

Electronic Supporting Information

ZnO photonic crystals with enhanced photocatalytic activity and photostability

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Experimental Section

Materials. The glasses used in the synthesis of polystyrene (PS) latex spheres were all cleaned in freshly chromic mixture and rinsed repeatedly with deionized water. Styrene was washed in 0.1 M NaOH solution (the volume ratio is 1:1) and deionized water to remove polymerization inhibitor. Potassium persulfate (KPS) was recrystallized twice from deionized water, and then lucifugal dried at 40 °C in the vacuum oven. The substrate (glass slide and fluorine-doped tin oxide (FTO) substrate) was immersed in the mixed H₂SO₄/H₂O₂ solution with the volume ratio of 3:1 for 3 h. Then, the substrate was cleaned with absolute ethanol and deionized water to make its surface hydrophilic and dried with nitrogen gas to keep its surface purity. 5, 5-dimethyl-1-pyrroline-N-oxide (DMPO) was obtained from Sigma Co. the electrical resistance of the used deionized water was *ca.* 12 MΩ. Unless specifically stated above, all chemicals used were analytic grade reagents.

Synthesis of Carboxyl-modified Polystyrene Spheres. Monodisperse PS latex spheres were synthesized by emulsifier-free emulsion copolymerization according to the literature using styrene as polymerized monomer, potassium persulfate as initiator, and methacrylic acid as functional monomer to provide carboxyl group on the surface of spheres.¹ The synthetic process was modified in our laboratory. In a typical synthesis of carboxyl-modified PS latex spheres with 270 nm diameter was as follows: Polymerization was conducted in a 250 mL reaction flask by magnetic stirring (350 rpm) under a nitrogen atmosphere. Firstly, 100 mL deionized water was added to a three-neck flask. Nitrogen was bubbled in the flask to blow away air. After 30 min, 6.2 mL prewashed styrene and 0.050 mL methacrylic acid were added to the flask. Then, the reaction flask was heated to 75°C, 0.1g prepurified KPS was added. After the reaction of 24 h, the flask was removed from the oil bath. The subsequently formed white latex was filtrated through glass filter to remove aggregates, and centrifuged, washed with deionized water for several times, finally the precipitate dispersed into water for use. Through change the volume ratio of styrene/methacrylic acid, other carboxyl-modified PS latex spheres with different diameter can be prepared.

Fabrication of the Opal Templates. The colloidal opal templates were fabricated by means of vertical deposition.² The substrate was submerged into the PS colloidal suspension with concentration of *ca.* 0.2 wt% at temperature 45 °C for about 20 h. Then the colloidal opal templates were obtained. To elucidate the photonic crystal effect, an inhomogenous PS template consist of different diameters PS spheres was fabricated to mold a random ZnO porous structure as a reference. The inhomogenous PS template was prepared by a similar procedure, except that the closely graded PS colloidal suspension replaced by the suspension contained different diameter PS spheres. In addition, the opal template with 270 nm, 295 nm and 351 nm PS was denoted as PS-270, PS-295 and PS-351, respectively.

Synthesis of ZnO Photonic Crystals. Before infiltration with the ZnNO₃ precursor solution, the opal templates were annealed at 90 °C for 30 min to promote their

mechanical strength. Then the opal templates were immersed vertically into ZnNO_3 water-ethanol solution bath at room temperature. After about 90 s, the templates were taken out of the ZnNO_3 solution slowly and placed horizontally on an experimental bench. As the solvent was evaporated and dried on the templates surface about 3 h at room temperature. The resultant samples (denoted as PSZ) were heated to 400 °C at a rate of 1 °C / min and kept at the temperature for 4 h. then the ZnO photonic crystals (denoted as ZnO-PCs) were obtained. Moreover, the ZnO-PC fabricated from the opal template with 270 nm, 295 nm and 351 nm diameter PS spheres was denoted as ZnO-270, ZnO-295 and ZnO-351, respectively.

The reference porous ZnO film (ZnO-P) was prepared by the same procedure except for using the inhomogenous PS template. Another reference nanoparticle ZnO film (ZnO-N) was also prepared as follows: The commercial ZnO powder was dispersed completely in deionized water by ultrasonication, then the same amount of ZnO as the porous ZnO film was coated on a substrate and followed by calcination at 120 °C for 3 h to remove water and enhance adhesion between the substrate and ZnO film.

Characterization. Fourier transform infrared (FT-IR) spectra of the polystyrene spheres in KBr pellets were recorded on a Nicolet Avatar 670 FT-IR spectrometer (Nicolet Corp., USA). The spectra were collected from 4000 to 400 cm^{-1} with a 4 cm^{-1} resolution over 32 scans. Zeta potential of the polystyrene latex spheres was measured on a ZETASIZER 3000 HSA (Malvern Instruments, UK). X-ray diffraction (XRD) pattern of the sample was collected on a Bruker D8 Advance X-ray diffractometer at 40 kV and 40 mA using Ni-filtered Cu $K\alpha$ radiation. UV-Vis diffuse reflectance spectra (DRS) were obtained on a UV-vis spectrophotometer (Cary 500) and BaSO_4 was used as a reference sample. X-ray photoelectron spectroscopy (XPS) analysis of the sample before and after photoreaction was conducted on an ESCALAB 250 photoelectron spectroscopy (Thermo Fisher Scientific) at 3.0×10^{-10} mbar with Al $K\alpha$ X-ray beam (1486.6 eV). The sample's morphology and energy dispersive X-ray spectroscopy (EDX) were investigated on field emission scanning electron microscopy (FESEM) (America, FEI Nova NanoSEM 230), Transmission electron microscopy (TEM) images and high-resolution transmission electron microscopy (HRTEM) images were determined on a JEOL model JEM 2010 Ex instrument at an accelerating voltage of 200 kV. The BET surface area was probed by using Micromeritics ASAP2020 (Micromeritics Instrument Corp.). The block inverse opal structure ZnO samples, which were used for measuring specific surface areas, were prepared via a general vacuum method.³

Photocatalytic Activity Evaluation. A 500 W Xe-arc lamp equipped with an IR-cutoff filter was used as a light source. The intensity of light at $300 \text{ nm} < \lambda < 800 \text{ nm}$ was measured to be about 130 mW / cm^2 using a laser power/energy detector (PhyScience Opto-electronics Co., Ltd., China). The photodegradation of environmental pollutions (methyl orange (MO) and 4-chlorophenol (4-CP)) in the liquid phase was implemented in a quartz cell (L 3.2 cm, W 1.2 cm, H 4.5 cm). The as-prepared ZnO film was immersed into the quartz cell contained 10 mL 5 ppm MO

(or 4 ppm 4-CP) solution vertically. Prior to irradiation, the above solution was stirred for 30 min in the dark to ensure the equilibrium of adsorption and desorption. Then, A 3 mL solution was taken out at given intervals; simultaneously, the light was shielded by a plate. The solution was poured into the quartz cell again after the solution analyzed on a UV-vis spectrophotometer (Cary-50, Varian Co.), and the plate was taken away. After reaction for 2 h, the MO solution was further analyzed by a Shimadzu TOC-V_{CPH} total organic carbon analyzer. To further evaluate the stability of the photocatalyst, the photocatalytic processes was repeated five cycles for degradation of MO under the same conditions.

Photoelectrochemical Measurement. The photoelectrochemical experiment was measured on an electrochemical station (CHI-660D, China) using a three-electrode system.⁴⁻⁵ The ZnO film on the FTO substrate (sheet resistance is *ca.* 14 Ω/cm², Nippon Sheet Glass, Japan) was used as the working electrode. Ag/AgCl soaked in 0.3 M KCl solution as the reference electrode, and a Pt wire served as the counter electrode. 0.1 M Na₂SO₄ solution was utilized as the electrolyte. In the photocurrent measurement, the ZnO photoanodes were illuminated at normal incidence of light through a quartz window, and the light was chopped manually at regular intervals.

Investigation of the Active Species. Electron spin resonance (ESR) spectra of the active species (superoxide radical •O₂⁻ and hydroxyl radical •OH) spin-trapped by 5, 5-dimethyl-1-pyrroline-N-oxide (DMPO) were detected using a Bruker model A300 spectrometer with normal incidence of light irradiation (300 nm < λ < 800 nm).⁶ In detail, for measuring hydroxyl radical and superoxide radical, the sample (*ca.* 1 mg) was dispersed in 0.5 mL purified ultrapure water and rarefied methanol into which 20 μL DMPO/water or DMPO/methanol solution was added, respectively. The settings for the ESR spectrometer were as follows: center field, 3512 G; microwave frequency, 9.86 GHz; power, 6.34 mW.

Figures and Captions

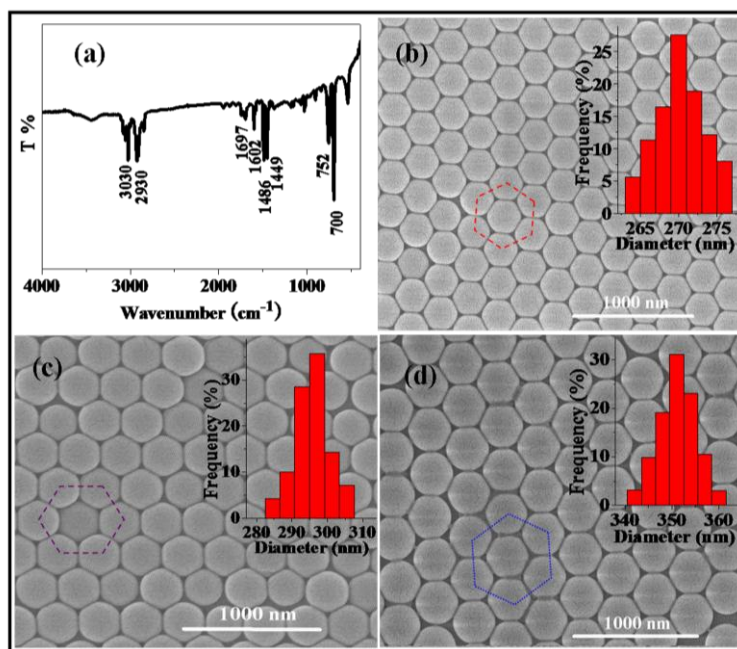


Fig. S1 (a) A typical FTIR pattern of the carboxyl-modified PS spheres. The SEM images of the opal templates self-assembled from (b) 270 nm, (c) 295 nm, and (d) 351 nm PS latex spheres, respectively (The insets were the corresponding size distributions).

Descriptions: A series of carboxyl modified PS latex spheres with uniform size distribution (270 ± 2 nm, 295 ± 3 nm, 351 ± 5 nm) were successfully prepared. Figure S1c showed the FTIR pattern of the gained carboxyl modified PS. Clearly, the peaks of 1449 cm^{-1} , 1486 cm^{-1} and 1602 cm^{-1} were belong to the vibration absorption of the benzene ring, 2930 cm^{-1} and 3030 cm^{-1} presented the C-H stretching vibrational absorption, these verified the existence of benzene ring. Two strong peaks could be observed at 700 cm^{-1} and 752 cm^{-1} which demonstrated the substitution of benzene ring. The peak located in 1697 cm^{-1} was the characteristic peak of C=O, the wide peak between 3200 cm^{-1} and 3600 cm^{-1} indicated the exist of hydroxyl.¹ The result illustrated that the surface of PS spheres modified by carboxyl groups was successfully synthesized.

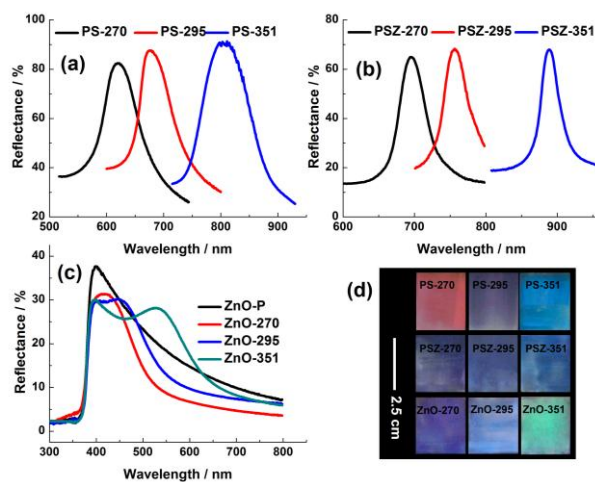


Fig. S2 Diffuse reflectance spectra of (a) the opal templates, (b) PSZs, and (c) ZnO-PCs. (d) The corresponding photographs under white light illumination.

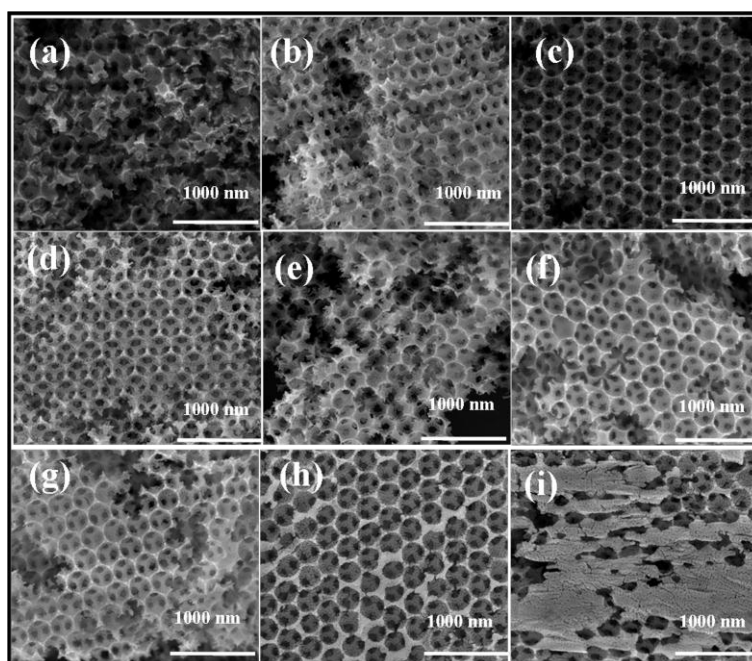


Fig. S3 The SEM images of ZnO-PCs prepared from the precursor with different (a-f) water/ethanol volume ratio: 20/0, 16/4, 12/8, 8/12, 4/16 and 0/20 (the mass of ZnNO_3 was fixed at 3 g); (g-i) the mass of ZnNO_3 : 1 g, 4 g, and 5 g (the water/ethanol volume ratio was fixed at 12/8), respectively.

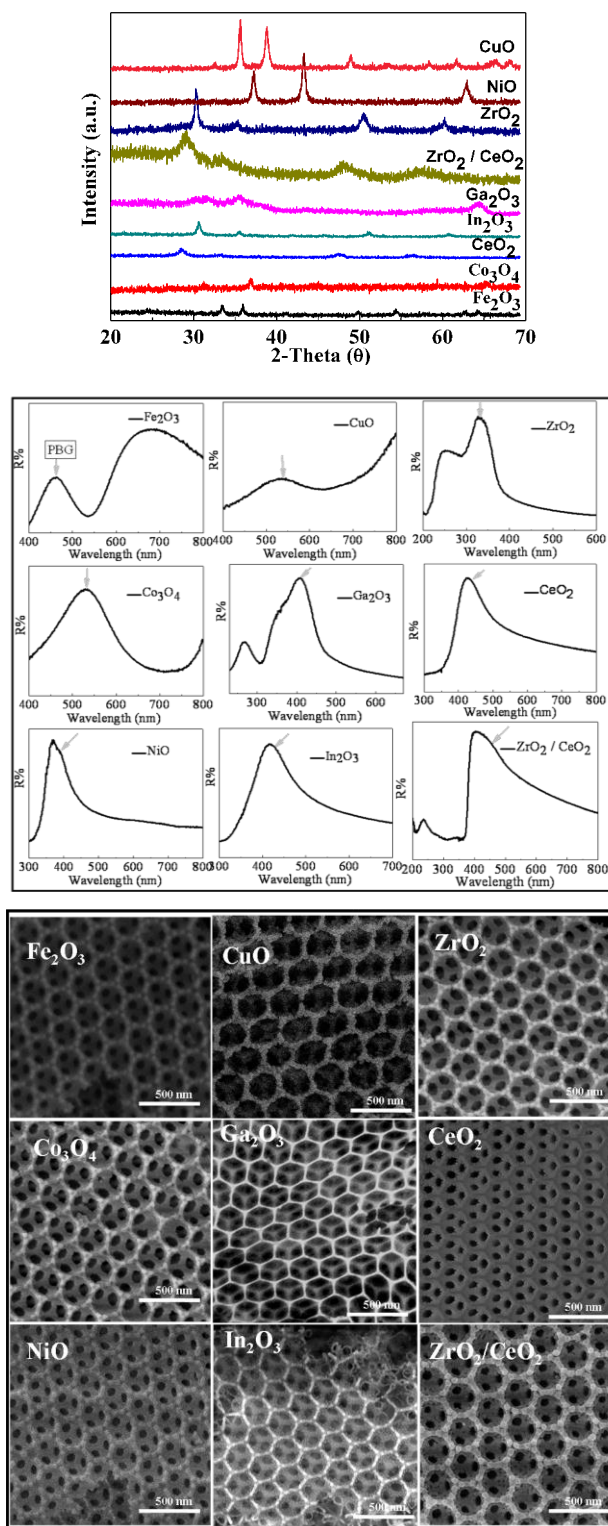


Fig. S4 XRD patterns, Reflectance spectra and SEM images of metal oxide inverse opals synthesized by this innovative and versatile approach.

Table S1 Parameters about ZnO PCs

Sample	ZnO-270	ZnO-295	ZnO-351
Average diameter of PS spheres (nm)	270	295	351
Average pore diameter of PC (nm)	260	280	320
Shrinkage (%)	4	5	9
Photonic stop band (nm)	416	450	530
Average wide of walls (nm)	22.2	25.1	28.3

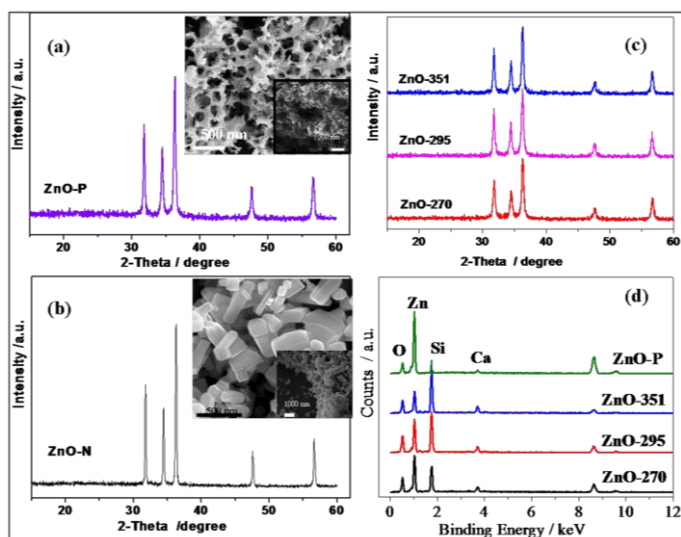


Fig. S5 XRD patterns of (a) ZnO-P, (b) ZnO-N, and (c) ZnO-PCs. The insets in (a) and (b) showed the corresponding SEM images (top view and cross-section view). (d) EDX patterns of photonic crystals and the reference porous ZnO.

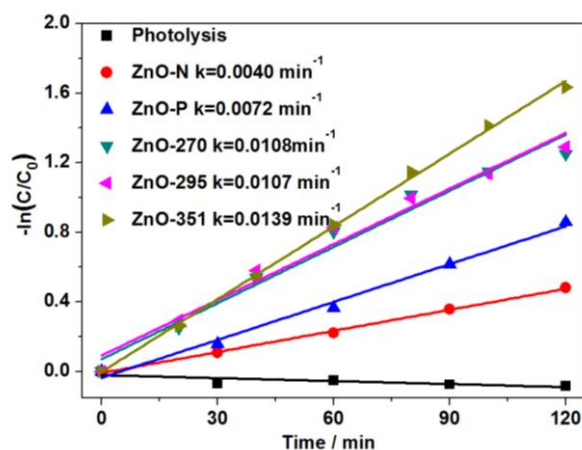


Fig. S6 Time profiles of photocatalytic degradation of 4-CP over ZnO under UV-Vis irradiation.

Table S2 the specific surface areas of the ZnO samples

Samples	ZnO-N	ZnO-P	ZnO-270	ZnO-295	ZnO-351
BET surface areas / $\text{m}^2 \text{g}^{-1}$	4.7	7.1	18.8	12.9	10.2

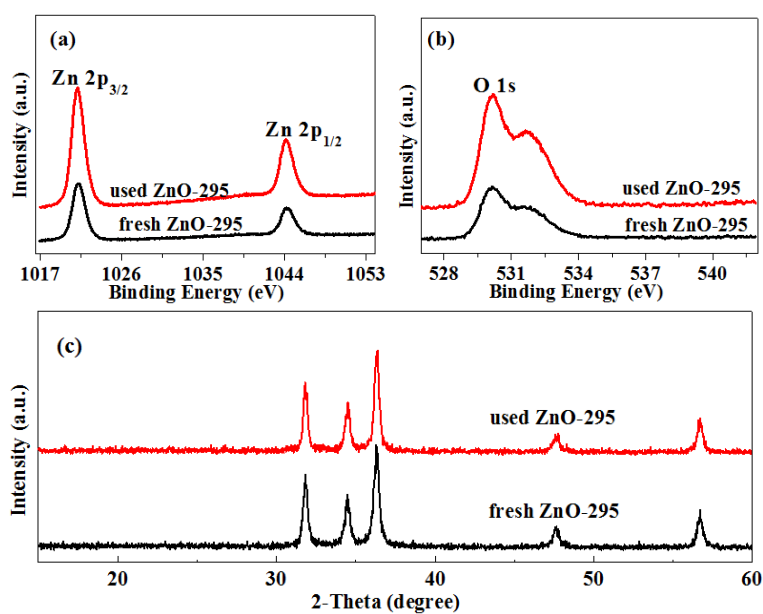


Fig. S7 Contrast XPS spectra of (a) Zn 2p and (b) O 1s and (c) XRD patterns of the ZnO-295 before and after photocatalytic degradation of MO.

The XRD patterns and the binding energies for Zn 2p and O 1s displayed no obvious change before and after photocatalytic degradation of MO, illustrating that ZnO-PCs had good chemical stability in the reaction process.⁷

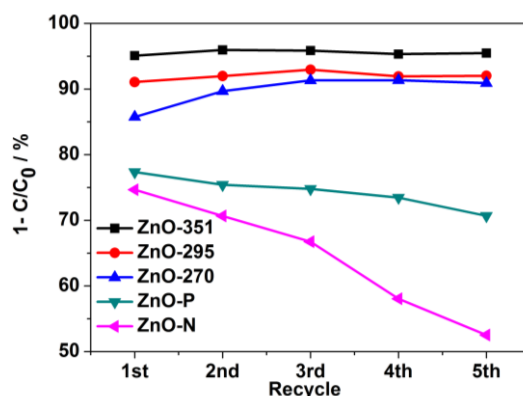


Fig. S8 Photocatalytic degradation of MO over ZnO photocatalysts during repetition operation upon UV-Vis light irradiation.

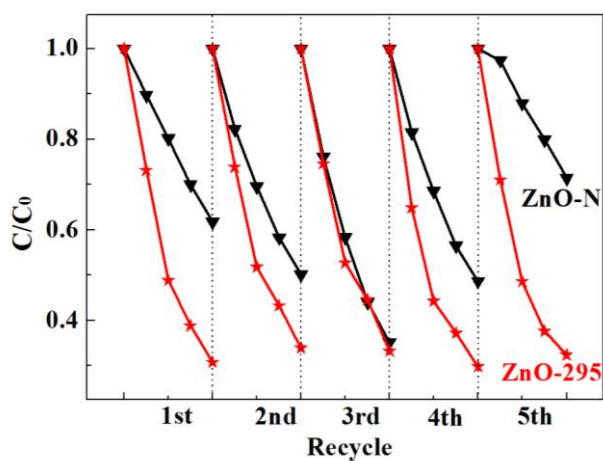


Fig. S9 Reusability of ZnO-295 and ZnO-N photocatalysts for the photocatalytic degradation of 4-CP under UV-Vis light irradiation.

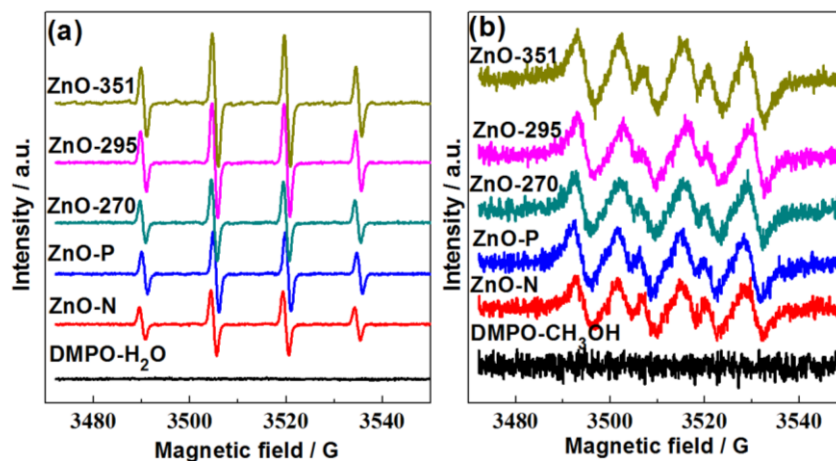


Fig. S10 (a) and (b) showed the ESR spectra of ZnO samples in irradiated aqueous dispersion for DMPO-•OH and methanol dispersion for DMPO-•O₂⁻, respectively.

Reference:

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