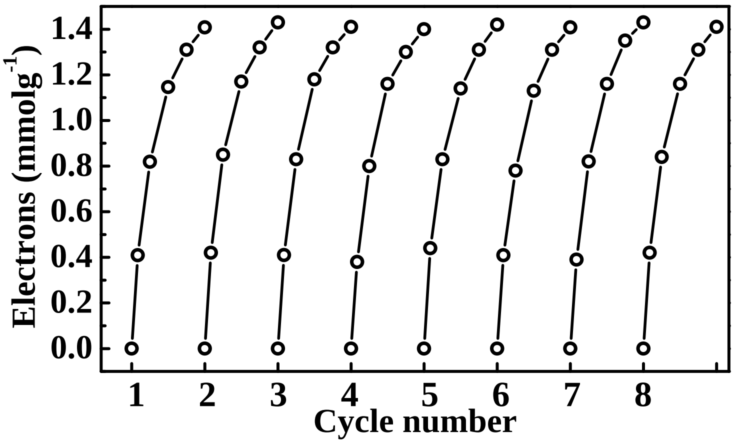

Figure S9. Cycles of light-induced electron storage for the as-prepared porous TiO_2. In each cycle, UV-irradiation lasts for 120 minutes.

Table S1. The BET surface areas and the electron-storing capacities of the as-prepared porous TiO_2, TiO_2(400), TiO_2(500) and P25.

Sample[a]	porous TiO_2	TiO_2(400)	TiO_2(500)	P25
BET surface area (m^2g^{-1})	534	124	89	50
electrons (mmol/g TiO_2)	1.4	0.21	0.14	0

[a] The UV-irradiation time is 120 minutes.

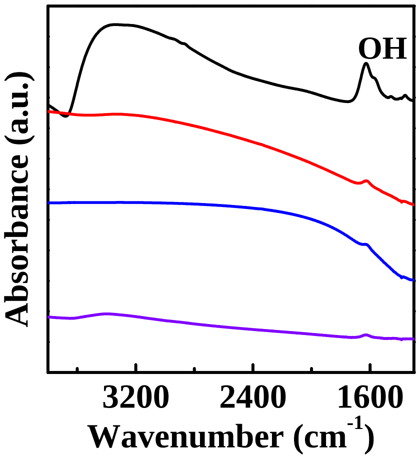

Figure S10. The FT-IR spectra of air-exposed porous TiO_2 (black line), TiO_2(400) (red line), TiO_2(500) (blue line) and P25 (violet line). For FT-IR measurements, the corresponding samples were mixed and ground with KBr powder followed by pressing into pellets.

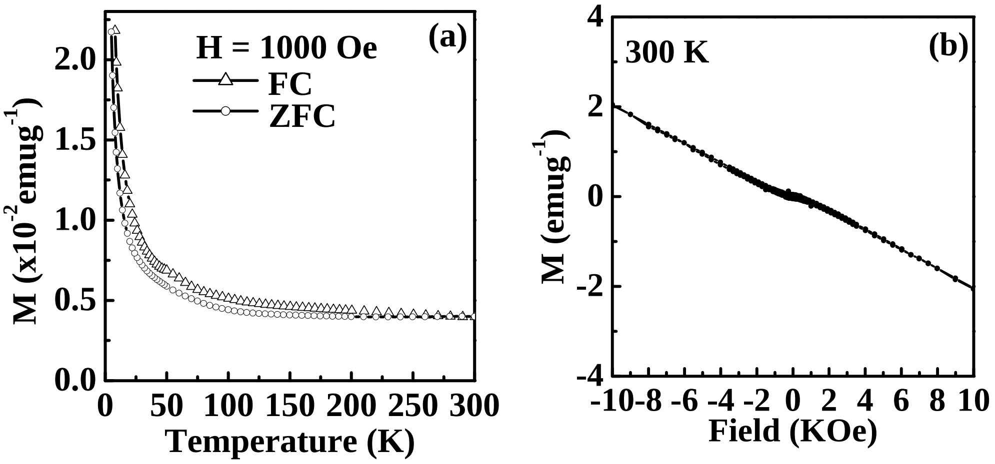

Figure S11. (a) Magnetization as a function of temperature for TiO_2 containing stored electrons (1.4 mmol electrons/g TiO_2) in the zero-field cooled (ZFC) and field-cooled (FC) conditions with H = 1000 Oe; (b) Magnetization as a function of applied magnetic field at 300 K for the sample after exposure to air.