Supporting Information

Two-Dimensional Single-Crystal Periodic Macroporous ZnO Sheets for Extraordinary Photocatalytic Performance for Antibiotics

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2.1 Synthesis of Ordered PS Template

500 mL of deionized water and 2.5 g of polyvinylpyrrolidone (PVP) were added to a 1 L three-necked round-bottomed flask and vented with nitrogen for 30 min, followed by 65 mL of styrene after removing the inhibitor, and continued to be vented with nitrogen for another 20 min. The solution was heated to 75 °C and then stirring on, the polymerization reaction was initiated by the rapid addition of an aqueous solution of $K_2S_2O_8$ (1 g $K_2S_2O_8$ / 50 mL H_2O) for 24 h. The resulting milky white dispersion was sonicated for 30 min and allowed to stand for 2 days. Then poured into a filtration funnel equipped with an organic filter membrane with a pore size of 0.2 µm, and the negative pressure was controlled to be 0.05 Mpa. After 3 days of filtration, a solid cake was obtained, and the ordered PS template was successfully prepared after drying at 50 °C overnight.

2.3 Characterization and measurement

X-ray diffractometer (XRD, SmartLab9kw) patterns were obtained by a Rigaku diffractometer using Cu K α radiation with a scanning speed of 20° min⁻¹ and a 2 θ range of 5-80°. The morphology and surface states of all samples were studied by scanning electron microscopy (SEM, Hitachi, SU8100). The Electron paramagnetic resonance (EPR) spectra were measured with a Bruker EMX PLUS spectrometer at room temperature. The optical absorption of the samples was tested by UV-vis diffuse reflectance spectroscopy (UV-vis DRS, PerkinElmer Lambda 365). X-ray S2 photoelectron spectroscopy (XPS) was performed on an X-ray photoelectron

spectrometer (XPS, ESCALAB-250Xi) with an Al K α X-ray source. Due to the presence of surface critical carbon, all binding energies were calibrated by the C 1s photoelectron peak at 284.6 eV. Time-resolved photoluminescence (TRPL) spectroscopy was performed on an Edinburgh steady-state transient fluorescence spectrometer (FLS1000) with an excitation wavelength of 325 nm. The specific surface areas of the samples were tested by the Brunauer-Emmett-Teller (BET, Kubo-X1000). An electrochemical station (CHI-660) with a standard three-electrode configuration was used to test photocurrent profiles, electrochemical impedance spectroscopy (EIS), and other optoelectronic tests in a 0.1 M Na₂SO₄ solution. Photocatalysts (ZnO-S and ZnO-H) were milled and coated on the FTO substrate for the electrode, and Pt sheets and saturated Ag/AgCl electrode were used as the working, counter and reference electrode, respectively. The surface area of the photoanode was 1 cm². Electrochemical impedance spectroscopy (EIS) was performed at a bias potential of 1.8 V.

Photocatalytic degradation experiments. The photocatalytic activity of the 2DSPM ZnO sheets material was evaluated by degradation of the medical antibiotic pollutants ciprofloxacin (20 mg/L CIP), norfloxacin (30 mg/L NF), tetracycline (50 mg/L TC), phenol (4×10^{-5} mol/L) and RhB (1×10^{-5} mol/L) under UV-visible light. Specifically, 20 mg of photocatalyst was added to 100 mL of a solution configured with a certain concentration of pollutants and dispersed by sonication. Then, sampling was carried out at 6 min intervals over a 30 min dark treatment period to ensure that an adsorption-desorption equilibrium was reached. Subsequently, 5 ml of sample solution was taken at 20 min intervals under light, centrifuged and analyzed for contaminant

concentrations by UV-vis spectrophotometer.

Photoelectrochemical measurement. Electrochemical impedance spectra (EIS), Linear sweep voltammetry (LSV) curves and Mott-Schottky plots were measured using an electrochemical workstation (PARSTA T4000) with a three-electrode system using 0.1 M Na₂SO₄ solution as electrolyte. In the system, Pt foil is the counter electrode and Ag/AgCl is the reference electrode. And, the working electrode was prepared by dipcoating the sample on FTO glass and heating it in an oven at 200 °C for 1 h.

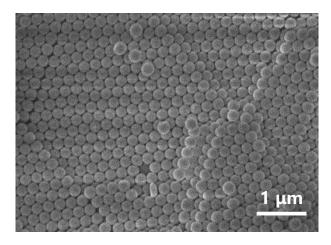


Fig. S1. SEM image of the PS template with a single sphere diameter of about 260 nm.

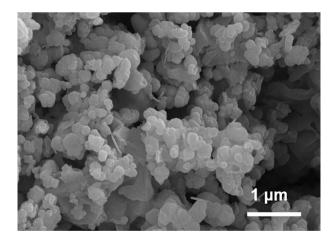


Fig. S2. SEM image of ZnO-R.

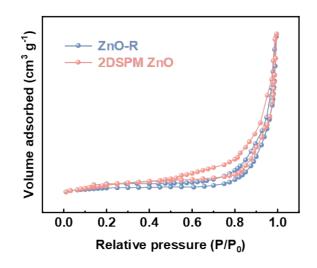


Fig. S3. N_2 adsorption-desorption isotherms for ZnO-R and 2DSPM ZnO.

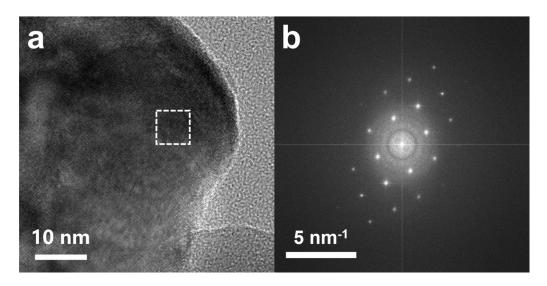


Fig. S4. (a) TEM image and (b) SAED pattern of another corresponding boxed area of 2DSPM ZnO.

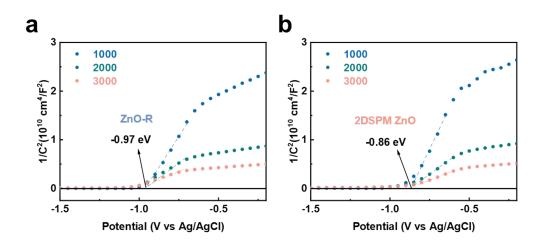


Fig. S5. Mott-Schottky curves of (a) ZnO-R and (b) 2DSPM ZnO relative to Ag/AgCl electrode at different frequencies.

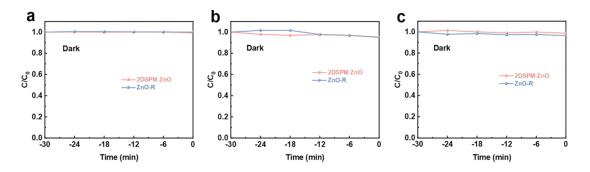


Fig. S6. Adsorption properties for CIP (a), NF (b) and TC (c) of 2DSPM ZnO and ZnO-

R in the dark.

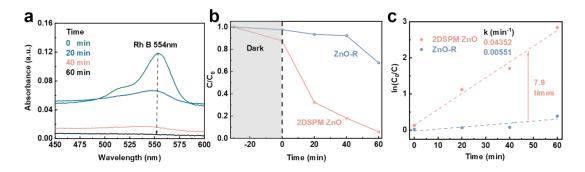


Fig. S7. (a) Light absorption curves of 2DSPM ZnO for RhB; (b) Photocatalytic degradation curves and (c) fitted curves of the degradation kinetic traces of RhB.

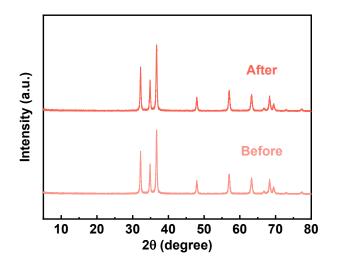


Fig. S8. XRD patterns before cycling and after cycling of 2DSPM ZnO.

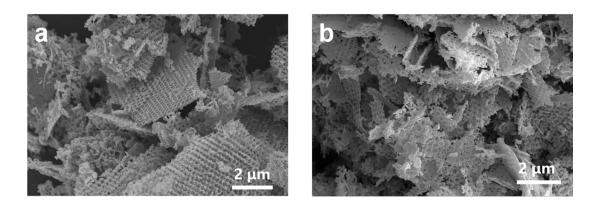


Fig. S9. SEM images of 2DSPM ZnO (a) before and (b) after the photocatalytic reaction.

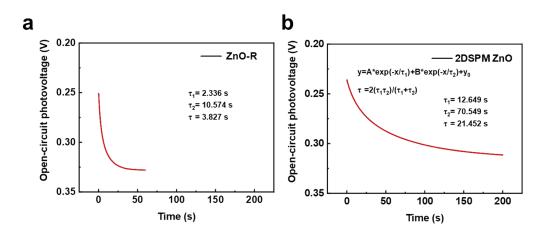


Fig. S10. Fitted curves for average carrier attenuation lifetimes of ZnO-R and 2DSPM ZnO.

Table S1. The specific surface area of ZnO-R and 2DSPM ZnO.

Sample	ZnO-R	2DSPM ZnO
S _{BET} /(m ² g ⁻¹)	15.49	32.45

Table S2. Recent reports on the use of ZnO for CIP, NF, TC and phenol photodegradation.

Material	Light source	Application	Ref.
ZnO nanotubes	UV-vis	6 mg/L CIP	[1]
ZnO nanoflowers	UV-vis	6 mg/L CIP	[2]
ZnO nanoflowers	UV-vis	5 mg/L NF	[3]
ZnO	UV-vis	5 mg/L TC	[4]
ZnO nanoparticles	UV-vis	1×10 ⁻⁵ M Phenol	[5]
ZnO nanosheets	UV-vis	1×10 ⁻⁶ M RhB	[6]
2DSPM ZnO sheets	UV-vis	20 mg/L CIP 30 mg/L NF 50 mg/L TC	TT1 1
		4×10 ⁻⁵ M Phenol 1×10 ⁻⁵ M RhB	This work

References:

1 C. Bojer, J. Schöbel, T. Martin, M. Ertl, H. Schmalz and J. Breu, *Appl. Catal. B-Environ.*, 2017, **204**, 561-565.

- 2 Y. Qu, X. Xu, R. Huang, W. Qi, R. Su and Z. He, Chem. Eng. J., 2020, 382, 123016.
- 3 S.-L. Zhou, S. Zhang, F. Liu, J.-J. Liu, J.-J. Xue, D.-J. Yang and C.-T. Chang, J. Photoch. Photobio. A., 2016, 328, 97-104.
- 4 L. Wang, Y. Zhu, T. Fu, K. Liu, J. Sun, J. Yan, L. Jiang, Z. Tong, Z. Zhou and H. Zhang, *Mater. Today Commun.*, 2023, **37**, 106967.
- 5 R. L. González, O. de la Fuente, R. L. García, M. del Carmen Uribe López, P. Q. Owen, M. C. H. López and M. A. A. Lemus, J. Chem. Technol. Biot., 2023, 98, 1826-1836.
- 6 R. Liu, X. Fu, Y. Guo, J. Zhang, W. Tian, Vacuum, 2023, 215, 112337