Supplementary Material (ESI) for Chemical Communications

Supplementary Information:

Characterization:

The X-ray diffraction (XRD) patterns, obtained on a Bruker D8 Advance X-ray diffractometer using Cu-Kα radiation ($\lambda = 1.54178$ Å) at a scan rate of 0.05^{o} 2θ s^{-1}, were used to identify the phase constitutions in samples and their crystallite size. The accelerating voltage and the applied current were 40 kV and 40 mA, respectively. The crystallite size was calculated from X-ray line broadening analysis by Scherrer formula. Scanning electron microscopy images and energy dispersive X-ray spectrum were performed on a LEO 1450VP scanning electron microscope with an energy-dispersive X-ray instrument (Oxford Instrument). X-ray photoelectron spectroscopy (XPS) measurements were performed on a PHI Quantum 2000 XPS System with a monochromatic Al-Kα source and a charge neutralizer. All the binding energies were referenced to the C1s peak at 284.8 eV of the surface adventitious carbon. The nitrogen adsorption and desorption isotherms of the resulting films on substrates at 77 K were measured using a Micromeritics ASAP2010 system after the film samples were vacuum-dried at 180^{o}C overnight. UV-visible diffuse reflectance spectra were achieved using a UV-Visible spectrophotometer (Cary 100 Scan Spectrophotometers, Varian, U.S.A.). Electron spin resonance (ESR) spectra were obtained using a Bruker model ESP 300E ESR spectrometer. The settings for the ESR spectrometer were center field 3480.00 G, microwave frequency 9.79 GHz, and power 5.05 mW.

Photocatalytic activity measurements:

The photocatalytic activities of the F-doped TiO_2 microspheres samples were measured by the degradation of 4-chlorophenol in an aqueous solution. O_2 was bubbled into the solution throughout the experiment. A 300 W tungsten halogen lamp with a 400 nm cut off filter was used as visible light source. 0.2 g of photocatalyst was suspended in a 200 mL aqueous solution of 2.5 x 10^{-4} M 4-chlorophenol. The concentrations of 4-chlorophenol and its degradation products were measured with a HPLC system (Waters Baseline 810) with a Waters 486 tunable UV absorbance detector. A Supelco LC-18-DB column (250 mm x 4.6 mm) was applied. The eluent consisted of a 40:60 methanol : water mixture, and the flow rate was 1 ml/min. The aromatic compounds were detected at 220 nm. Millipore discs were used to separate the catalysts before analysis of the solution.

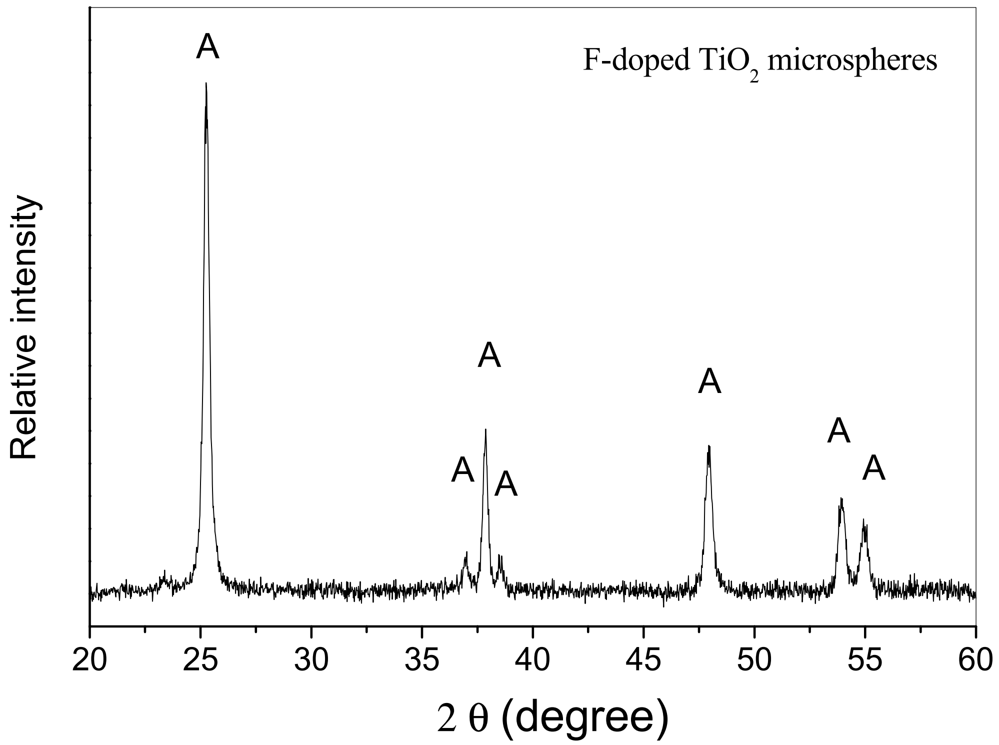

Fig. S1 XRD patterns of porous F-doped TiO_2 microspheres "A" represents the peaks of anatase phase.

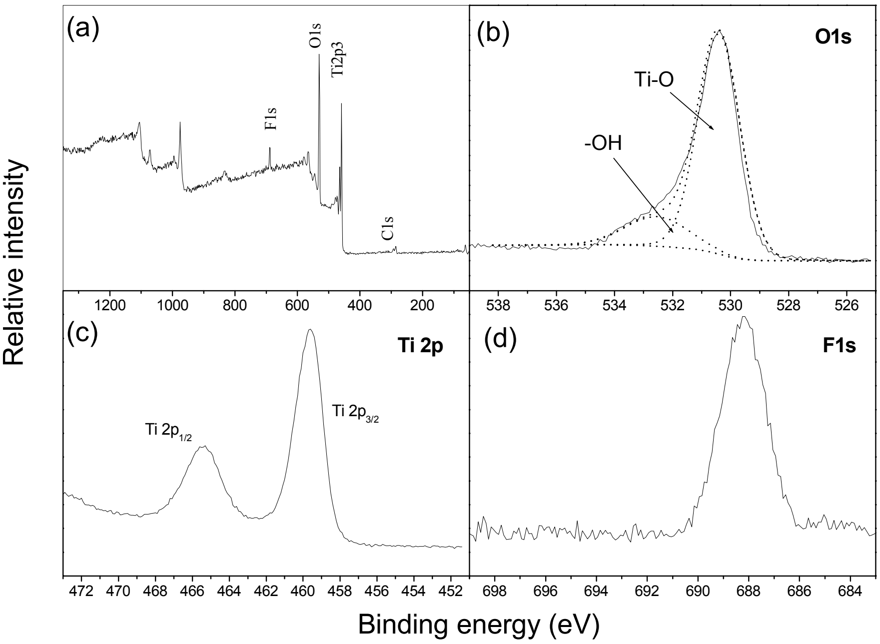

Fig. S2 (a) Survey XPS spectrum of F-doped TiO_2 microspheres; High-resolution XPS spectra of the (b) O1s, (c) Ti2p and (d) F1s regions for the porous F-doped TiO_2 microspheres. The large O1s peak at 530.5 eV is assigned to the lattice oxygen atom of TiO_2 and the small peak at 532.6 eV to the surface hydrated oxygen.

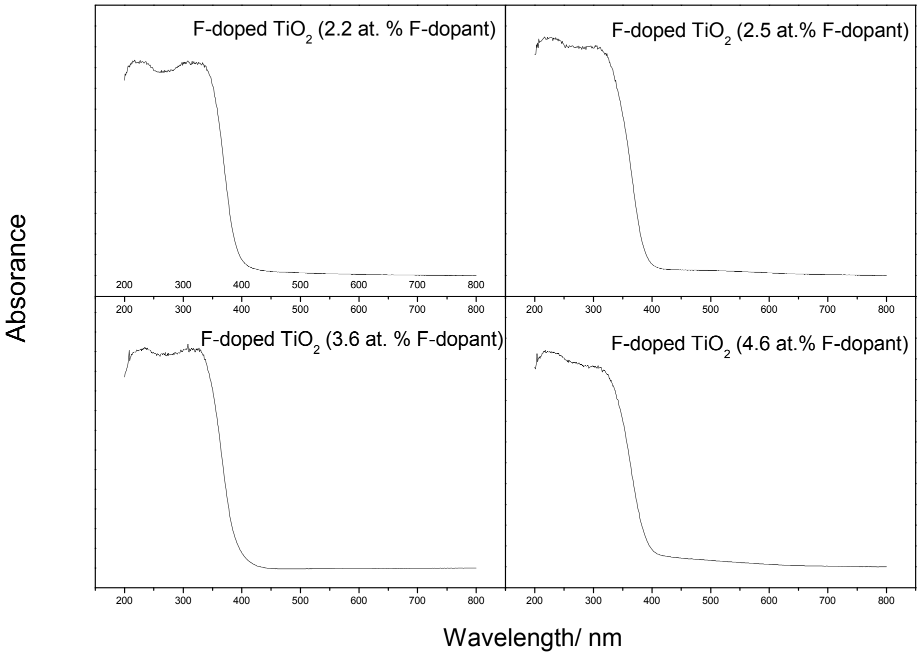

Fig. S3 UV-vis diffuse reflectance spectra of porous F-doped TiO_2 microspheres with different fluorine contents.

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Table S1: Crystalline sizes, F-dopant concentrations, visible light photocatalytic activity of F-doped TiO_2 microspheres with different concentrations of TiF_4 used in the hydrothermal synthesis.

samples	Crystalline size [a] (nm)	Conc. of F-dopant [b] (%)	Photocatalytic activity [c] (C_t/C_o, t = 6h)
Without Photocatalyst	-	-	0
F-TiO_2 (0.5M)[d]	11	2.2	0.45
F-TiO_2 (1M)	15	2.5	0.36
F-TiO_2 (2M)	13	3.6	0.43
F-TiO_2 (5M)	12	4.6	0.50

[a] Crystalline size of anatase calculated from (101) by the Scherrer equation.

[b] Atomic percentage of fluorine in the F-doped TiO_2 measured from the XPS results.

[c] C_o = initial concentration of 4-chlorophenol, C_t = concentration of 4-chlorophenol after 6 h visible light irradiation measured by HPLC.

[d] Concentration of TiF_4 used for hydrothermal synthesis.