Electronic Supplementary Information

Doping High-Surface-Area Mesoporous TiO_2 Microspheres with Carbonate for Visible Light Hydrogen Production

Bin Liu,[ab] [†] *Li-Min Liu,*[c†] *Xiu-Feng Lang,*[c] *Hsin-Yi Wang,*[a] *Xiong Wen (David) Lou,**[a] *and Eray S. Aydil**[b]

[a] School of Chemical and Biomedical Engineering, Nanyang Technological University, 62 Nanyang Drive, Singapore 637459, Singapore. Email: xwlou@ntu.edu.sg

[b] Department of Chemical Engineering and Materials Science, University of Minnesota, 421 Washington Avenue SE, Minneapolis, MN 55455, USA. Email: aydil@umn.edu

[c] Beijing Computational Science Research Center, Beijing 100084, China

[†] These authors contributed equally to this work.

Experimental Section

Materials Preparation. Mesoporous TiO_2 microspheres were prepared via a nonaqueous solvothermal process. In a typical synthesis, 1–8 ml of titanium isopropoxide was mixed with 60 ml of anhydrous acetone. The mixture was stirred at ambient conditions for 30 min and then transferred to a Teflon-lined stainless-steel autoclave (125 ml volume, Parr Instrument Co.), which, during synthesis, was held at varying temperatures between 25 ^{o}C and 200 ^{o}C for 30 min to 24 h. After synthesis, the white precipitate was separated by centrifugation and washed several times with deionized water and acetone. In some control experiments, ethanol, 2-propanol, and mixtures of acetone and deionized water were used instead of anhydrous acetone to study the effect of the solvent. Carbonate doping was achieved in a subsequent 2 h calcination in a furnace. The effect of calcination temperature was studied between 50 ^{o}C and 400 ^{o}C.

Photocatalytic Reactivity. Photocatalytic potential of the mesoporous TiO_2 microspheres was evaluated by measuring their efficiency in photocatalytic decomposition of methyl orange. In a typical experiment, 20 mg of TiO_2 microspheres was dispersed in 45 ml of deionized water via sonication in a 100 ml beaker. Following, 5 ml of 100 mg l^{-1} methyl orange solution, which had been bubbled with air for 1 hour, was added to the TiO_2 microsphere dispersion. The mixture was stirred at room temperature for 2 hours before illumination with light from a mercury lamp (100 W, Opti Quip Inc., Model 770) filtered with a cutoff filter (λ = 420 nm) to remove UV photons. During the 120-minute long illumination, 4 ml of solution together with the solid catalyst was drawn out every 15 minutes to determine the concentration of the remaining methyl orange using UV-visible spectrophotometry; the solution was separated from the catalyst through syringe filtration.

Photocatalytic Hydrogen Evolution. Photocatalytic hydrogen evolution was carried out in a gas-closed circulation system. 1 mg of photocatalyst particles was dispersed in 3 ml of water-methanol solution in a 14 ml quartz cell. Argon (~ 1300 Torr) was introduced into the reaction system after deaeration. The reaction system was irradiated using a 450 W Xe lamp with a long-pass cutoff filter (λ = 400 nm). The illumination intensity is ~ 300 mW cm^{-2} (~ 3 sun). The cumulative amount of hydrogen evolved during the reaction was determined every 2 h using an online gas chromatography (Agilent 3000A Micro GC).

Materials Characterization. The X-ray diffraction (XRD) patterns from the TiO_2 microspheres were recorded using a Bruker-AXS Microdiffractometer (model D5005) with Cu Kα radiation (λ = 1.5406 Å) from 20^o to 70^o at a scanning speed of 2.4^o min^{-1}. The X-ray tube voltage and current were set at 45 kV and 40 mA, respectively. The morphology and composition of the TiO_2 microspheres were studied using field emission scanning electron microscopy (FESEM, JSM-6500F and JSM-6700F), energy-dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM/HRTEM, FEI Tecnai G2 30), and selected area electron diffraction (SAED). The nitrogen adsorption/desorption isotherms were measured at 77 K using a Micromeritics ASAP 2000 system. Prior to the measurements, the particles were degassed at 353 K overnight. Surface area and pore size distribution of the TiO_2

microspheres were calculated using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively. The diffuse reflectance spectra were recorded using a UV-vis-NIR spectrophotometer equipped with an integration sphere, a combination of deuterium and tungsten halogen lamps (Ocean Optics, DH-2000-Ball) and a spectrometer (Ocean Optics, HR 2000). The spectrometer was equipped with a grating and a silicon detector, sensitive in the 200-1100 nm range. The optical density was displayed as $F(R) = (1-R)^2/2R$ in Kubelka-Munk units, where R is the measured diffuse reflectance. Chemical composition of the microspheres was examined with X-ray photoelectron spectroscopy (XPS, Surface Science SSX-100). All binding energies were referenced to the C1s peak (284.6 eV) arising from adventitious hydrocarbons. Thermal behaviour of the TiO_2 microspheres was studied using thermogravimetric analysis (TGA, Perkin Elmer Diamond TG/DTA Thermogravimetric). About 10 mg of TiO_2 microspheres was heated at 10 ^{o}C min^{-1} from room temperature to 900 ^{o}C while flowing 100 ml min^{-1} of air through the system. The product solution obtained after solvothermal synthesis was filtered to remove any remaining particles and then analyzed using ^{13}C liquid-state NMR (Varian UNITY-300 VAC-300).

Computational Details. To calculate the electronic structure of carbonate-doped anatase TiO_2, a 48-atom (2x2x1) supercell was used. The structure of carbonate-doped TiO_2 with C@Ti was modeled by replacing one Ti atom with one C atom. The cell parameters and the atomic positions of the model-doped structure were optimized by performing spin-polarized Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional within the generalized gradient approximation (GGA).[1] Since PBE functional usually underestimates the bandgap of the semiconductor, the cell parameters and the atomic positions of the supercell were also optimized by PBE+U calculations,[2] where a U(Ti_d) value of 4.2 eV was applied to the Ti d states. The projector augmented-wave method (PAW) was employed to treat valence-core interactions with cores of [Ar] for Ti and [He] for O and C.[3] The plane-wave cutoff energy of 400 eV, and the Monkhorst-Pack grid with 4x4x4 k-point mesh for the integration in the Brillouin zone were used. The convergence threshold for self-consistent-field iteration was set at $2\text{x}10^{-5}$

eV, and all of the atomic positions were fully optimized until all components of the residual forces were smaller than 0.02 eV Å^{-1}. All of the calculations were carried out using the Vienna ab-initio simulation package.[4]

[1] J. P. Perdew, K. Burke, M. Ernzerhof, *Physical Review Letters* **1996**, *77*, 3865.

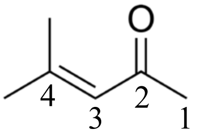
[2] S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, A. P. Sutton, *Physical Review B* **1998**, *57*, 1505.

[3] G. Kresse, D. Joubert, *Physical Review B* **1999**, *59*, 1758.

[4] G. Kresse, J. Furthmüller, *Physical Review B* **1996**, *54*, 11169.

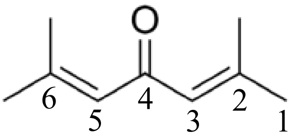
^{13}C NMR Data:

Mesityl oxide (4-methyl-3-penten-2-one):



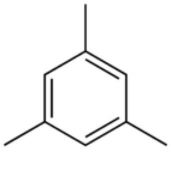
^{13}C NMR δ = 198.6 (C2), 155.1 (C4), 124.1 (C3), 31.5 (C1), 27.5, 20.4 (CH_3).

Phorone (2,6-dimethyl-2,5-heptadiene-4-one):



^{13}C NMR δ = 191.5 (C4), 154.2 (C2 and C6), 126.1 (C3 and C5), 27.7, 20.4 (CH_3).

Mesitylene (1,3,5-trimethylbenzene):



^{13}C NMR δ = 137.6, 126.8 (C_{ph}), 21.1 (CH_3)

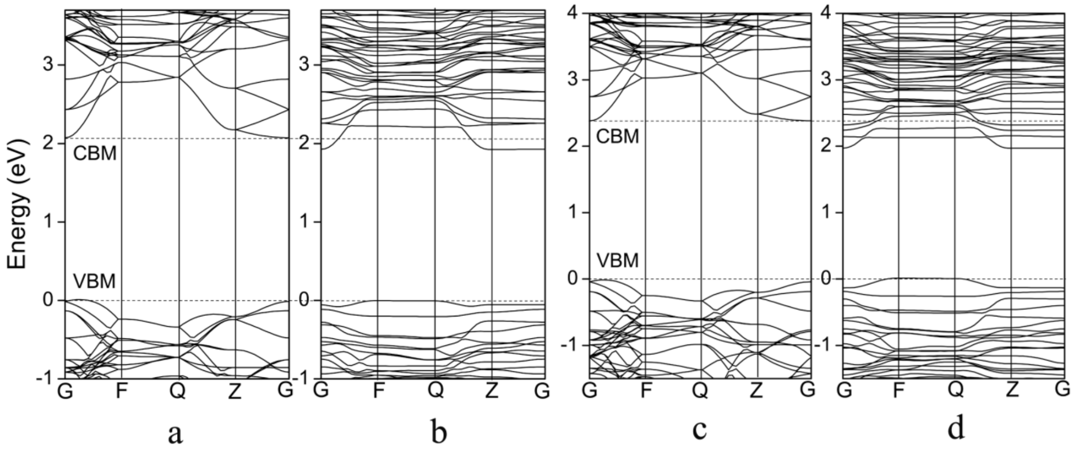


Fig. S1 Band structures for undoped TiO_2 (a and c) and carbonate-doped TiO_2 (b and d). Band structures in a and b (c and d) are obtained by the PBE (PBE+U) calculations, respectively. All the energies of undoped TiO_2 and carbonate-doped TiO_2 are aligned by their valence band maxima (VBM). The dashed lines indicate the VBM and conduction band minimum (CBM) of undoped TiO_2

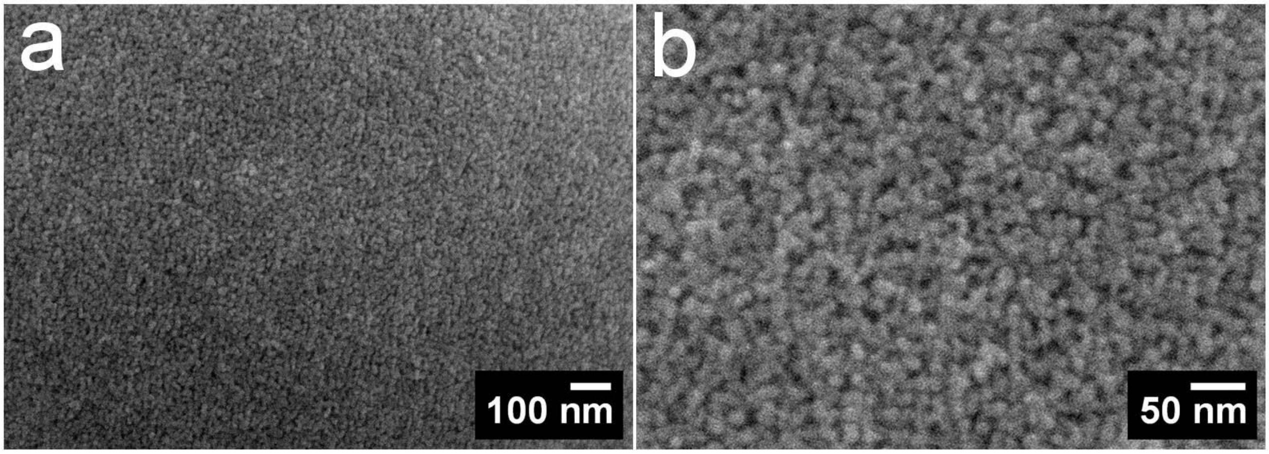


Fig. S2 High-magnification FESEM images of TiO_2 microspheres prepared at 200 °C for 12 h, using 2 ml of titanium isopropoxide.

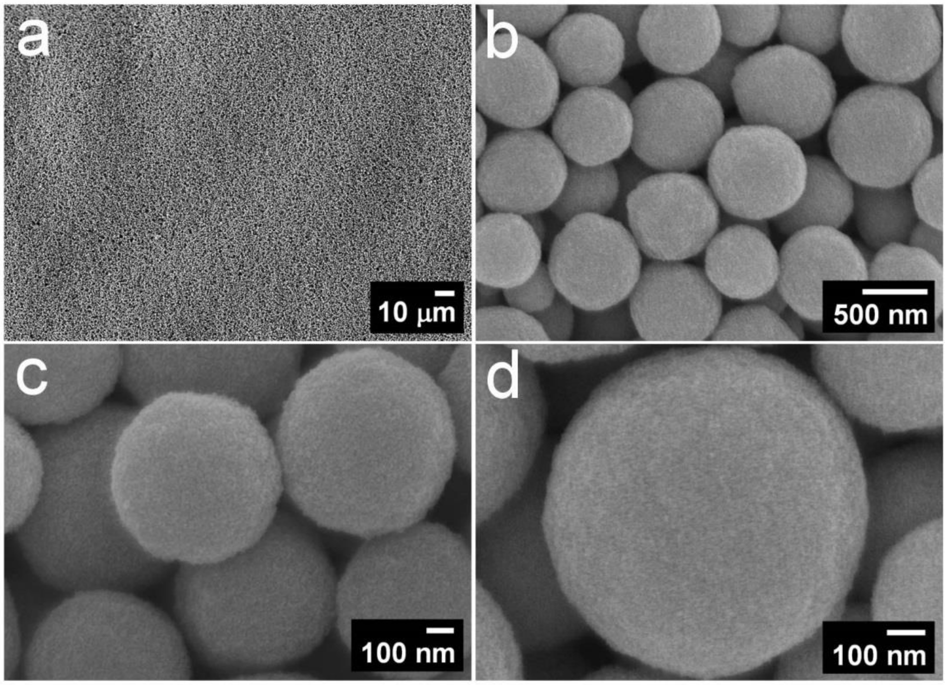


Fig. S3 FESEM images of TiO_2 microspheres prepared at 200 ^oC for 12 h, using 1 ml of titanium isopropoxide.

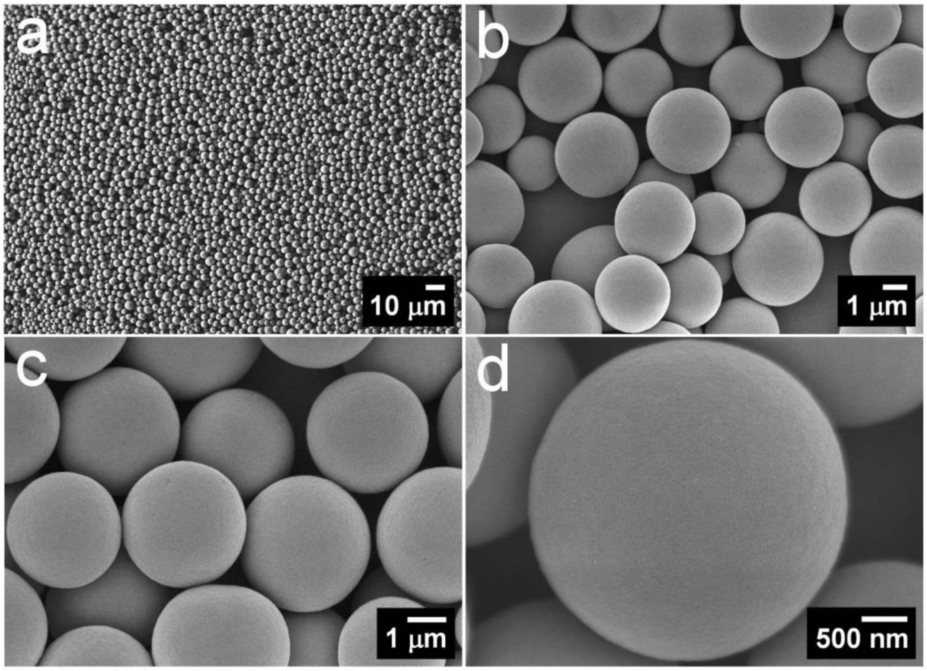


Fig. S4 FESEM images of TiO_2 microspheres prepared at 200 ^oC for 12 h, using 4 ml of titanium isopropoxide.

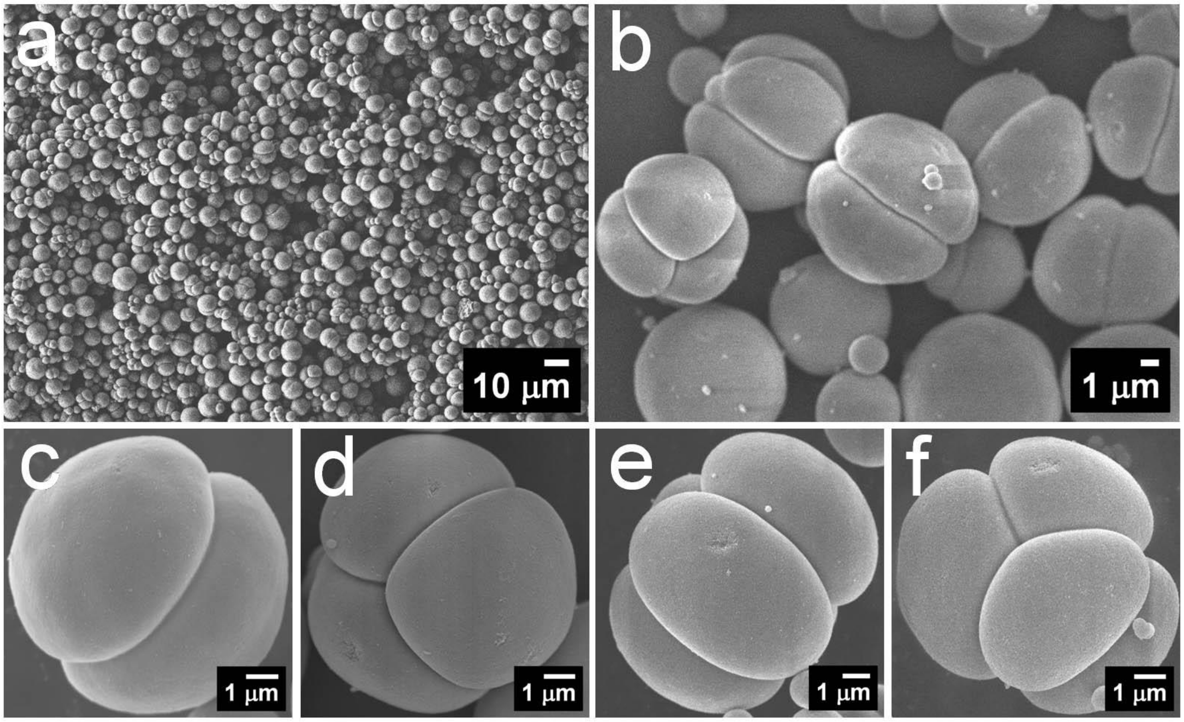


Fig. S5 FESEM images of TiO_2 multimers prepared at 200 ^{o}C for 12 h, using 8 ml of titanium isopropoxide.

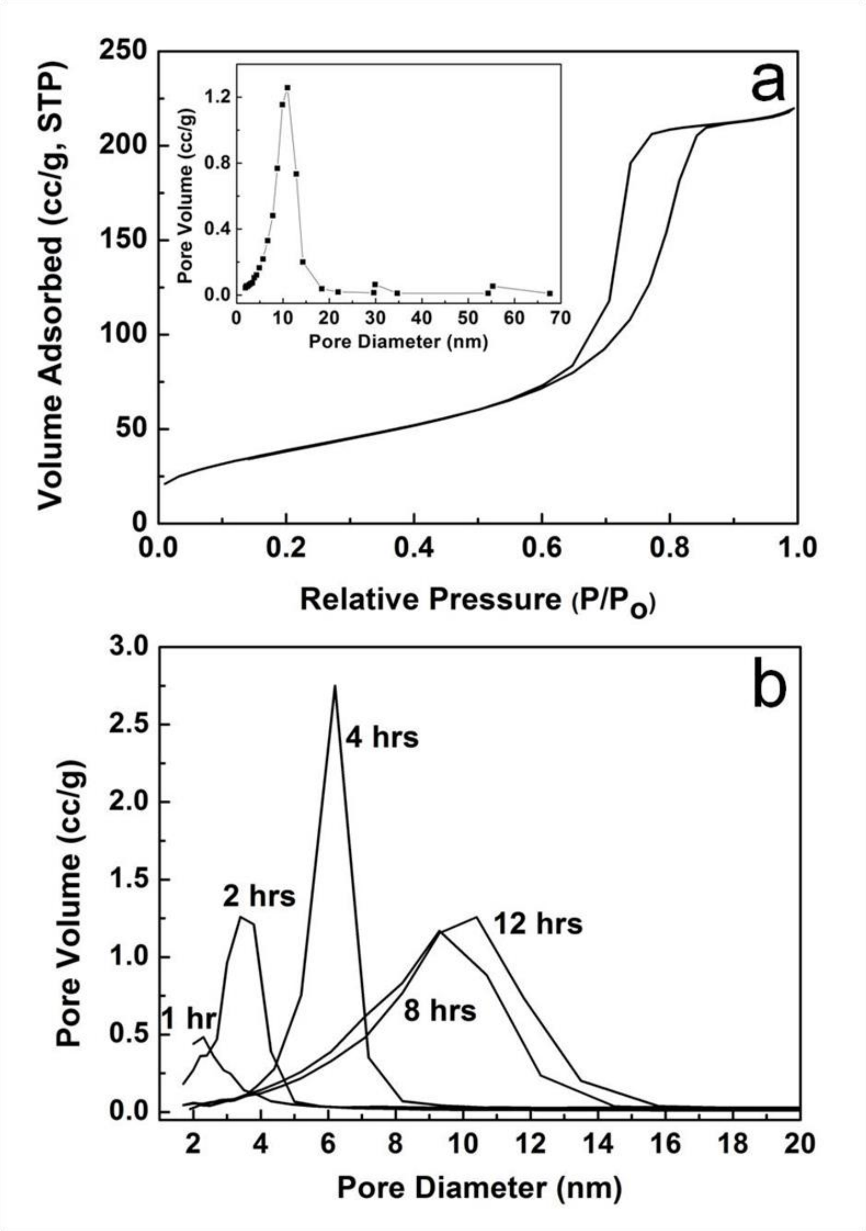


Fig. S6 (a) Nitrogen adsorption-desorption isotherm of TiO_2 microspheres prepared at 200 ^{o}C for 12 h, using 2 ml of titanium isopropoxide in 60 ml anhydrous acetone. Inset is the corresponding BJH pore size distribution. (b) BJH pore size distribution of TiO_2 microspheres prepared at 200 ^{o}C for various solvothermal reaction times.

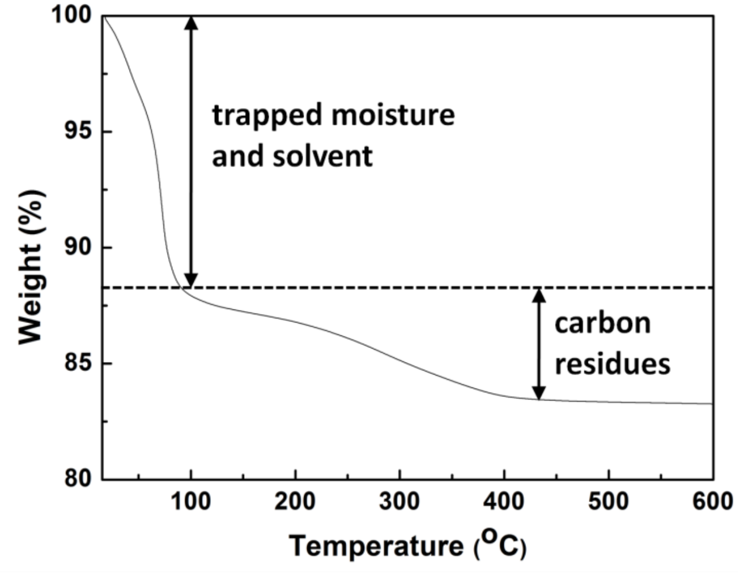


Fig. S7 TGA curve of TiO_2 microspheres prepared at 200 °C for 12 h, using 2 ml of titanium isopropoxide in 60 ml anhydrous acetone.

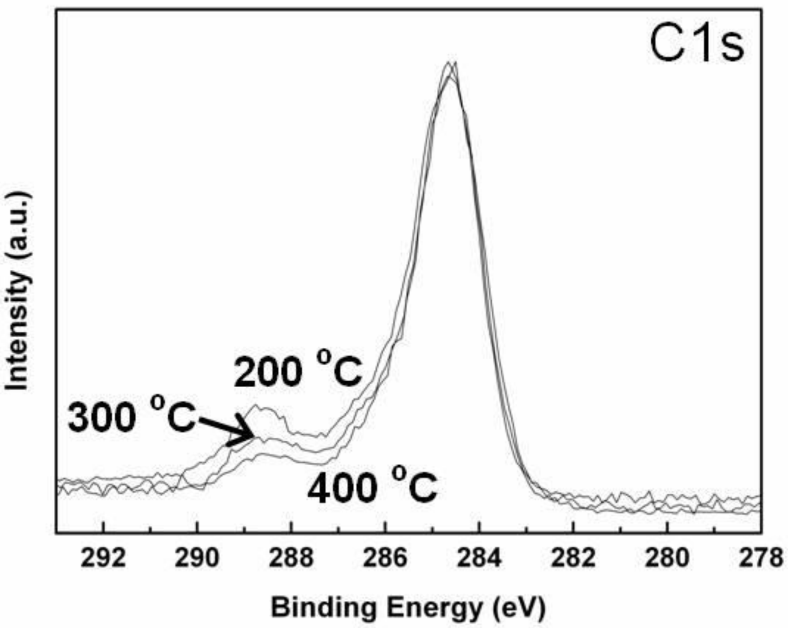


Fig. S8 XPS spectra of C1s band for TiO_2 microspheres prepared at various calcination temperatures.

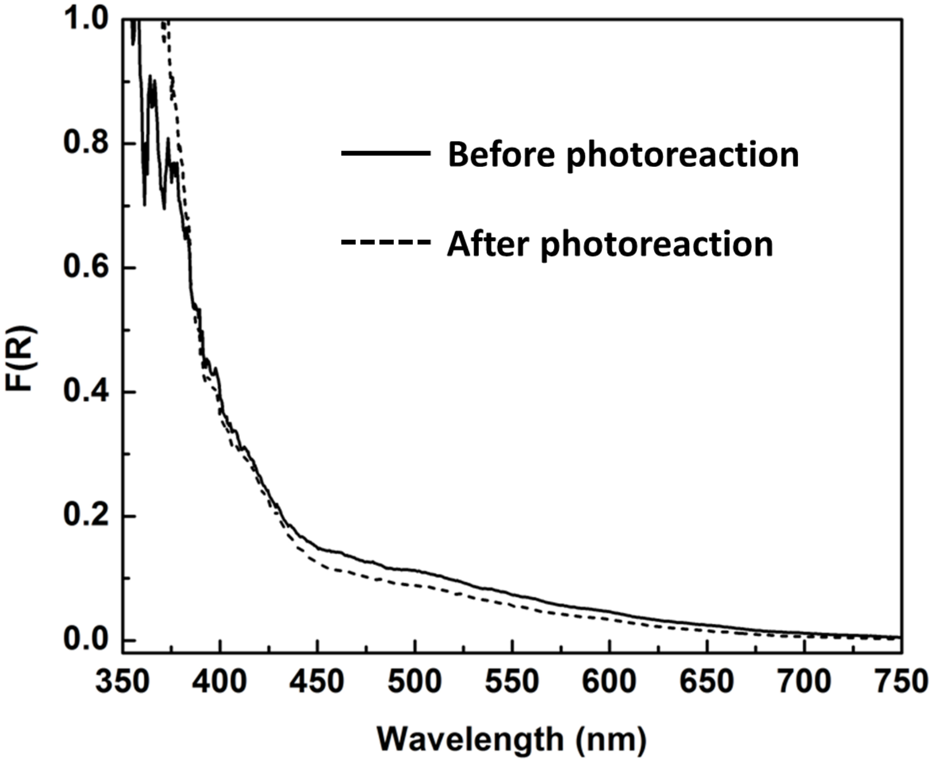


Fig. S9 Diffuse reflectance spectra of TiO_2 microspheres prepared after annealing at 200 ^{o}C for 2 h before and after photoreaction for 12 h.

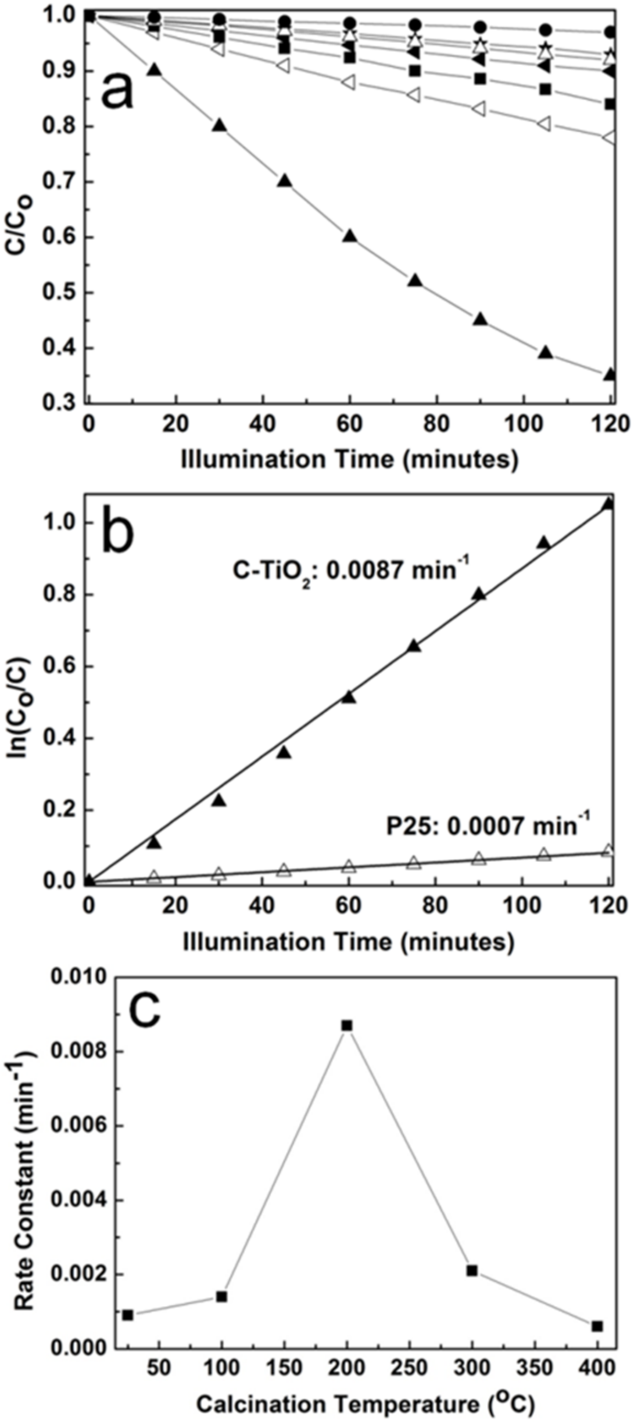


Fig. S10 (a) Photocatalytic degradation of methyl orange using different TiO_2 photocatalysts under visible light irradiation ($\lambda > 420$ nm). C_o and C are initial concentration and concentration at time *t* of methyl orange, respectively. (◀) As-prepared TiO_2 microspheres, (■) TiO_2 microspheres calcined at 100 ^{o}C for 2 h, (▲) TiO_2 microspheres calcined at 200 ^{o}C for 2 h, (◁) TiO_2 microspheres calcined at 300 ^{o}C for 2 h, (★) TiO_2 microspheres calcined at 400 ^{o}C for 2 h, (Δ) P25 nanoparticles, and (●) control with no photocatalyst. (b) Semilog plots based on the data from (a) to determine the first order rate constants. (▲) TiO_2 microspheres calcined at 200 ^{o}C for 2 h and (Δ) P25 nanoparticles. (c) Rate constant of photocatalytic degradation of methyl orange as a function of microsphere calcination temperature.