Electronic Supplementary Information

Novel Fe-incorporated anatase TiO_2 nanosheets hierarchical spheres with 94% {001} facets for efficient visible-light photodegradation of organic dye

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Experimental Section

1. Preparation of {001}-Fe-anatase TiO_2 nanosheets hierarchical spheres

The Fe-incorporated anatase TiO_2 nanosheets hierarchical spheres with a high percentage of {001} facets were synthesized by a one-pot solvothermal method. Typically, 0.05 mL of diethylenetriamine (DETA, 98 wt% purity) was added to 71 mL of isopropyl alcohol (IPA). After the solution was gently stirred for a few minutes, 3.35 mL (10 mmol) of titanium (IV) isopropoxide (TIP, 98 wt% purity) was added and then a proper amount of $FeCl_3•6H_2O$ (2.7mg, 0.01 mmol or 5.4 mg, 0.02 mmol) was added. After sonicating for 5 min, the resultant solution was transferred into a 100 mL Teflon-lined stainless steel autoclave and kept in an electric oven at 200^oC for 24 h. The autoclave was then taken out of the oven and left to cool naturally to room temperature. The precipitate was harvested via centrifugation, washed thoroughly with absolute ethanol, and dried at 60^oC overnight. Resultants were calcined at 400^oC in static air for 2 h with a heating rate of 1^oC min^{-1} leading to the slight yellow product. The obtained Fe-incorporated anatase TiO_2 nanosheets hierarchical spheres with expected high percentage of {001} facets were named as {001}-*x*Fe-AHSs, where *x* refers to the nominal molar ratio of Fe to Ti, i.e., $x = n_{Fe}/n_{Ti}$ = 0.1% or 0.2% according to the above synthesis parameters. A pure {001}-AHSs without Fe incorporation was also prepared as a reference.

2. Characterizations

Powder X-ray diffraction (XRD) data were taken on a Shimadzu XRD-6000 diffractometer using Cu Kα radiation (λ = 1.5418 Å, 40 kV, 30 mA). The samples, as unoriented powders, were step-scanned in step of 0.02° (2θ) in the range of 10-70° using a count time of 4 s per step. Raman spectroscopy measurements were performed at room temperature using a LabRAM ARAMIS spectrometer with the excitation light of 532 nm in the range of 75-800 cm^{-1}. The scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) measurements were carried out on an Oxford Instruments INCAx-act EDX detector attached to a Zeiss Supra 55 field emission scanning electron microscopy (FESEM) using a 15 kV electron beam and 60 s acquisition time. The transmission electron microscopy (TEM) was carried out on a Hitachi H-800 instrument with an accelerating voltage of 100 kV. The high resolution TEM graphs were recorded on a JEM 2010 transmission electron microscope with an accelerating voltage of 200 kV. The specific surface areas and the pore size distributions of the catalysts were determined from low temperature nitrogen adsorption-desorption isotherms on a Quantachrome Autosorb-1C-VP System by using the Brunauer-Emmett-Teller (BET) and the Barrett-Joyner-Halenda (BJH) method, respectively. X-ray photoelectron spectroscopy (XPS) was recorded on a Thermo VG ESCALAB250 X-ray photoelectron spectrometer at a base pressure of 2×10^{-9} Pa using Al Kα X-ray (1486.6 eV) as the excitation source. All the binding energies were referenced to the C1s peak (284.6 eV) of the surface adventitious carbon. Solid-state spectra (DRS) were recorded on a Shimadzu UV-3000 spectrometer equipped with an integrating sphere attachment in the range of 200-800 nm at room temperature in air. $BaSO_4$ was used as a reflectance standard in the UV-visible diffuse reflectance experiments.

3. Catalytic reaction

The liquid phase photocatalytic degradation of methylene blue (MB) was performed at 298 K in a 200 mL quartz reactor containing 0.050g of catalyst (Degussa as reference) and 100 ml MB aqueous solution (10 mg/L) under visible light irradiation. After stirring in dark for 30 min until reaching adsorption equilibrium, the photocatalytic reaction was initiated by irradiating the system with a 300 W xenon lamp (Beijing Trusttech Co. Ltd, PLS- SXE-300UV) located 15 cm away from the reaction solution. All UV lights with wavelengths less than 420 nm, were removed by a glass filter. Each run of reactions lasted for 1 h, and the MB was analyzed by a UV spectrophotometer (Shimadzu UV-3000) at its absorption maximum (λ = 665 nm) to determine the degradation yield. Preliminary tests indicates that less than 10% MB decomposed after reaction for 1 h in the absence of either the photocatalyst or the light irradiation and thus could be neglected in comparison with MB degradation yields resulting from real photocatalysis.

Cycle regeneration experiment After the photocatalytic degradation reaction, the catalyst was centrifuged and dried at 60^{o}C overnight. The resultant was further calcined at 400^{o}C in static air for 30 min with a heating rate of 1^{o}C min^{-1} to remove the organic residue adsorbed on the catalyst. The obtained regeneration catalyst was subjected to the degradation reaction of MB under visible light irradiation again. The cyclic regeneration experiment was performed three times.

Analysis of hydroxyl radical (•OH) The generation of hydroxyl radicals (•OH) at photo-illuminated samples/water interface was detected by the photoluminescence (PL) technique using terephthalic acid (TA) as a probe molecule. The experimental procedure is similar to the measurement of photocatalytic activity except replacing the MB aqueous solution by the TA aqueous solution. In detail, 10 mg of the catalyst was suspended in 40 ml aqueous solution containing 0.01 M NaOH and 3 mM TA aqueous solution. After stirring in dark for 30 min until reaching adsorption equilibrium, the photocatalytic reaction was initiated by irradiating the system with a 300 W xenon lamp. Then 4 mL of the solution was taken out after every 20 min, for the visible light irradiation, and centrifuged for fluorescence spectrum measurements. During the photoreactions, no oxygen was bubbled into suspension. A Shimadzu RF-5301PC fluorescence spectrophotometer was used to measure the fluorescence signal at 425 nm of the 2-hydroxyterephthalic acid generated. The excitation light employed in recording fluorescence spectra was 310 nm.

Equation S1

Scherrer equation[1]

$D = 0.89\lambda/(\beta\cos\theta)$, where λ is the X-ray wavelength (Cu Kα, 0.1542 nm), θ is the Bragg diffraction angle (deg.), and β is the FWHM (rad.) of the XRD lines.

Equation S2

Langmuir-Hinshelwood kinetics equation[2]

$\ln(C_t/C_0) = - k_{app}t$, where k_{app} is the pseudo-first-order rate constant (min^{-1}), C_0 is the initial concentration and C_t is the concentration of different reaction time t.

Table S1 Kinetic values derived from equation S2 for the degradation of MB on different catalysts under visible light irradiation.

Catalysts	$k_{app} \times 10^3$（min^{-1}）	R
{001}-0.1%Fe-AHSs	61.07	0.96844
{001}-0.2%Fe-AHSs	24.13	0.99585
{001}-AHSs	37.33	0.98053
P25	6.68	0.99731

Reference

1 Y. M. Wu, J. L. Zhang, L. Xiao and F. Chen, *Appl. Catal. B*, 2009, **88**, 525.

2 I. K. Konstantinou, T. A. Albanis, *Appl. Catal. B*, 2004, **49**, 1.

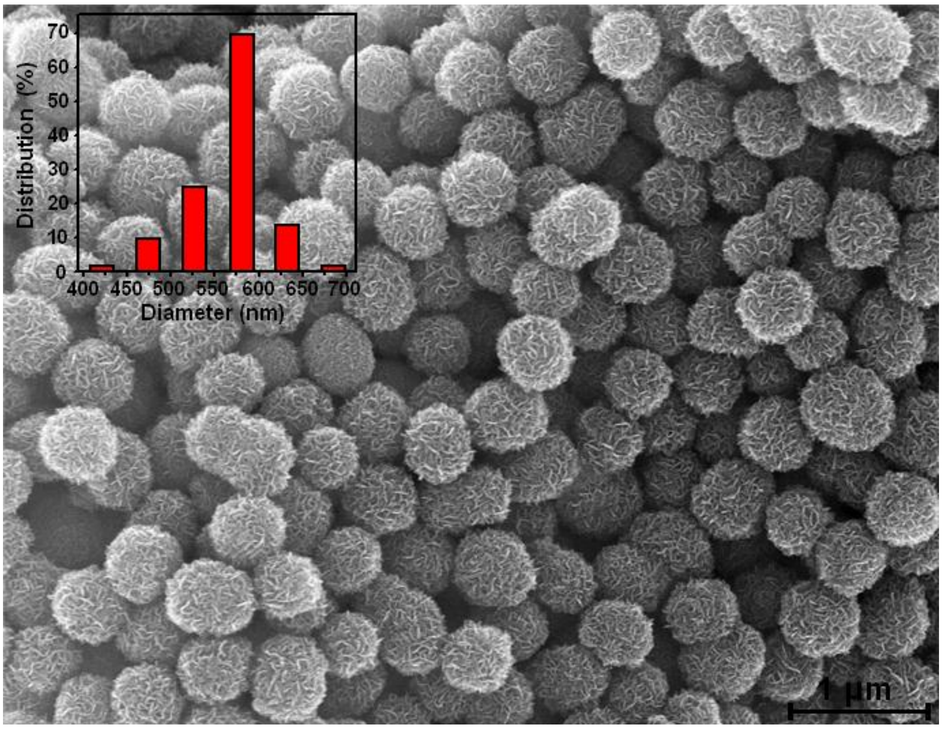

Fig. S1 The low-magnified SEM image and Particle size distribution of {001}-0.1%Fe-anatase TiO_2 nanosheets hierarchical spheres catalyst.

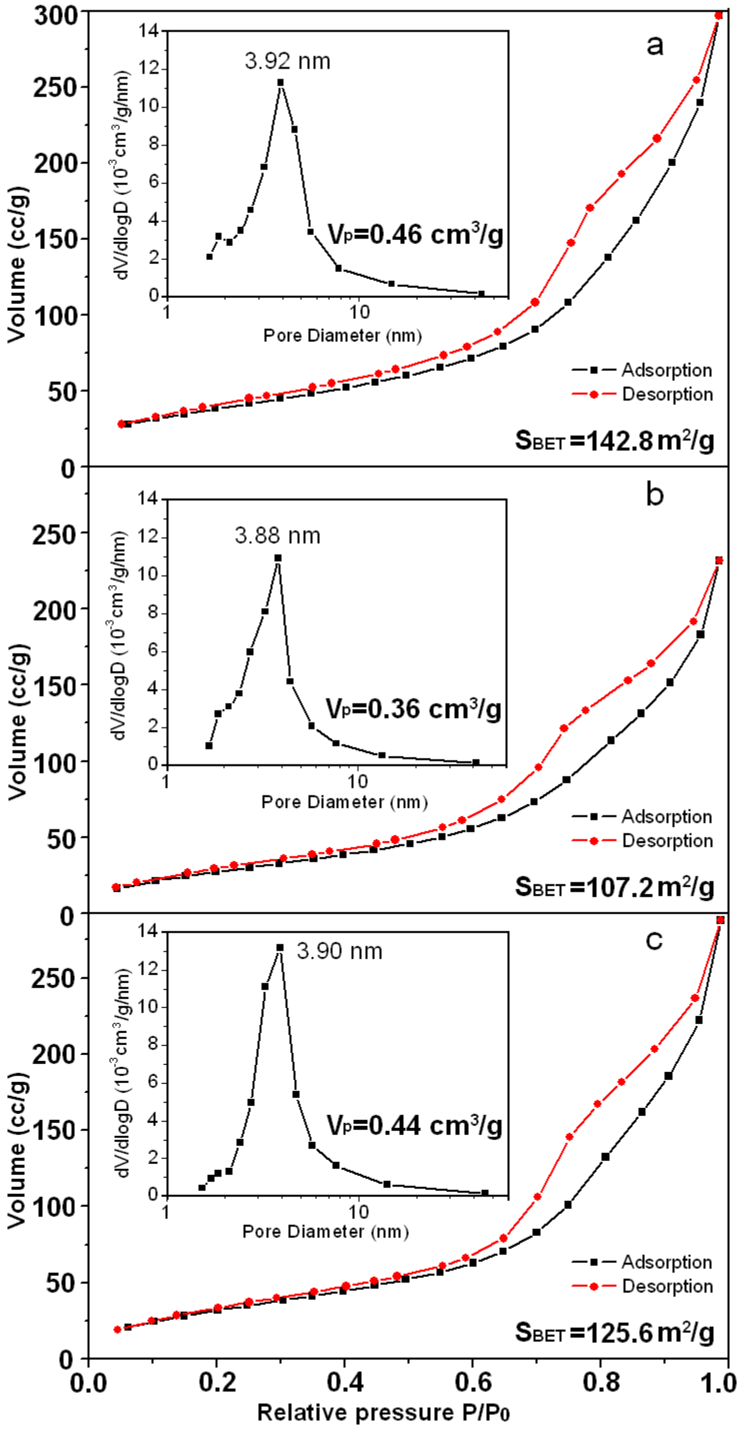

Fig. S2 N_2 adsorption-desorption isotherm of {001}-xFe-TiO_2 anatase nanosheets hierarchical spheres catalysts {001}-0.1%Fe-AHSs (a), {001}-0.2%Fe-AHSs (b) and {001}-AHSs (c) (Insets show the corresponding pore size distribution curves calculated by the Barrett-Joyner-Halenda (BJH) method).

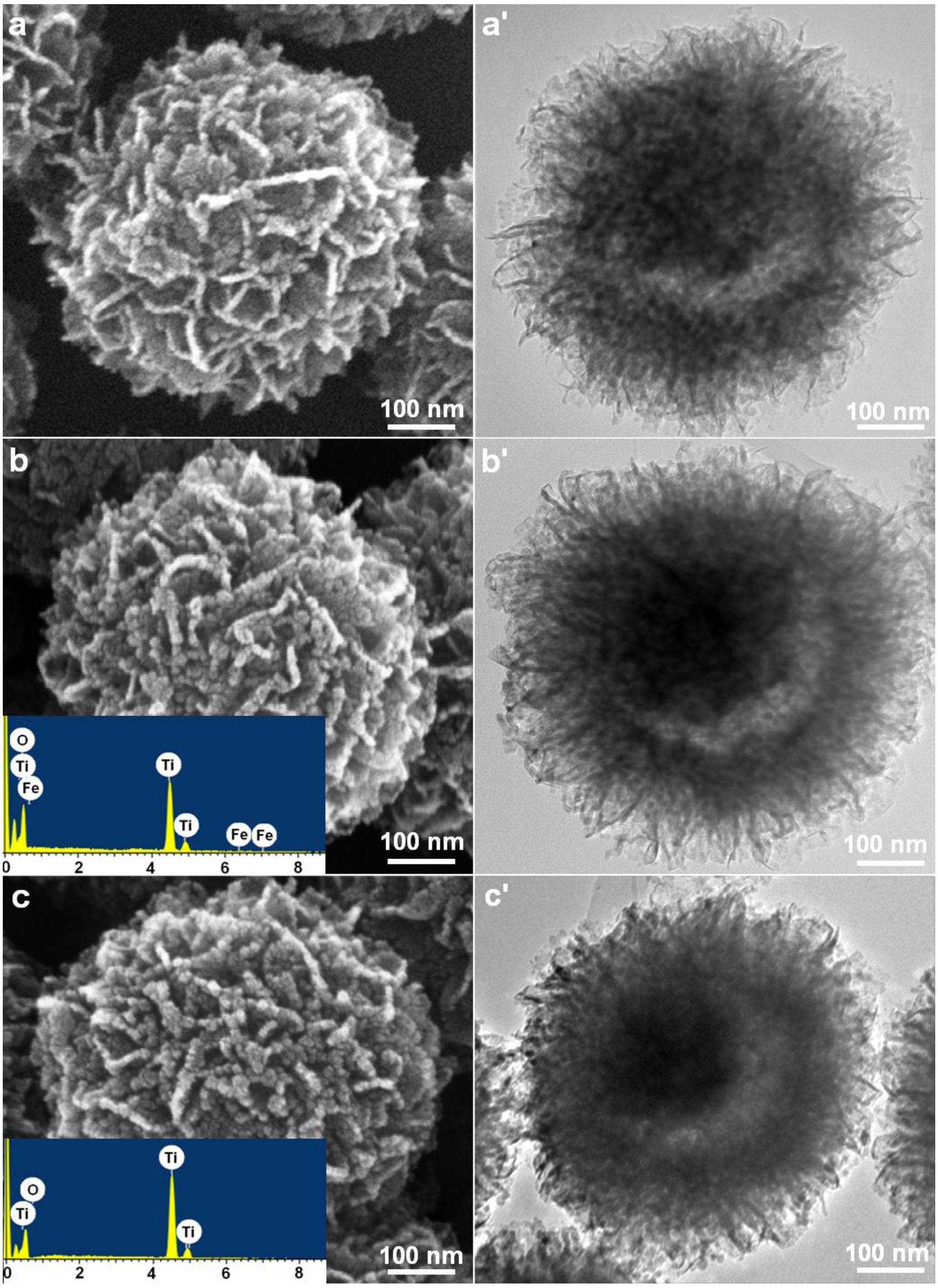

Fig. S3 SEM and TEM images of {001}-0.1%Fe-AHSs (a, a’), {001}-0.2%Fe-AHSs (b, b’) and {001}-AHSs (c, c’) (Insets present the EDX results).

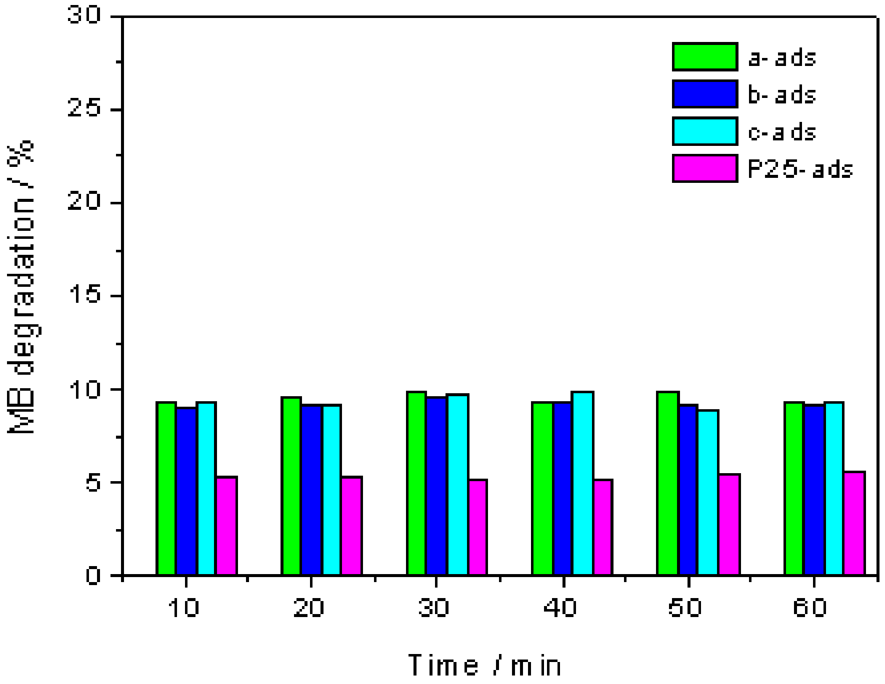

Fig. S4 Photodegradation results of MB upon the adsorption on {001}-0.1%Fe-AHSs (a), {001}-0.2%Fe-AHSs (b), {001}-AHSs (c) and P25 without visible light irradiation.

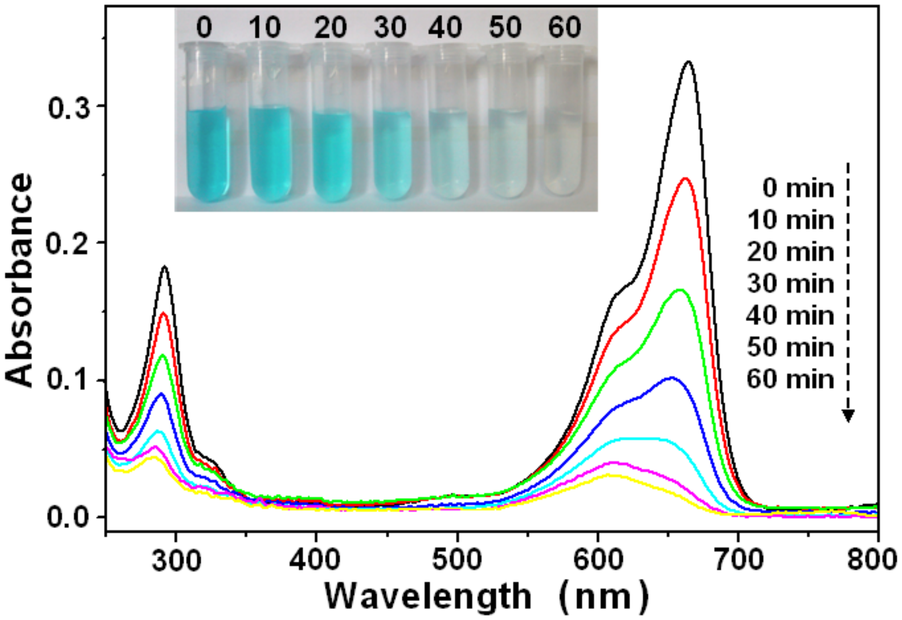

Fig. S5 UV-vis absorbance spectral changes of the MB aqueous solutions at different irradiation time under visible light in the presence of {001}-0.1%Fe-AHSs.

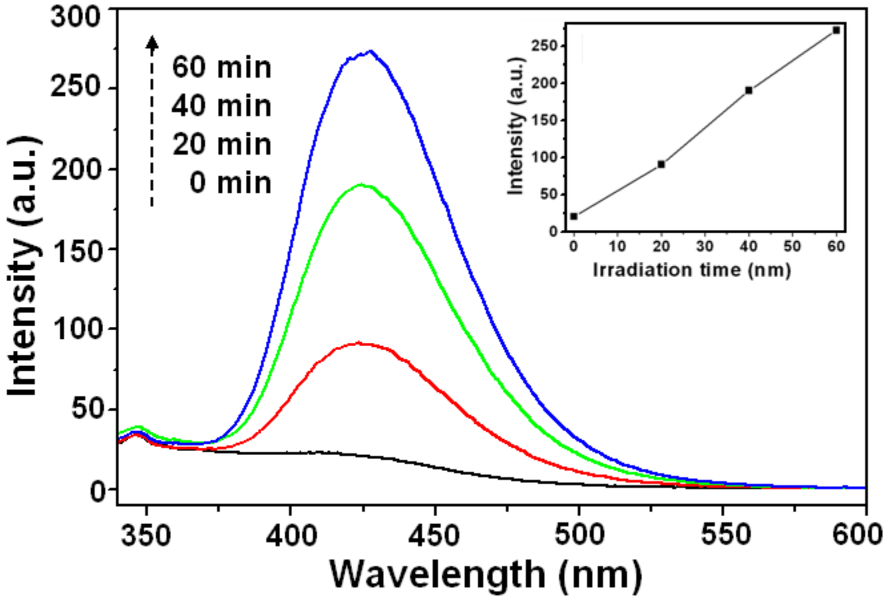

Fig. S6 Fluorescence spectral changes with visible light (420~770 nm) irradiation time for {001}-0.1%Fe-AHSs in a 3 mM terephthalic acid (Insets are the dependence of the fluorescence signal intensities at 425 nm on the irradiation time). The nearly linear relationship between PL intensity and irradiation time confirms the stability of {001}-0.1%Fe-AHSs.