

Electronic Supporting Information (ESI)

For

Photoinduced Charge Separation Enhanced by Confinement of Electron Donor and Acceptor at Different Surface of Porous TiO₂ Nanotube and Its Application in Olefins Oxidation

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1. Chemicals

Zinc acetate, sodium hydrate, manganese chloride tetrahydrate, hexachloroplatinic acid hexahydrate, tetrabutyl titanate (TBOT), ammonium molybdate tetrahydrate, urea, ethanol, ethylene glycol, ethyl acetoacetate (EAA), dimethyl sulfoxide (DMSO), acetonitrile, acetone, and N, N-Dimethylformamide (DMF) were purchased from Sinopharm Chemical Reagent Company. Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol)(P123), polyethyleneglycol-400(PEG400), 1, 2, 4-benzenetricarboxylic anhydride, styrene, α -methylstyrene, 1-octene, cyclohexene, trichloroethylene, 1, 5-cyclooctadiene, isoprene and leaf alcohol were purchased from Aladdin Chemistry Co. Ltd. All the chemicals were of AR grade except that acetonitrile and acetone were of GC grade. Ultrapure water used in the experiment was purified with Mill-Q (electric resistivity 18.2 M Ω ·cm) water purification system.

2. Synthesis Process

2.1 Synthesis of 2, 9, 16, 23-tetracarboxyl manganese(II) phthalocyanine (TCMnPc)

TCMnPc was prepared by a solid-phase synthesis method, which was reported elsewhere.¹ In a typical procedure, 9.61g 1, 2, 4-Benzenetricarboxylic anhydride, 3.96g MnCl₂·4H₂O, 0.3g (NH₄)₂Mo₄O₁₃·2H₂O and 20g urea were mixed and heated to 220°C in one hour and the reaction was kept for 6 hours. The resulting mixture was ground and washed with hot water for several times until the filtrate became colorless. Then, it was added into a 500mL 2M NaOH solution, refluxed at 120°C for 12 hours under N₂ atmosphere in darkness. The resulting solution was diluted by 500mL water and filtrated.

The filtrate was acidified by 1M HCl to pH 2.0 with dark green TCMnPc deposition. It showed a strong absorbance at 728 nm in a DMSO solution (Figure S1).

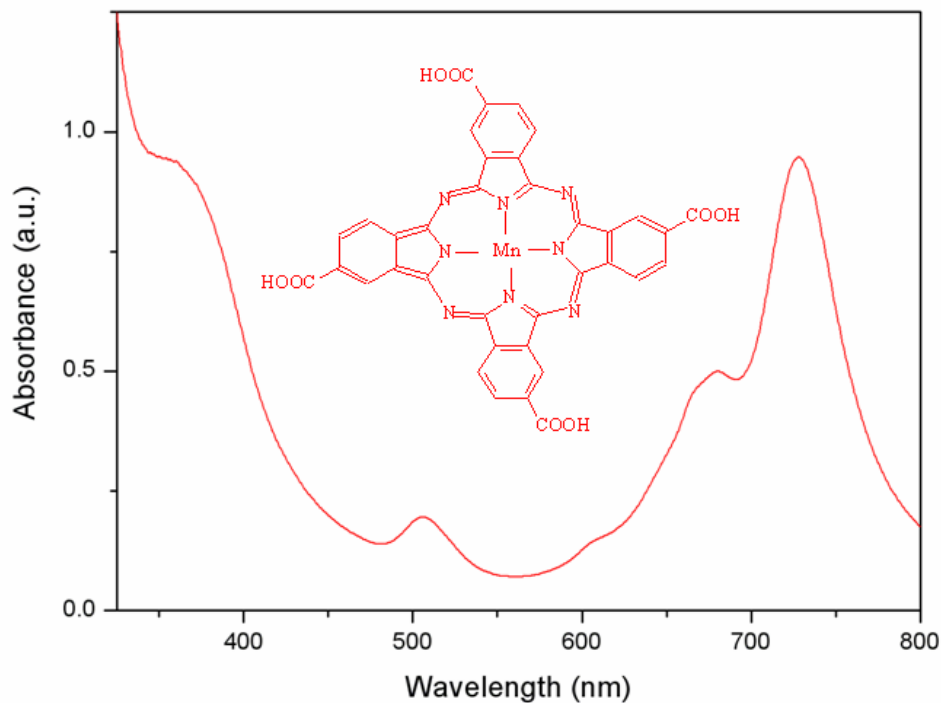


Figure S1. UV-vis spectrum of TCMnPc

2.2 Synthesis of ZnO nanorod

In a typical procedure, 2.0g Zinc acetate, 25mL PEG400, 55mL ethanol and 5g NaOH were sequentially added into a 100 mL Teflon-lined autoclave with stirring for 10 minutes. Then, the Teflon-lined autoclave was heated at 120°C for 12 hours. The system was then allowed to cool to room temperature naturally. The final product was washed with deionized water, ethanol for three times and dried at 70°C for 4 hours. ZnO nanorod with diameter of 40~50nm and length of 1~2µm was obtained (Figure S2).

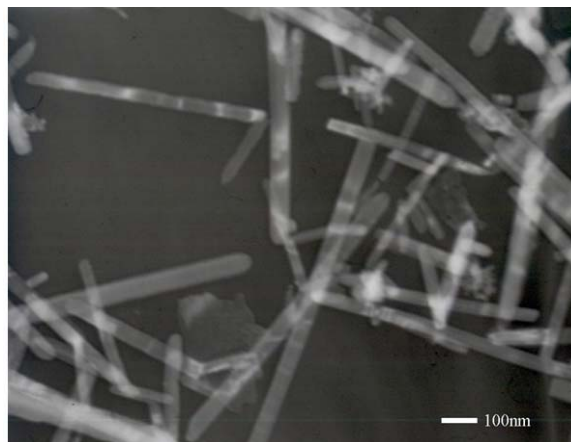


Figure S2. TEM image of ZnO nanorods

2.3 Deposition of Pt on the ZnO nanorods

Pt nanoparticles with diameter of 3~5 nm were uniformly deposited on ZnO nanorod by a modified polyol method.² 2.0g ZnO nanorods were dispersed in 200 mL H₂O, 3.0 mL 0.077M H₂PtCl₆ solution was added in 200 mL ethylene glycol. Then, the prepared H₂PtCl₆ ethylene glycol solution was added slowly into the ZnO nanorods dispersed phase. A gray suspension was obtained after reaction at 140°C for 8 hours. The final product was centrifugated and washed with water, ethanol, then dried at 70°C for 4 hours (Figure S3).

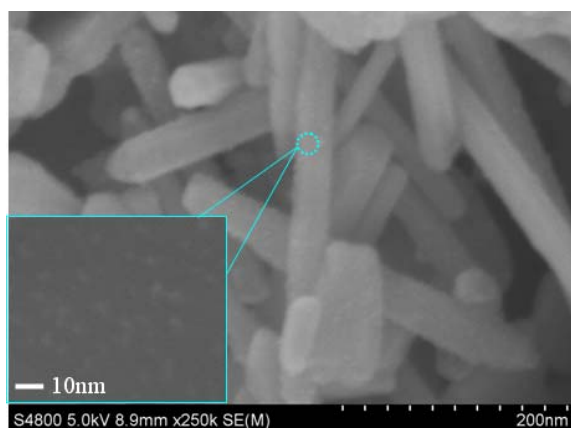


Figure S3. SEM image of Pt-ZnO

2.4 Synthesis of Pt/ZnO@TiO₂

In a typical procedure, 0.3g P123 was dissolved in 20 mL ethanol with stirring for 2 hours, then two drops of EAA and 0.15g TBOT were orderly added stirring for more 30 minutes. 0.05g Pt/ZnO was dispersed in 150 mL ethanol. The as-prepared solution was dropped into the Pt/ZnO suspension in 2 hours. Last, 20 mL H₂O was dropped into the system at a rate of 0.008 mL/s. The final product was centrifugated, washed with water and ethanol, dried at 70°C for 4 hours, then, calcined at 450°C for 3 hours (Figure S4).

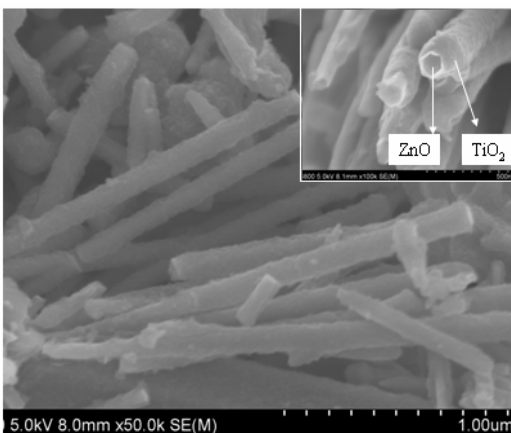


Figure S4. SEM image of Pt-ZnO@TiO₂

2.5 Synthesis of Pt@TiO₂-TCMnPc

The as-prepared Pt/ZnO@TiO₂ was dispersed in 10⁻³ M TCMnPc solution of DMSO and DMF (V_{ratio},2:1), refluxed at 140°C for 12 hours in darkness, then washed with DMSO and ethanol. The final product was dispersed in a 0.1 M HCl for two hours to remove the ZnO template, and then washed with water, dried in a vacuum vessel.

3. Characterization

A JEM-100CXII transmission electron microscope (TEM) was used to characterize the

morphology of the product in each step. The crystalline structures of the samples were evaluated by X-ray diffraction (XRD) analyses, carried out on a Bruker D8 Advance Diffractometer with Cu K α radiation (1.5418 Å). A HITACHI S-4800 Scanning Electron Microscope (SEM) equipped with a field-emission gun operated at 5.0 kV was used to characterize the morphology of the as-obtained product. The XPS data were collected in an ultrahigh vacuum chamber equipped with an Al K α ($h\nu = 1,486.6$ eV) X-ray excitation source by a ThermoFisher SCIENTIFIC ESCALAB 250 X-Ray Photoelectron Spectroscopy. The UV-Vis diffuse reflectance spectrum was measured on a VARIAN Cary 50 spectrophotometer with BaSO₄ powder used as a reference (100 % reflectance). The fluorescence spectrum was carried out with an Edinburgh FLS920 spectrofluorimeter (Edinburgh Instruments Ltd, England) equipped with a xenon lamp. ESR spectroscopic experiments were carried out at room temperature (298 K) with a Bruker ESP 300E spectrometer. Nitrogen adsorption-desorption isotherm measurements were carried out on a Micromeritics ASAP2020 Surface Area and Porosity Analyzer.

The X-ray diffraction (XRD) pattern showed that the porous titania layer was amorphous (Figure S5). The broad and weak diffraction peaks attributed to TiO₂ or anchored TCMnPc, indicated a small crystal size or a poor crystallinity of the two phases in the nanostructures. The discriminable diffraction peaks are sharp and intense, attributed to crystalline Pt nanoparticles. The data ($2\theta = 39.3(111)$, $45.7(200)$, $66.7(220)$, $80.5(311)$, $84.5(222)$) are in agreement with the Joint Committee on Powder Diffraction Standards (JCPDS) card for Pt (JCPDS 89-7382).

The XPS survey scan spectra (Figure S6) demonstrated that C, N, Mn, O and Ti elements existed in the hierarchical nanostructures. The absence of Pt element peaks in the survey scan spectra was owing to the surface depth detection limit of XPS (<10 nm), which indicated that Pt nanoparticles were anchored in the channel of TiO₂ tube (the wall thickness >10 nm) from another perspective. Pt element existed mainly in the form of Pt (0) which was demonstrated by XPS of Pt/ZnO composite (Figure S7).³ The C, N, Mn and O elements can be ascribed to TCMnPc. The peak located at 464.32 eV corresponds to the Ti 2p_{1/2} and another one located at 458.67 eV was assigned to Ti 2p_{3/2} (Figure S8).⁴ The peak centered at 642.49 eV corresponded to the Mn 2p_{3/2} and another one centered at 655.17 eV was assigned to Mn 2p_{1/2}, indicating a Mn(II) in the TCMnPc molecule (Figure S6, b, inner),⁵ which was also demonstrated by the ESR spectrum (Figure S16).⁶ Using the XPS Peak fitting program, version 4.1, the shape of a wide and asymmetric peak of O 1s spectrum indicated that it could be existing in four chemical states included crystal lattice oxygen (Ti-O*), hydroxyl groups (-*OH), carbonyl bond C=O*, and ester group(-C(O)-O*-), peaks centered at 530.2 eV, 533.1 eV, 531.4 eV and 532.2 eV, respectively (Figure S9).⁷ C1s existed in three chemical states included carbon of aromatic ring (-C*=C*-), ester group (-C*(O)-O-) and -N=C*-, peaks centered at 284.6 eV, 288.5 eV and 286.2 eV, respectively (Figure S10).⁸

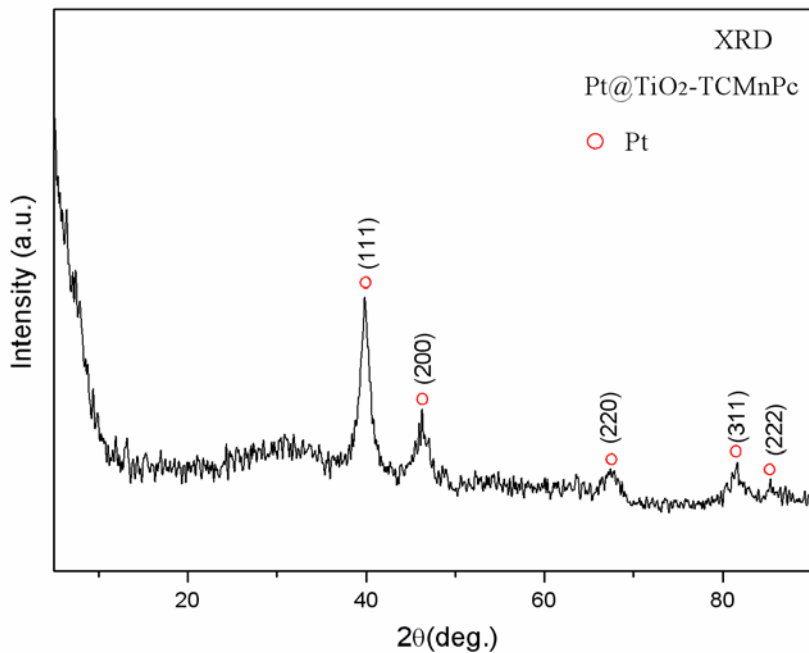


Figure S5. XRD patterns of the Pt@TiO₂-TCMnPc

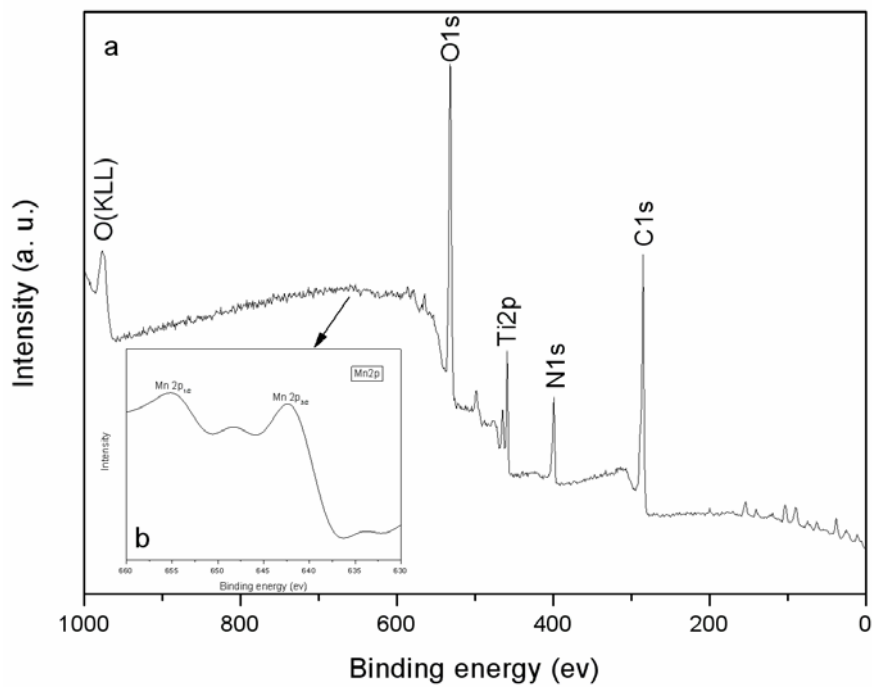


Figure S6. XPS survey of Pt@TiO₂-TCMnPc

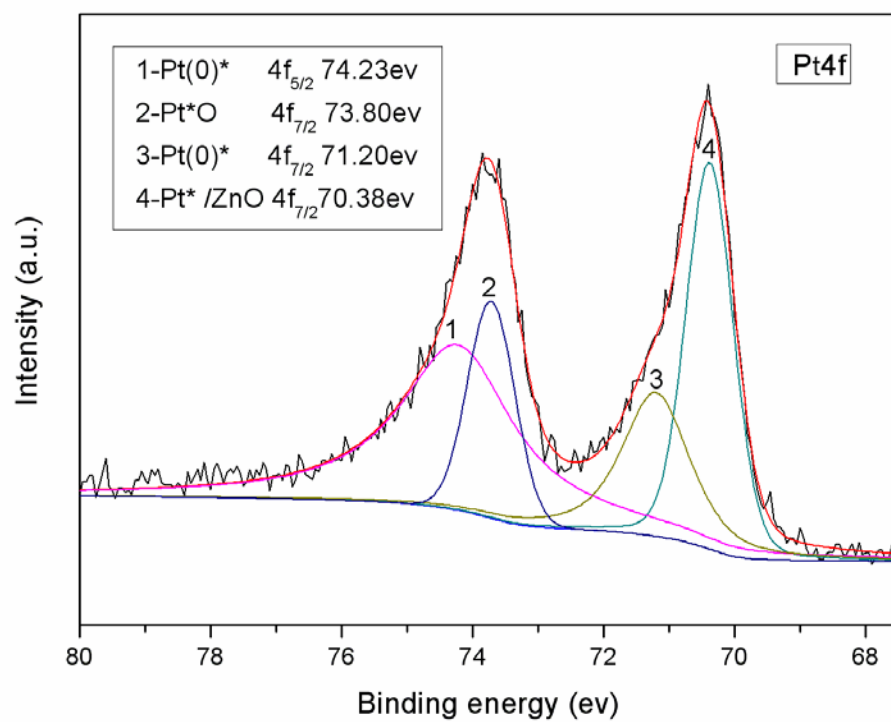


Figure S7. XPS Pt 4f spectra for Pt/ZnO

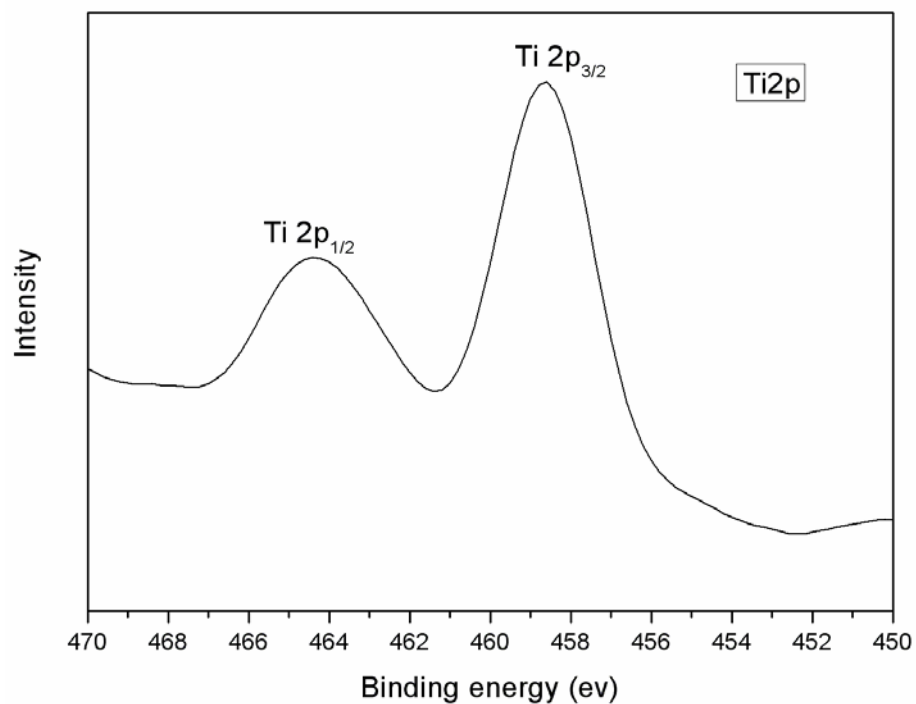


Figure S8. XPS Ti 2p spectra for Pt@TiO₂-TCMnPc

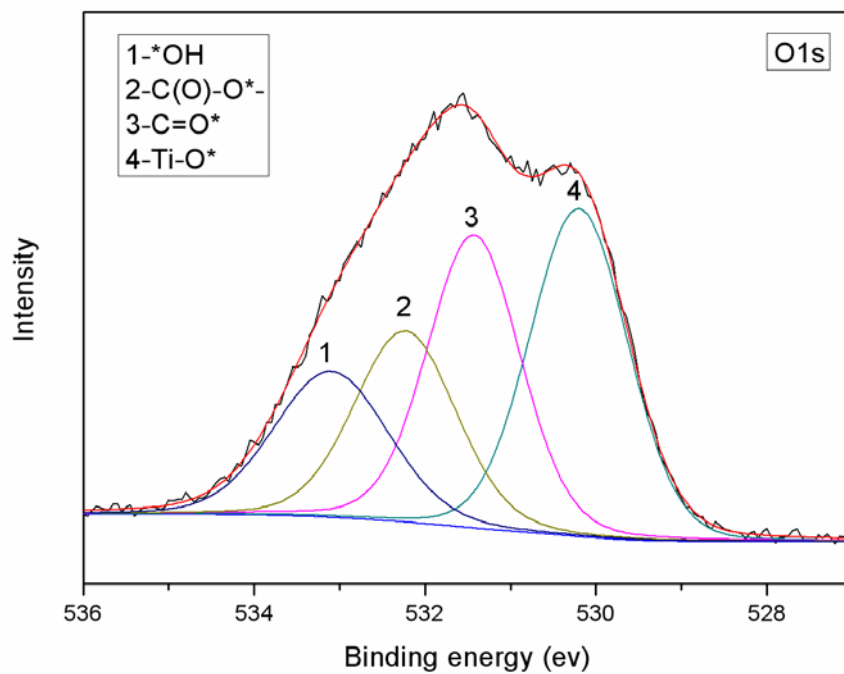


Figure S9. XPS O 1s spectra for Pt@TiO₂-TCMnPc

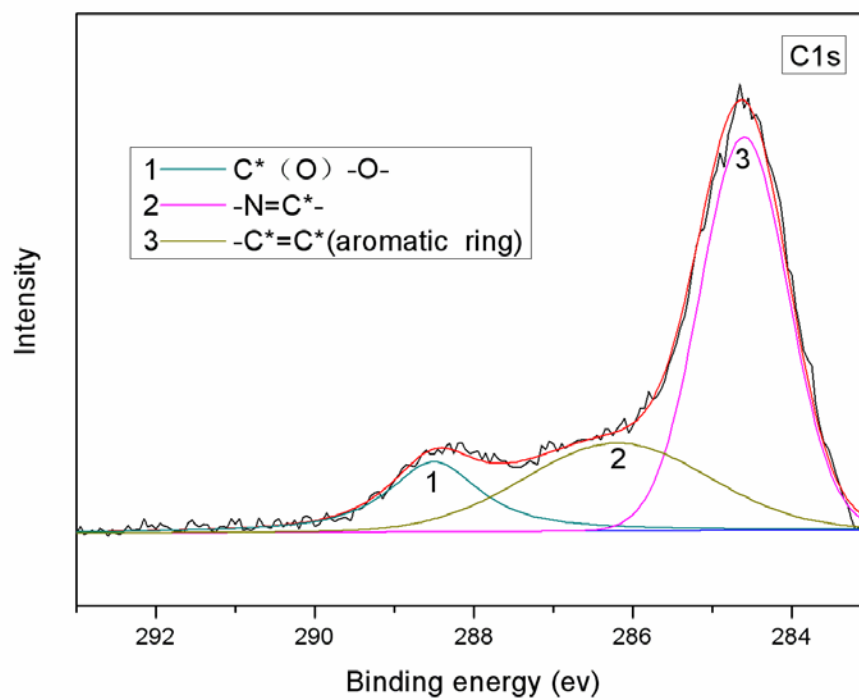


Figure S10. XPS C 1s spectra for Pt@TiO₂-TCMnPc

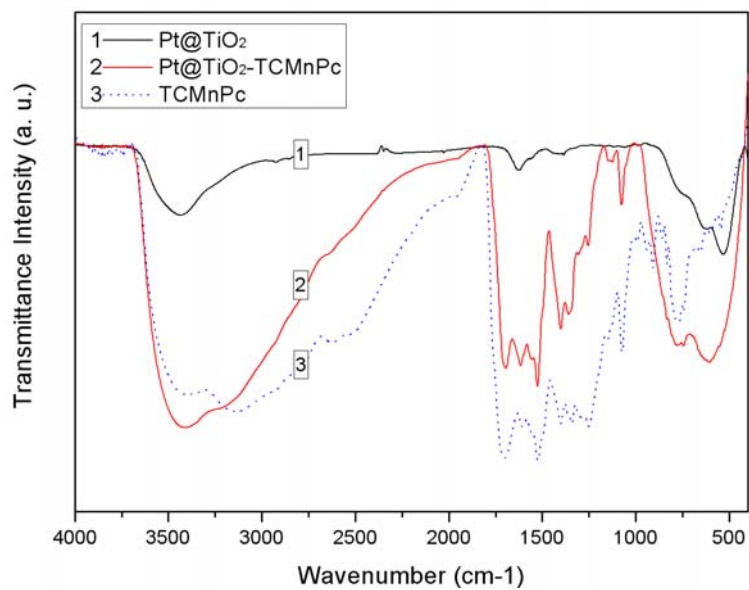


Figure S11. IR spectrum for Pt@TiO₂(1), Pt@TiO₂-TCMnPc(2) and TCMnPc(3).

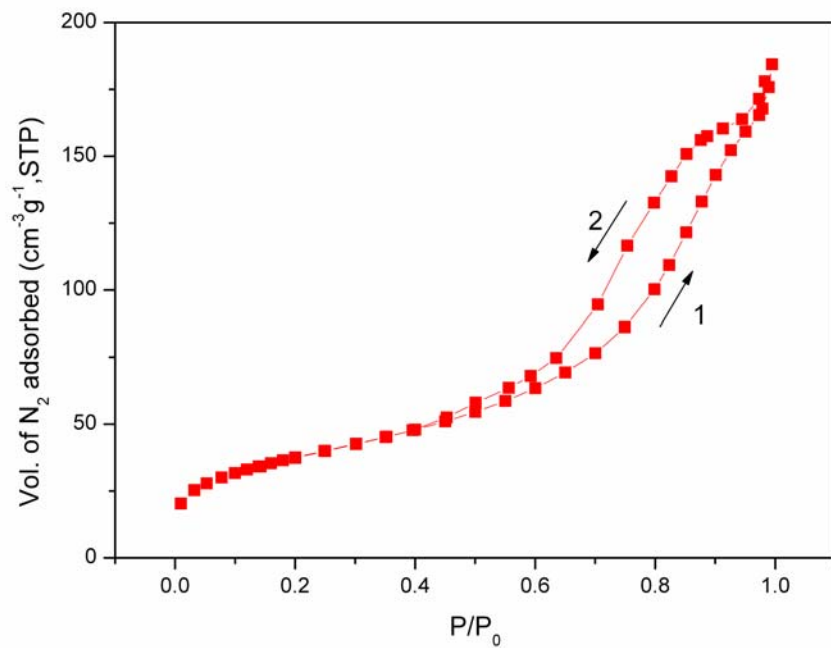
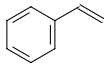
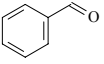
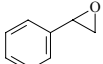
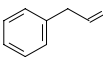
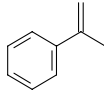


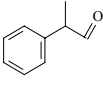




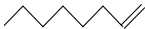

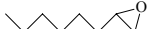
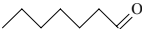
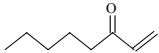
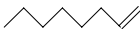
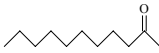
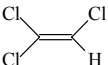
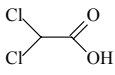




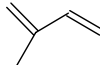

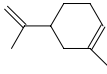
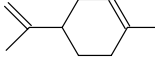



Figure S12. Isotherm of low temperature nitrogen adsorption (1) and desorption (2) on the surface of Pt@TiO₂-TCMnPc.

4. Photocatalytic activity measurement

The photocatalyst (20 mg), styrene (10 mmol), and acetonitrile (15 mL) were added into a quartz reaction vessel, which was then sealed with a rubber septum. The resulting mixture was sonicated and bubbled with oxygen for 30 minutes in the dark. Subsequently, the sample was irradiated from the side with a Xe lamp (1000W) with magnetic stirring at ambient pressure and room temperature. The resulting solution was centrifuged and the supernatant was analyzed by GC with a Agilent 6890N GC with a flame ionization detector equipped with HP-5 columns. The structures of the products were confirmed by comparison with standard samples and by GC-MSD(Agilent 5973N).

Table S1. Results of the oxygen photooxidation of olefins

Entry	Substrate	t[h]	Conv. [%]	Product & Selectivity.[%]		
1		48	100	 (90)	 (8)	 (2)
2		48	100	 (82)	 (9)	 (9)
3		48	100	 (75)	 (17)	 (8)
4 ^[a]		48	60	 (44)	 (22)	 (15)
				 19		
5 ^[b]		48	45	 100		
6		48	100	 (100)		
7		48	90	 (60)	 (28)	 (12)
8		48	96	 (4)	 (74)	 (22)
9		48	0	-		

[a] In the absence of solvent. [b] In acetone solvent.

The position and number of the double bond markedly affect the selectivity. As shown in Table S1, the terminal double bond was favorable for the oxidation reaction (Table S1, entries 1 and 2), whereas, leaf alcohol with an inner double bond was inert to this photocatalyzed reaction (Table S1, entry 9). The oxidation reaction usually took place at α -H position on double bond of cycloolefine (Table S1, entries 3 and 7). Isoprene with two terminal double bonds showed poor conversion and selectivity to the oxidation chemicals. Interestingly, a high conversion and selectivity of monoterpene was observed (Table S1, entry 8). 1-Octene also showed low conversion and selectivity without solvent (Table S1, entry 4), but when it was oxidized in acetone, an addition reaction between 1-Octene and acetone was observed with a result of producing of 2-undecanone with high selectivity (Table S1, entry 5).⁹ When H atom of the double bond was substituted by Cl atom, a carboxylic acid was produced with a high conversion and selectivity (Table S1, entry 6).

Photo-inert solvents without H₂O are usually required in the photocatalytic synthesis system for avoiding the side reactions, which is different from the degradation of organic pollutants by a photocatalyst.¹⁰ As shown in Figure S14, the presence of H₂O markedly depressed the reaction rate in a contrast experiment. This result was well consistent with the previous report.¹¹ It was caused by the competitive absorption between water and the reaction substrates.

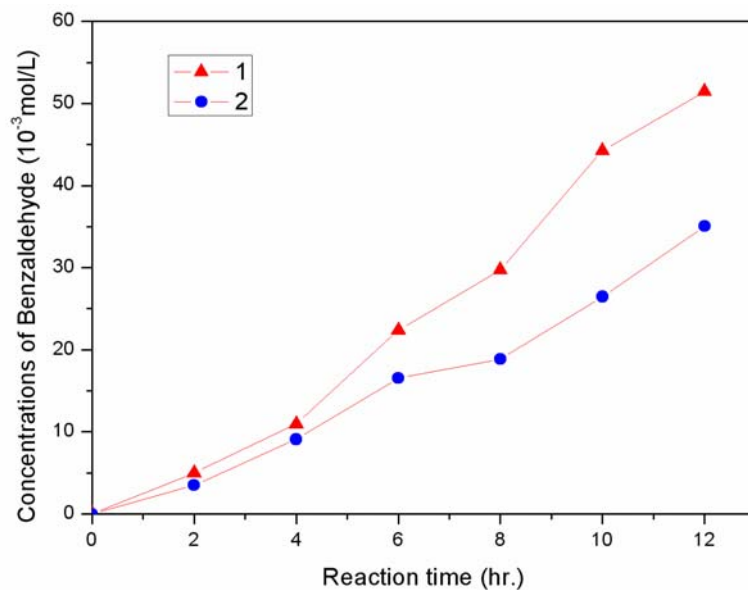


Figure S13. Photooxidation reaction of styrene catalyzed by Pt@TiO₂-TCMnPc under 1000W Xe lamp irradiation without light filtration (1) and with a glass filter ($\lambda > 400$ nm, visible-light irradiation) (2).

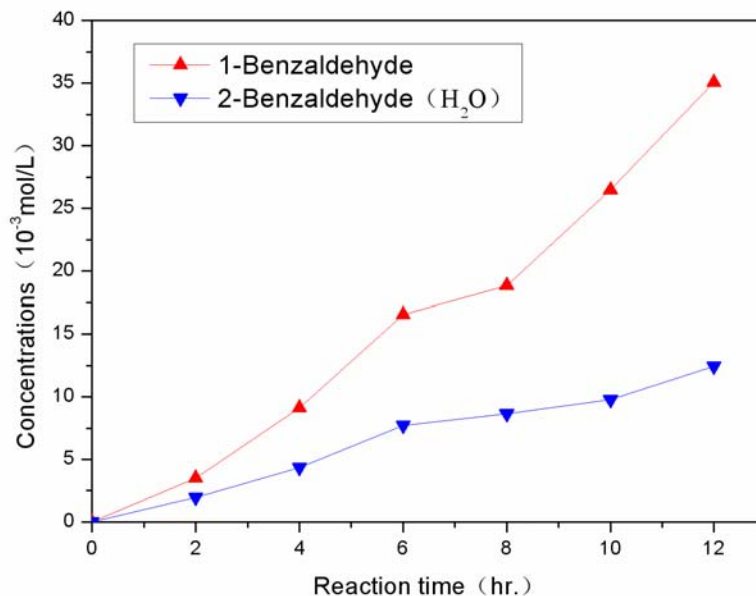
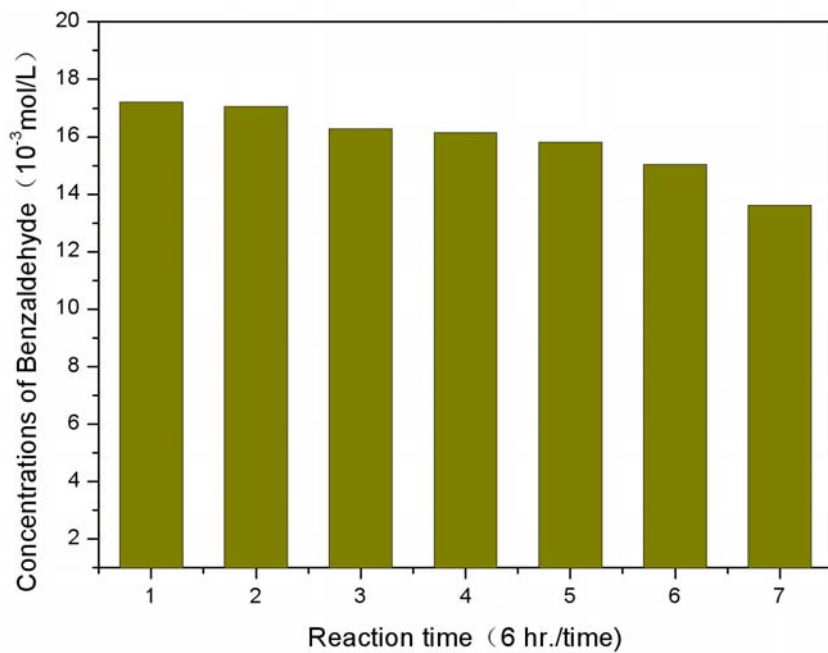


Figure S14. Effect of H₂O for the photooxidation reaction of styrene catalyzed by Pt@TiO₂-TCMnPc. (1) Reaction performed without H₂O, (2) Reaction performed in the presence of H₂O.



**Figure S15. Repeating photooxidation reaction of styrene catalyzed by
 $\text{Pt@TiO}_2\text{-TCMnPc}$.**

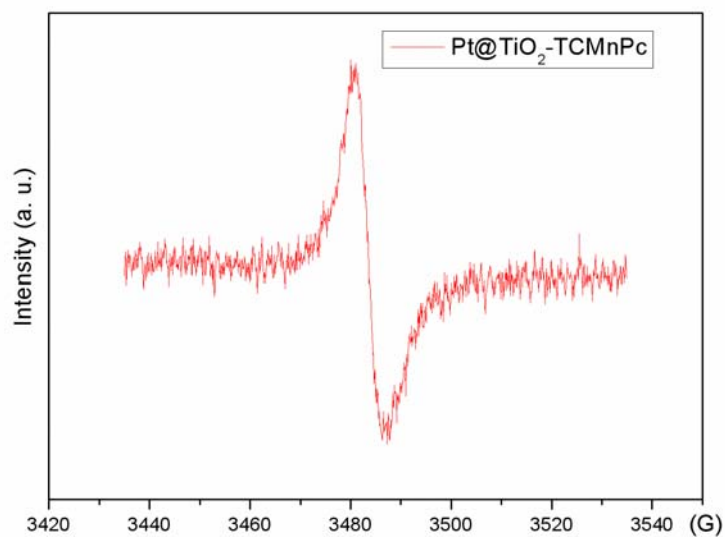


Figure S16. ESR spectrum of $\text{Pt@TiO}_2\text{-TCMnPc}$

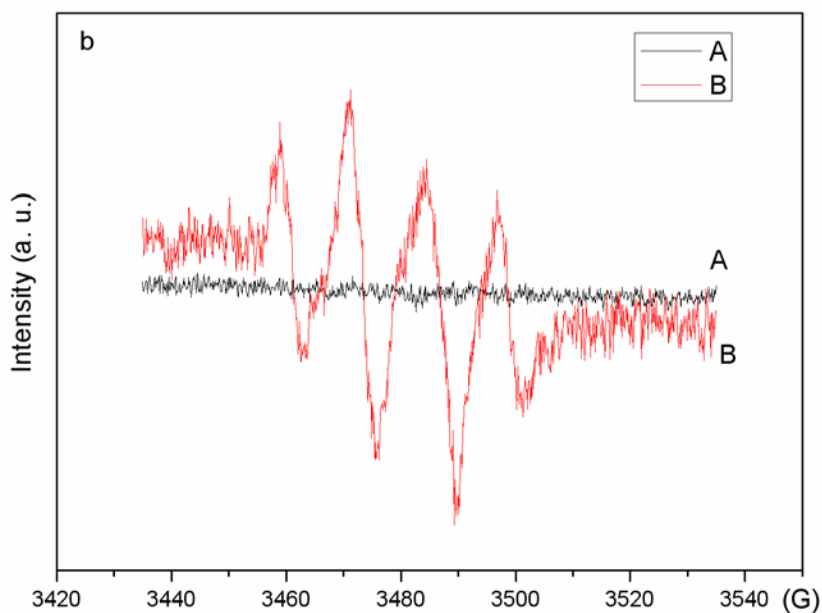


Figure S17. ESR spectrum of the composite of O_2^- and DMPO: (A) in darkness, (B) in visible light.

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