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反蛋白石结构ZnO@PDA用于增强光催化产H_2O_2性能

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Enhanced Photocatalytic H_2O_2 Production over Inverse Opal ZnO@ Polydopamine S-scheme Heterojunctions

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1 Material Characterization

The crystal phases of the as-prepared nanofibers were tested by an X-ray diffractometry (Shimadzu XRD-6100) with Cu K_α radiation. Fourier transform infrared (FT-IR) spectra of samples were collected using the Nicolet iS50 spectrometer (Thermo Scientific, USA). The morphology and microstructure observations were studied by a field-emission scanning electron microscopy (FESEM; JSM 7500F, JEOL, Japan) and a transmission electron microscopy (TEM; Talos F200S, USA). The ultraviolet-visible diffuse reflectance absorption spectrum was recorded on a UV-Vis spectrophotometer (UV-2600, Shimadzu, Japan). X-ray photoelectron spectroscopy (XPS) analysis was performed on a Thermo Scientific ESCALA 210 XPS spectrometer system (USA) with 300 W Al K_α radiation to investigate the chemical composition of the samples and the chemical states of the elements. The binding energies were calibrated by the C 1*s* peak at 284.8 eV from adventitious carbon. Contact potential difference (CPD) was measured on a kelvin probe apparatus (Instytut Fotonowy, Poland). And the work function of the probe is calibrated to be 4.25 eV by the gold tip as a standard reference surface. Photoluminescence (PL) spectra of the samples were analyzed by a fluorescence spectrophotometer (F-7000, Hitachi, Japan) with the excitation wavelength at 325 nm. The time-resolved photoluminescence (TRPL) spectra were obtained from a fluorescence lifetime spectrophotometer (FLS 1000, Edinburgh, UK).

2 Photoelectrochemical measurements

Electrochemical measurements were measured on an electrochemical workstation (CHI660C, China) in a standard three-electrode system. The photoelectrodes were prepared as follows. 20 mg of powdered sample was dispersed into 20 μL of Nafion and 250 μL of ethanol under grinding for 30 min. The as-prepared samples coated on FTO glasses acted as the working electrode with an active area of about 1.0 cm^2 and a Pt wire and Ag/AgCl (saturated KCl) were used as the counter and reference electrode, respectively. 50 mL of 0.5 mol·L^{-1} Na_2SO_4 aqueous solution was selected as the electrolyte.

3 Photocatalytic performance test

The photocatalytic H_2O_2 production experiments were carried out in a 50 mL three-necked flask using a 300 W Xenon arc lamp as the light source. In a typical photocatalytic reaction, 20 mg of the photocatalyst was suspended in a 50 mL glycol (4 vol%) aqueous solution. Before irradiation, the system was bubbled with oxygen through the flask for 30 min. During the photocatalytic experiments, a 1 mL solution was sampled from the reactor and the photocatalytic H_2O_2 evolution activity was analyzed by a UV-visible spectrophotometer (Shimadzu UV/Vis 1240, Japan) with an iodometry method. Briefly, the obtained solution was added to 1 mL of 0.4 mol·L^{-1} potassium iodide (KI) aqueous solution and 1 mL of 0.1 mol·L^{-1} $C_8H_5KO_4$ aqueous solution. Then the solution was mixed and kept for 30 min in the dark. The concentration of H_2O_2 was estimated according to the concentration of triiodide anions (I^{3-}) obtained from the reaction. Due to the strong absorbance of I^{3-} at 350 nm, the amount of I^{3-} was determined by UV-Vis spectroscopy. The H_2O_2 evolution cycling tests were conducted using the same procedure of photocatalytic reactions. Then, the reacted photocatalyst in the cycle experiments was centrifuged and rinsed with deionized water for the next cycle. The degradation behavior of H_2O_2 over the as-synthesized photocatalysts was investigated by degrading 1 mmol·L^{-1} H_2O_2 under 300 W xenon lamp irradiation.

4 Apparent quantum yield (AQY) calculation

To calculate the apparent quantum yield (AQY), incident light at 365 nm was used as the light source to trigger the photocatalytic reaction. The average intensity of irradiation was determined to be 1.9 mW·cm^{-2} and the irradiation area was 10.5 cm^2. The number of incident photons (N) is 1.73 × 10^{22} as calculated by equation (1). The amount of H_2O_2 molecules generated in 1 h was 15.3 μmol. The AQY is calculated from the following equation (2).

$$N=\frac{E\lambda}{hc}=\frac{1.9\times10^{-9}\times10.5\times3600\times365\times10^{-9}}{6.626\times10^{-34}\times3\times10^{8}}=1.32\times10^{20} \tag{1}$$

$$\begin{aligned}\text{AQY}&=\frac{2\times\ \text{the number of evolved } \mathrm{H_2O}}{\text{the number of incident photons}}\times100\\&=\frac{2\times6.02\times10^{23}\times1.53\times10^{-5}}{1.32\times10^{20}}=13.96\%\end{aligned} \tag{2}$$

5 Band gap (E_g)

Band gap (E_g) of PDA and ZnO was obtained by the following formula S1 proposed by Tauc, Davis and Mott:

$$(\alpha h\nu)^{1/n}=A(h\nu-E_g) \tag{S1}$$

where α is the absorbance index, h is the Planck constant, ν is the frequency, A is the constant and E_g is the band gap of the semiconductor. And n is related to the type of semiconductor, where n = 2 for direct and n = 1/2 for indirect allowed transition.

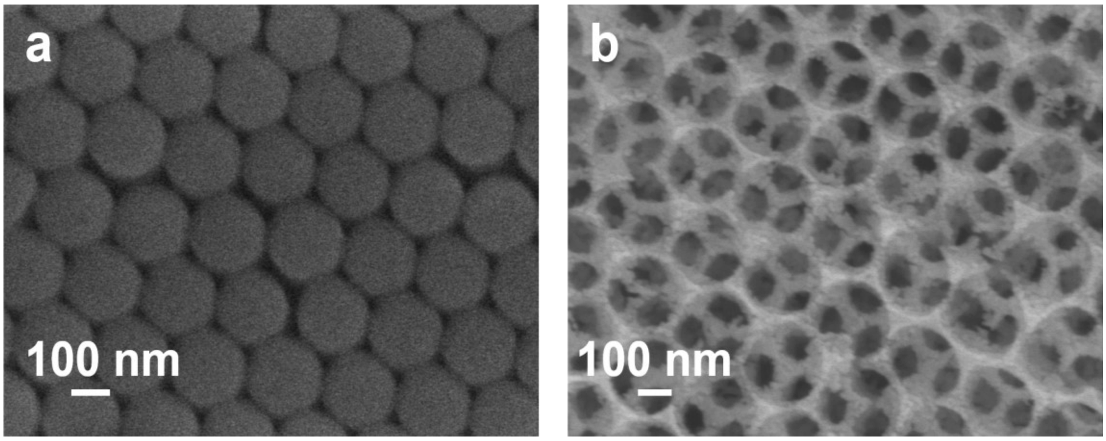

Fig. S1 FESEM images of PS opals (a) and 3DOM ZnO (b).

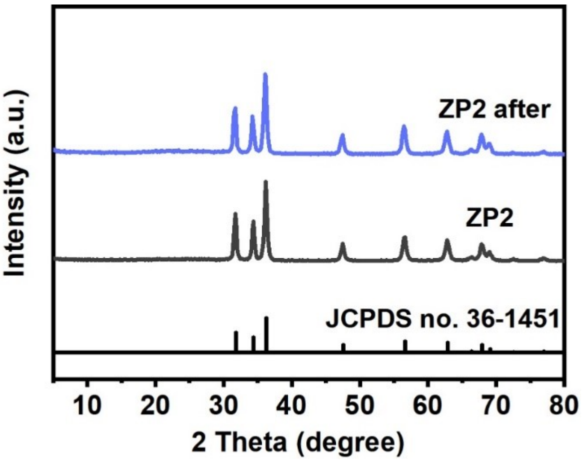

Fig. S2 XRD patterns for ZP2 before and after photocatalytic reactions.

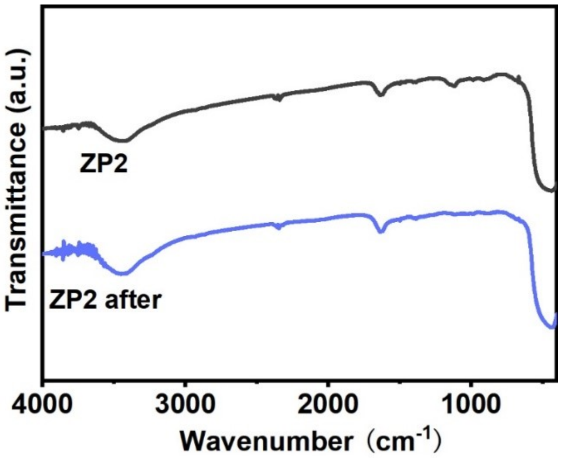

Fig. S3 Comparison of FTIR spectra for ZP2 sample before and after photocatalytic reactions.

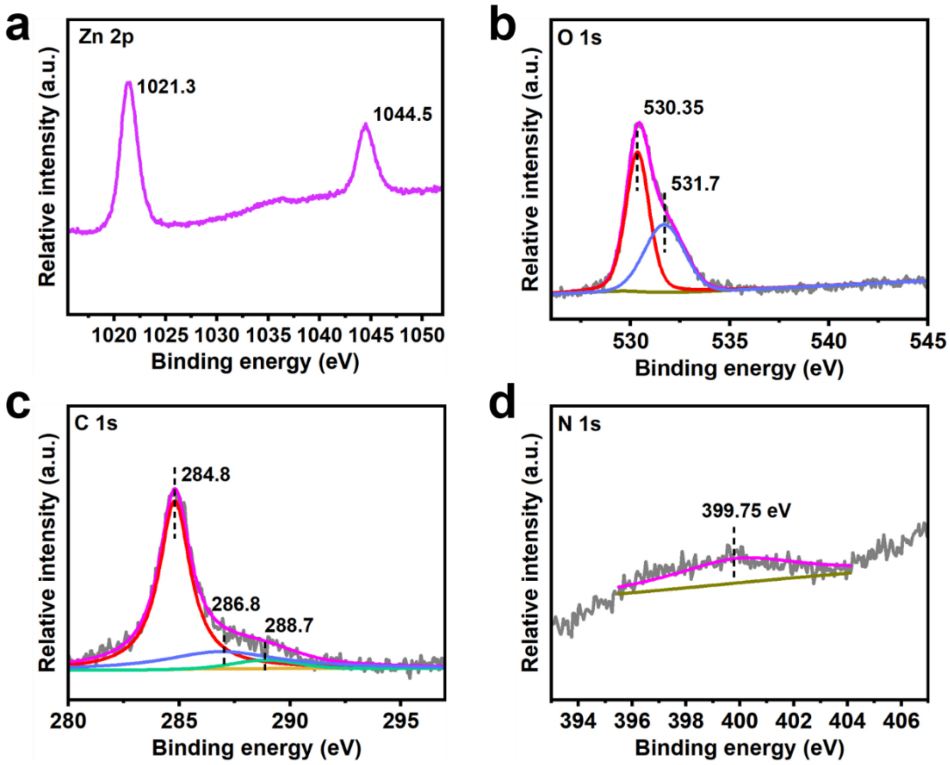

Fig. S4 High-resolution XPS spectra of Zn 2*p* (a), O 1*s* (b), C 1*s* (c) and N 1*s* (d) of ZP2.

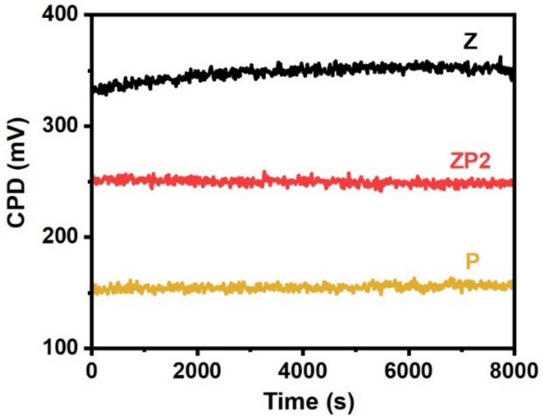

Fig. S5 CPD profile of Z, ZP2 and P under dark conditions.

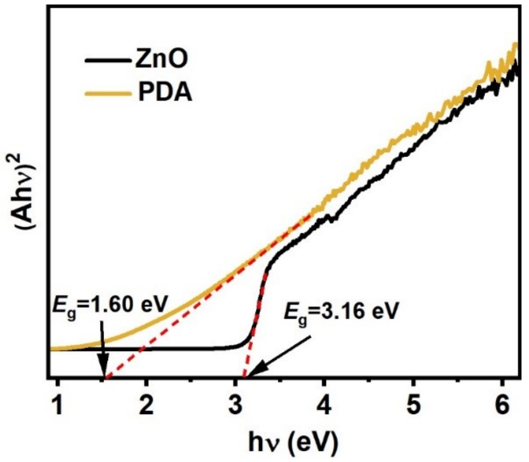

Fig. S6 Kubelka-Monk plots of the pure PDA and ZnO.