Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Improved photoactivities of TiO_2/Fe_2O_3 nanocomposites for visible light water splitting after phosphate bridging and mechanism

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Supporting Information (SI).

SI-Experimental section

Synthesis of materials.

TiO_2 was synthesized by a sol-hydrothermal method.[1] A typical process was as follows: 5 mL $Ti(OBu)_4$ was dissolved in 5 mL anhydrous ethanol in a dry atmosphere, and then the mixed solution was added dropwise into another mixture consisting of 20 mL anhydrous ethanol, 5 mL water and 1 mL 70% HNO_3 at room temperature under vigorously stirring, forming a yellowish transparent sol. Subsequently, 30 mL of resulting sol was kept at 160 ℃ for 6 h in a Teflon-lined stainless-steel vessel to carry out hydrothermal reactions, and afterwards cooled naturally to room temperature. After washed with deionized water and absolute ethanol in turn, and dried at 80 ℃ in air, spherical TiO_2 was obtained.

Film preparation.

To fabricate the Fe_2O_3, phosphate-modified Fe_2O_3, TiO_2-Fe_2O_3 and different phosphate-bridged TiO_2-Fe_2O_3 nanocomposite films for photoelectrochemical (PEC) measurements, the corresponding pastes were synthesized as follows: 0.5 g nanopowder was dispersed in 2 mL iso-propyl alcohol, and then treated by an ultrasonic process for 30 min and stirring for 30 min. Then, 0.25 g of Macrogol-6000 was added to the above system, and another treated by an ultrasonic process for 30 min and stirring for 30 min. Subsequently, 0.1 mL of acetylacetone was introduced to the above mixture, followed by a 30 min-ultrasonic treatment and continuously stirring for 24 hours, forming the paste. Conductive fluorine doped tin oxide (FTO)-coated glasses, used as the substrates for the nanocomposite films, were cleaned by sonicating in acetone for 30 min and then in deionized water for another 30 min. After dried in air, the FTO was sintered at 450 ℃ for 30 min prior to use. Typically, nanocomposite film was prepared by the doctor blade method using Scotch tape as the spacer, followed by drying in air for 30 min. Then, films were sintered at 450 ℃ for 30 min. After that, the FTO glass covered by the nanocomposite film was cut into 1.0 cm × 3.0 cm pieces with nanocomposite film surface area of 1.0 cm × 1.0 cm. To make a photoelectrode, an electrical contact was made with FTO substrate by using silver conducting paste connected to a copper wire which was then enclosed in a glass tube. The working geometric surface area of nanocomposite was 0.5 cm × 0.5 cm where the remaining area was covered by epoxy resin.

Measurement of O_2 evolution.

To measure the produced O_2 amount in the PEC water oxidation, the as-prepared films were used as working electrodes in a sealed quartz cell with 0.5 M Na_2SO_4 solution of 80 mL as electrolyte, and high-purity nitrogen gas was employed to bubble through the electrolyte before the experiment. The films were illuminated from the FTO glass side, whose illuminated working area was about 0.5 cm × 0.5 cm, at the constant bias of 0.4 V. During the experiment, the produced O_2 amount was detected quantitatively with an Ocean Optics fluorescence-based oxygen sensor (NFSC 0058) by putting the needle probe into the electrolyte, near to the working electrode, and the irradiation was lasted for 10 min using a 500 W Xenon light with a 420 cutoff filter as the illumination source.

Measurement of hydroxyl radical (•OH).

In the analysis of hydroxyl radical, 50 mg sample and 20 mL 5 mg/L^{-1} coumarin aqueous solution were fixed in a 50mL quartz reactor. Utilize a 150 W high-pressure Xenon lamp as its irradiation source with a cutoff filter ($\lambda > 420$ nm) placed at about 10 cm from the reactor under magnetically stirring for 1 h. Finally, a certain amount of the solution was transferred into a Pyrex glass cell for the fluorescence measurement of 7-hydroxycoumarin under the light excitation of 332 nm.

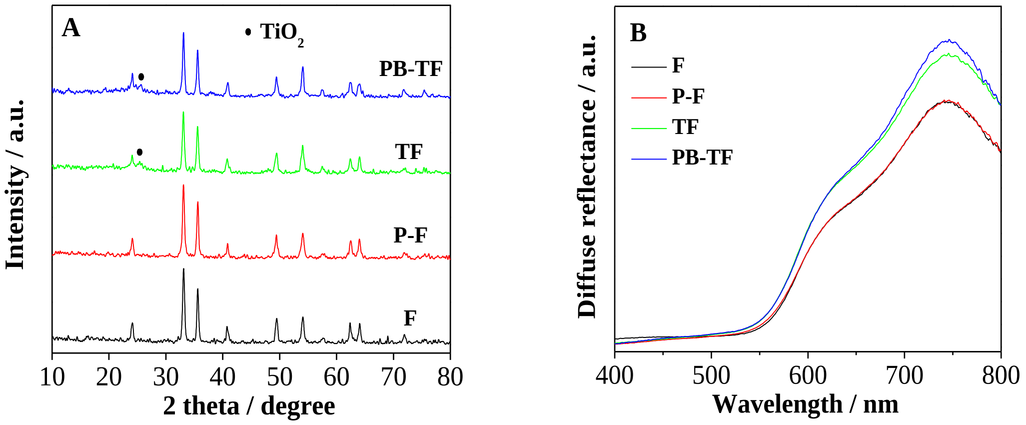
Photocatalytic degradation of pollutants.

Phenol as a typical recalcitrant contaminant without sensitizing as a dye and acetaldehyde as a kind of volatile organic compound widely existing in industrial production are harmful to human health and natural environment. Thus, phenol and acetaldehyde were chosen as liquid-phase and gas-phase representative pollutants to evaluate the photocatalytic activity of the fabricated nanocomposite samples under visible irradiation, respectively. The liquid-phase photocatalytic experiments were carried out in a 100 mL of open photochemical glass reactor, and irradiation was provided from a side of the reactor by using a 150 W GYZ220 high-pressure Xenon lamp made in China with a cutoff filter ($\lambda > 420$ nm), which was placed at about 10 cm from the reactor. During the photocatalytic degradation of phenol, 0.2 g of photocatalyst and 60 mL of 10 mg/L phenol solution were mixed by a magnetic stirrer for 0.5 h to reach the adsorption saturation and then begin to irradiate. After photocatalytic reaction for 1 h, the phenol concentration was analyzed by the colorimetric method of 4-aminoantipyrine at the characteristic optical adsorption of 510 nm with a Model Shimadzu UV2550 spectrophotometer after centrifugation.

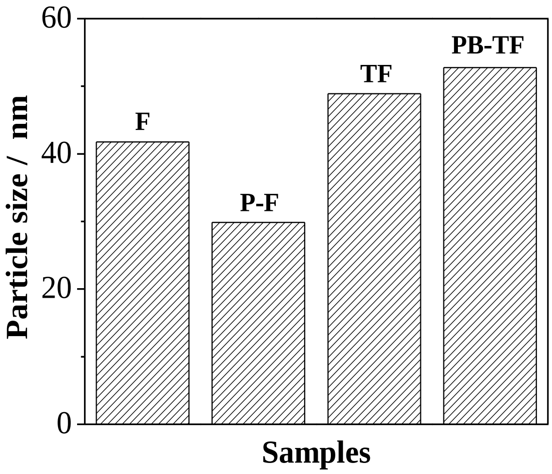
For the photocatalytic degradation of gas-phase acetaldehyde, it was conducted in a 640 mL of cylindrical quartz reactor with 3 mouths for introducing a planned amount of photocatalyst powders and a planned concentration of acetaldehyde gas. The reactor was placed horizontally and irradiated from the top side by using a 150 W xenon lamp with a cutoff filter ($\lambda > 420$ nm). In a typical process, 0.2 g of photocatalyst was used, and a premixed gas system, which contained 810 ppm acetaldehyde, 20% of O_2, and 80% of N_2, was introduced into the reactor. To reach adsorption saturation, the mixed gas continuously moved through the reactor for half an hour prior to the irradiation. The determination of acetaldehyde concentration at different time interval in the photocatalysis was performed with a gas chromatograph (GC-2014, Shimadzu) equipped with a flame ionization detector.

1 L. Q. Jing, Y. C. Qu, H. J. Su, C. H. Yao and H. G. Fu, *J. Phys. Chem. C*, **2011**, *115*, 12375.

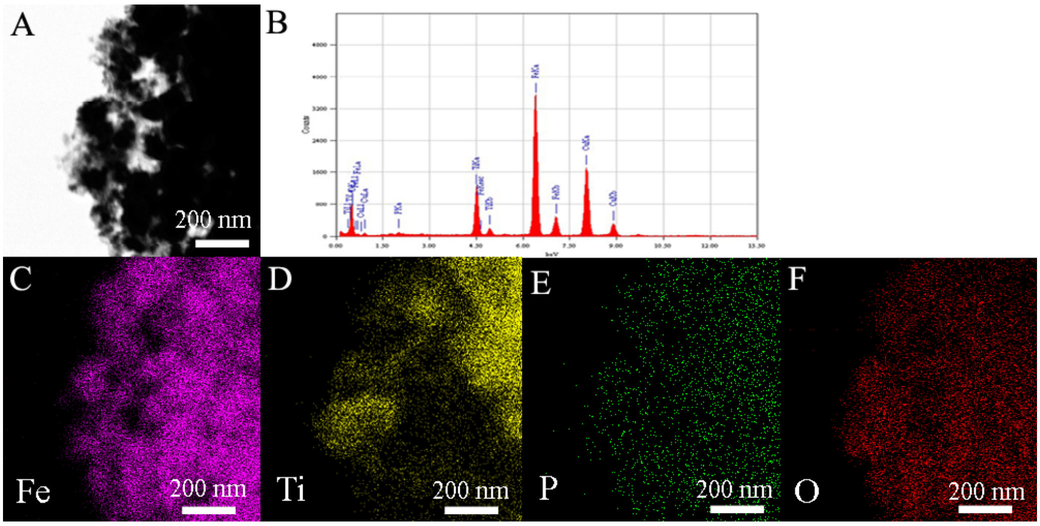
SI-Fig. 1 XRD patterns (A) and UV-Vis DRS spectra (B). (F: α-Fe_2O_3, P-F: 0.5% phosphate-modified α-Fe_2O_3, TF: TiO_2-coupled α-Fe_2O_3, and PB-TF: 0.5% phosphate-bridged TiO_2-Fe_2O_3, 0.5% means mole ratio of P to Fe in P-F and PB-TF, and the same elsewhere unless stated)



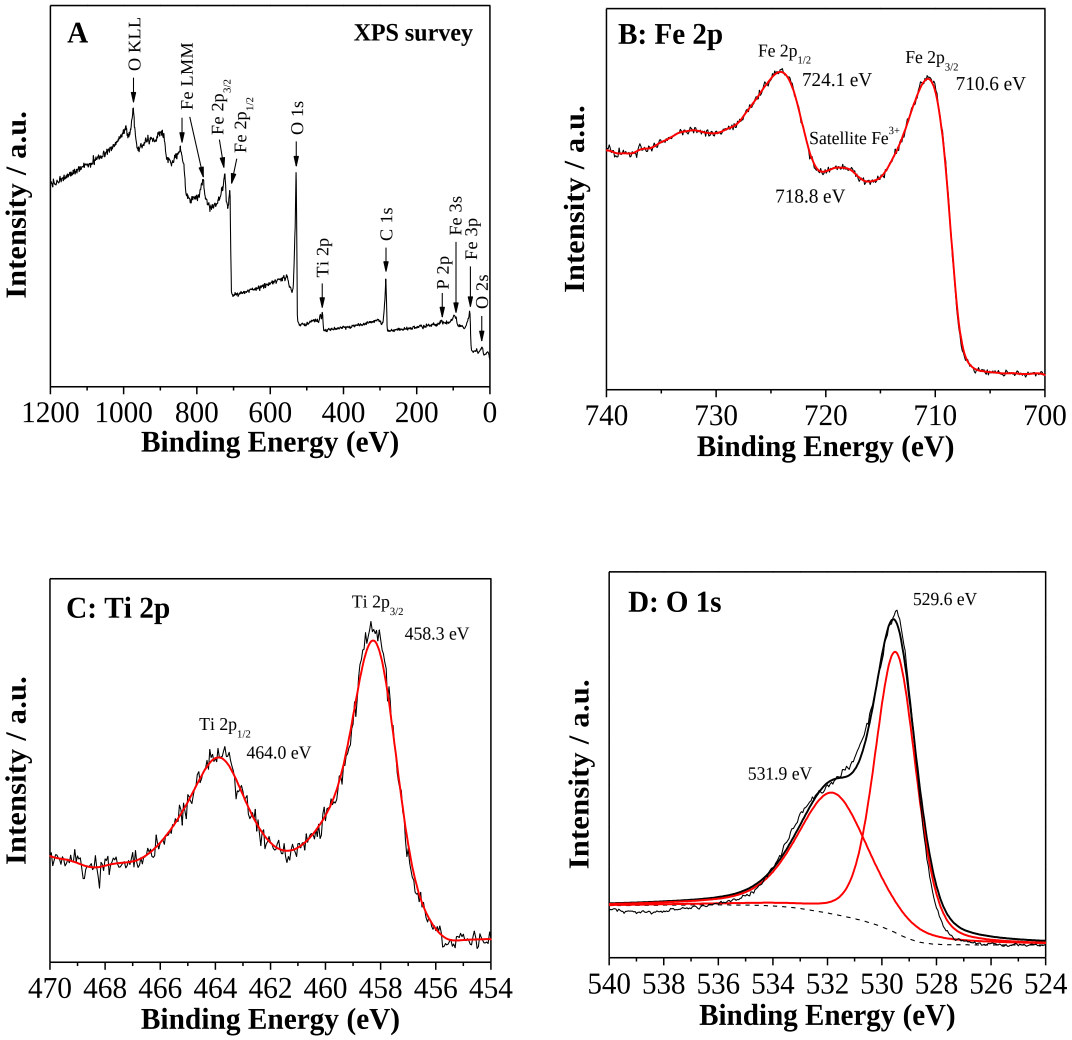
SI-Fig. 2 Average particle size histograms of F, P-F, TF, PB-TF.



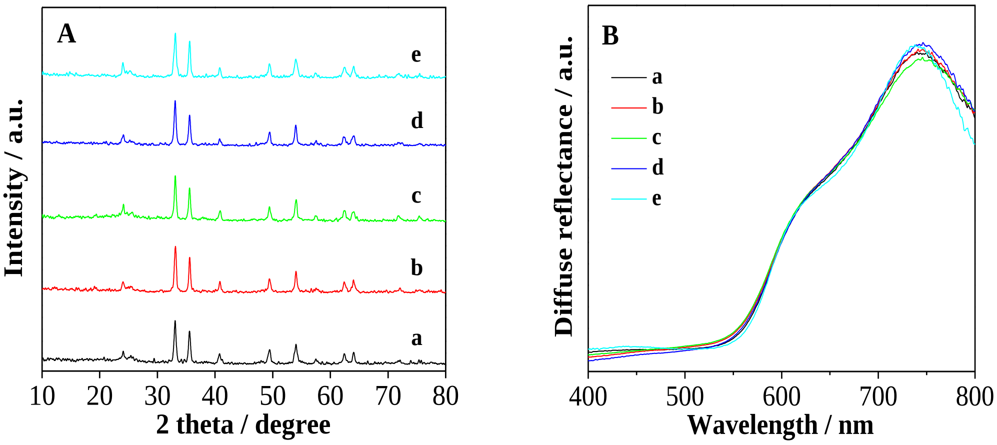
SI-Fig. 3 TEM image (A), TEM-EDS spectrum (B) and TEM-EDS mapping of PB-TF to show the spatial distribution of Fe, Ti, P, O (C-F).



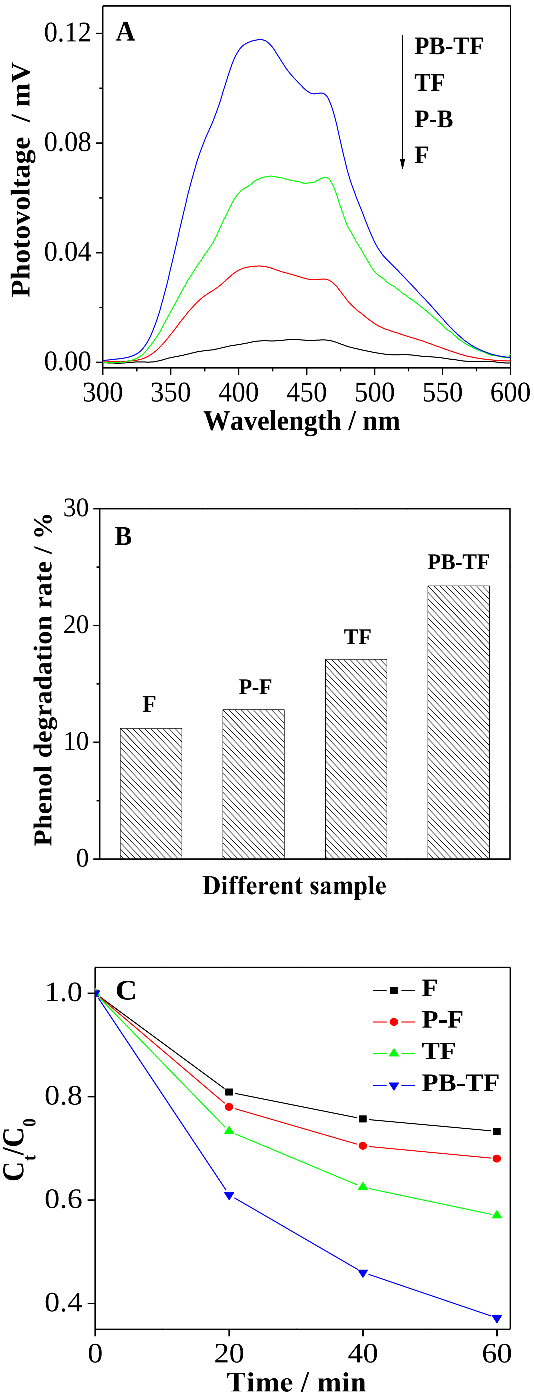
SI-Fig. 4 The whole XPS spectrum (A), Fe 2p XPS spectrum (B), Ti 2p XPS spectrum (C), O 1s XPS spectrum (D) of PB-TF.



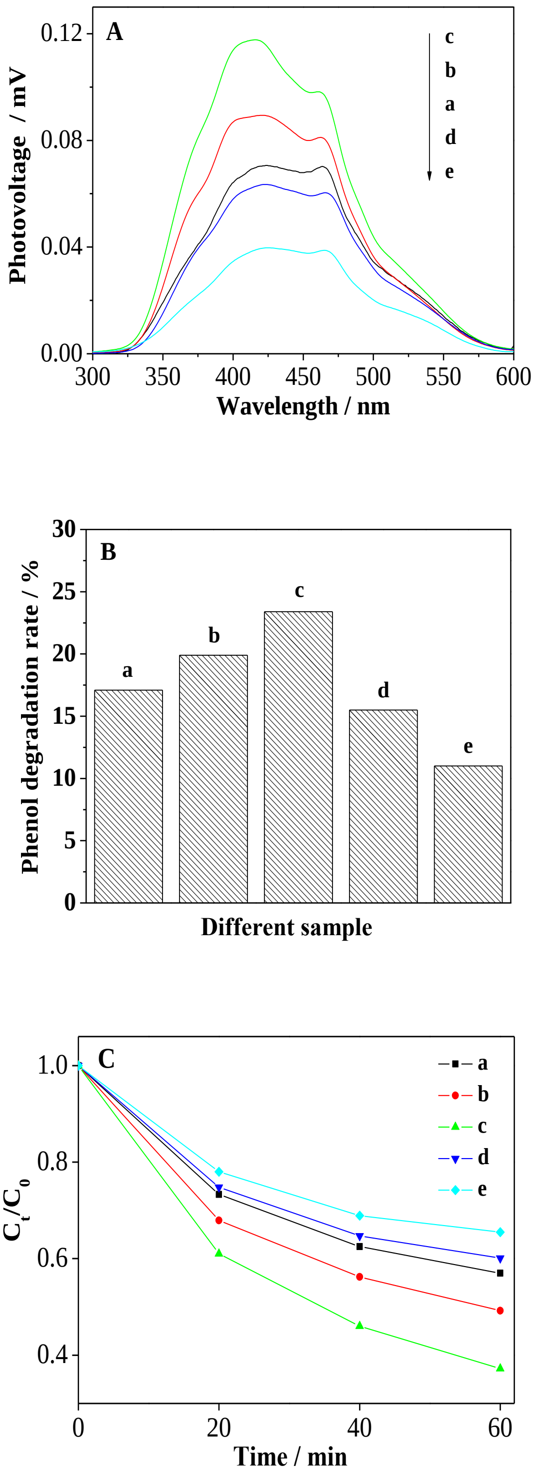
SI-Fig. 5 XRD patterns (A) and UV-Vis DRS spectra (B) of different phosphate-bridged TiO_2-Fe_2O_3. (a-e: phosphate-bridged TiO_2-Fe_2O_3 with mole ratio of P to Fe of 0%, 0.2%, 0.5%, 0.8% and 1.0% respectively, and the same elsewhere unless stated)



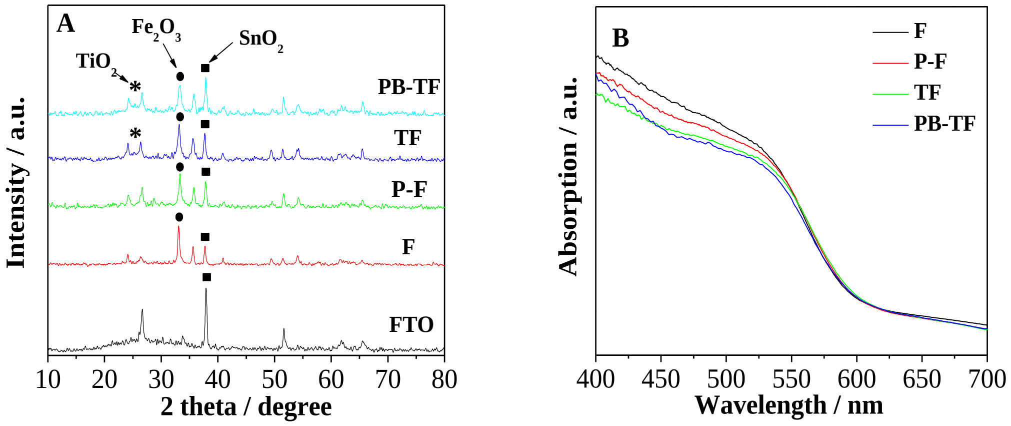
SI-Fig. 6 SS-SPS responses in air (A), visible light photocatalytic activities for degrading phenol (B) and acetaldehyde (C) of F, P-F, TF, PB-TF.



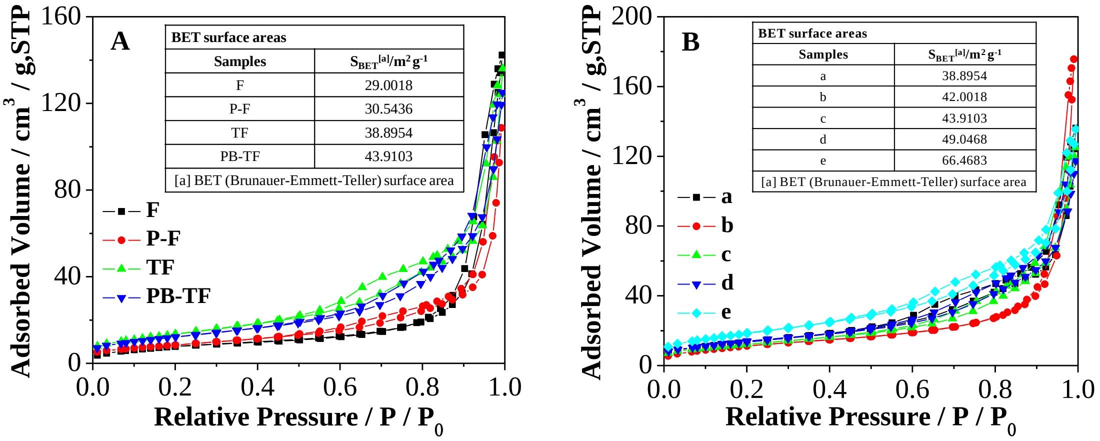
SI-Fig. 7 SS-SPS responses in air (A), visible light photocatalytic activities for degrading phenol (B) and acetaldehyde (C) of a, b, c, d, e.



SI-Fig. 8 XRD patterns (A) and UV-Vis absorption spectra (B) of fabricated films.



SI-Fig. 9 Nitrogen adsorption-desorption isotherms of F, P-F, TF, PB-TF (A) and a, b, c, d, e (B).



BET surface areas

Samples	S_{BET}[a]/$m^2 g^{-1}$
F	29.0018
P-F	30.5436
TF	38.8954
PB-TF	43.9103

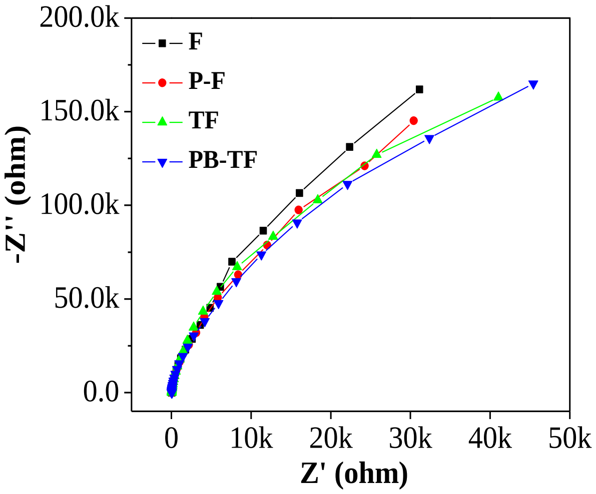
[a] BET (Brunauer-Emmett-Teller) surface area

BET surface areas

Samples	S_{BET}[a]/$m^2 g^{-1}$
a	38.8954
b	42.0018
c	43.9103
d	49.0468
e	66.4683

[a] BET (Brunauer-Emmett-Teller) surface area

SI-Fig. 10 Electrochemical impedance spectra (EIS) Nynquist plots in dark.



SI-Fig. 11 Electron paramagnetic resonance (EPR) response of TF was measured at 1.8 K and the sample was irradiated by one laser beam with wavelength of 532 nm.