Oxygen-defective ZnO porous nanosheets modified by carbon dots for improving visible-light photocatalytic activity and mechanism insight

Supporting Information

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1. Characterization

The crystal structures of the as-prepared samples were determined by X-ray diffraction (XRD) using Cu Ka radiation (D/MAX-2500 diffractometer, Rigaku, Japan). Fourier transform infrared (FT-IR) spectra were obtained on KBr pellets on a Nicolet NEXUS470 FTIR in the range of 400-4000cm$^-$.Raman spectroscopy was obtained by laser confocal Raman spectroscopy (in Via) from Renishaw, UK. The X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) were determined by a Thermo ESCALAB 250X (America) electron spectrometer using 150 W Al Ka X-ray sources. The transmission electron microscopy (TEM), high-resolution TEM (HRTEM) images, and selected area energy dispersive X-ray spectra (EDX) were observed by field emission electron microscopy (JEM-2100F, Japan) with an accelerating voltage of 200 kV. The UV-vis diffused reflectance spectra (DRS) of the samples were measured on an UV-vis spectrophotometer (UV-2450, Shimadzu, Japan). The electrochemical impedance spectra (EIS) tests were performed by using a CHI 660 C (Chenhua Instruments, China) electrochemical workstation in a standard three-electrode configuration. Specific surface area (BET) and pore size were determined using a Microfor TriStar II Plus 2.02.The photoluminescence (PL) spectra were analyzed with a Perkin-Elmer LS 55 at room temperature using a fluorescence spectrophotometer. Time-resolved PL was conducted using the time-correlated single photon counting (TCSPC) technique with an excitation laser wavelength of 320 nm. The electron spin resonance (ESR) acquired on a Bruker A200-9.5/12 spectrometer was used to detect the radical intermediates.

2. Photocatalytic experiments

The photocatalytic activity of the prepared samples was evaluated by the degradation of TC, 50 mg photocatalyst was put into 100 mL of TC aqueous solution with concentration of 10 mg L^{-1} and stirred in the dark for 30 min to reach the adsorption equilibrium. A 300 W xenon lamp was selected as the light source and a 420 nm cut-off filter was mounted. At certain time intervals, 3.5 mL of the mixture was extracted and the catalyst was centrifuged, and the absorption spectra were recorded on ultraviolet-visible spectrophotometer with max wavelength of 357 nm (TC). Keep the temperature at 25 °C during photocatalysis to rule out degradation due to the temperature change. The degradation efficiency was calculated using the following equation (1):

$$\text{Degradation (\%)} = (1-C/C_0)\times 100\% \qquad (1)$$

Where C represents the residual concentration of antibiotics at different times, and C_0 displays the initial concentration after adsorption equilibrium.

3. Cyclic experiment

After the first photocatalytic reaction, the suspensions were collected and centrifugated to obtained the used photocatalyst powder. Then, the used photocatalyst was washed with water several times and dried in oven. The used photocatalyst was employed to the next photocatalytic degradation reaction. The above steps were repeated twice for three cycles degradation to investigate the reproducibility of the photocatalyst.

4. Actives capturing experiments

Briefly, in order to detect superoxide radical ($\bullet O_2^-$), holes (h^+) and hydroxyl radical (•OH), ascorbic acid (VC), disodium ethylenediamine tetra-acetic acid (EDTA) and 2-propanol (IPA) were separately added in the photodegradation process of TC. The amount of all scavengers in the photocatalytic process is controlled at 1 mmol.

5. ESR measurements

The electronic spin resonance (ESR) technique was measured on an electron paramagnetic resonance spectrometer (A300-10/12, Bruker) to further confirm the generation of $\bullet O_2^-$ and •OH during the photocatalytic reaction under visible light ($\lambda > 420$ nm). The $\bullet O_2^-$ and •OH can be captured by 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) in methanol and water, respectively. As the $\bullet O_2^-$ capturing for example, 10 mg photocatalysts were dispersed in 0.5 mL methanol, then 45 μL DMPO was added with ultrasonic disperse for 5 min. Finally, superoxide radicals (DMPO-$\bullet O_2^-$)

signals with the 10 min irradiation time were determined and recorded. The •OH capturing was similar to the process of $•O_2^-$ capturing but replaces methanol with water.

6. Figures and Table

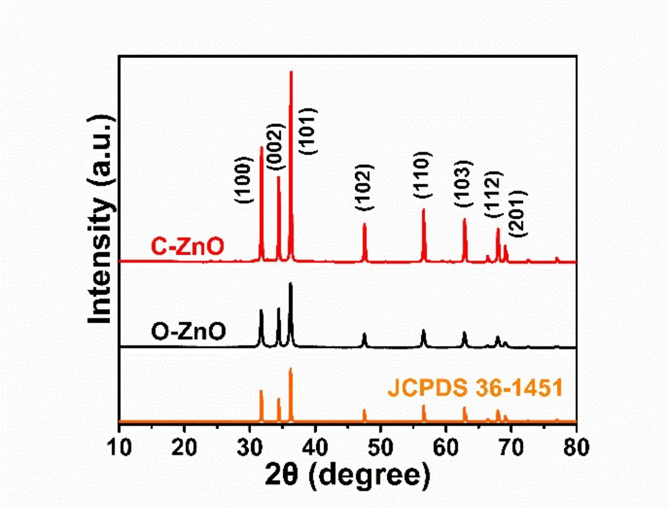

Fig.S1 XRD patterns of C-ZnO and O-ZnO.

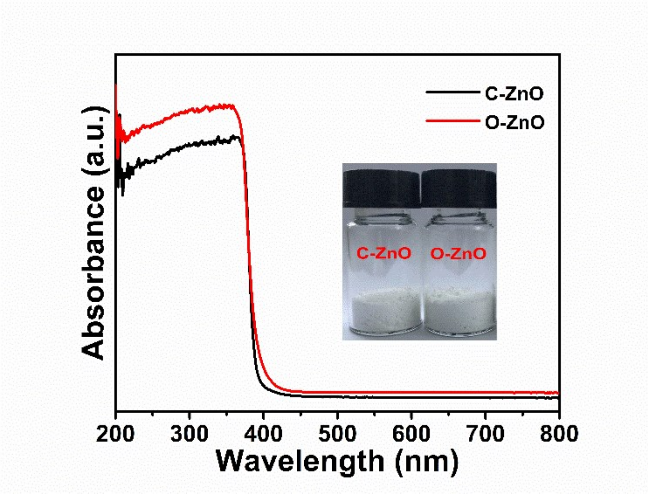

Fig.S2 UV-Vis diffuse reflectance spectra of C-ZnO and O-ZnO.

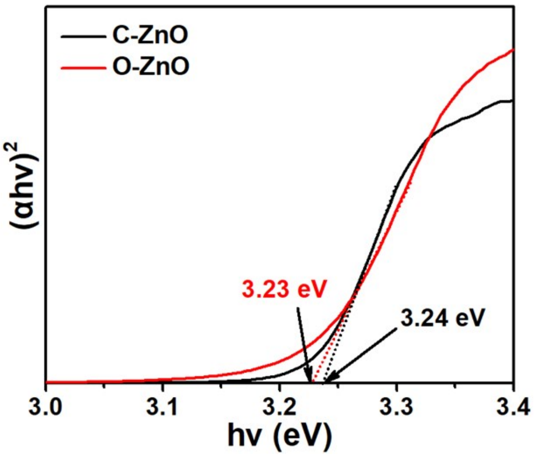

Fig.S3 Plots of $(ahv)^2$ versus photon energy (hv) of C-ZnO and O-ZnO.

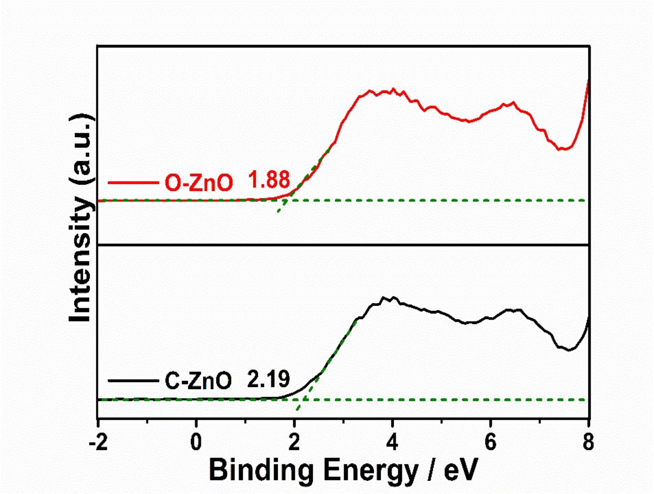

Fig.S4 Valence band XPS measurements of C-ZnO and O-ZnO.

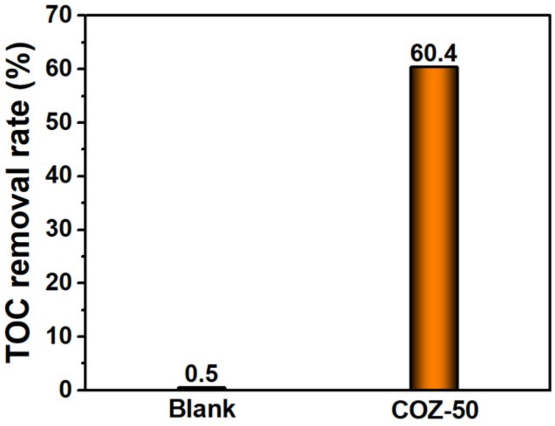

Fig.S5 TOC removal ratio of TC (C_0=10 mg/L) over the COZ-50 and directly photolysis under visible light irradiation (λ > 420 nm).

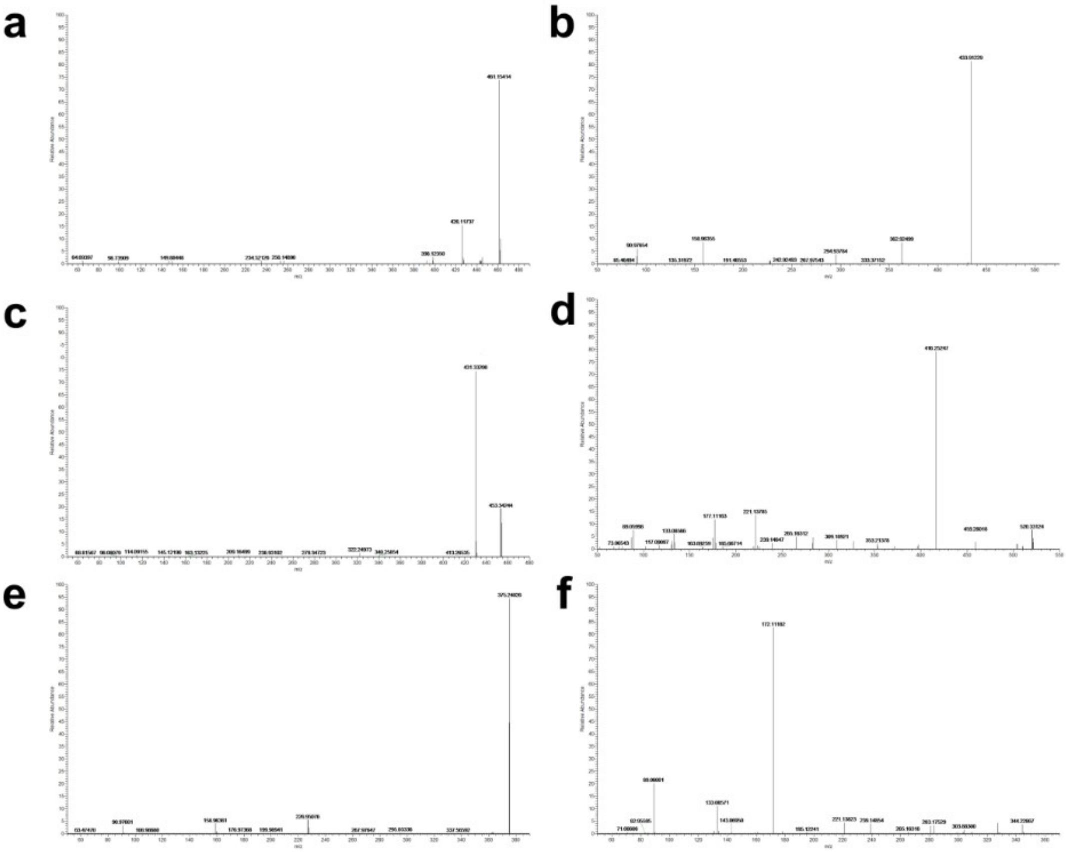

Fig.S6 .MS spectra of the TC and possible intermediates.

Table S1 XPS O1s spectra results of C-ZnO and O-ZnO

	Zn-O-Zn (%)	Oxygen ions near the oxygen vacancy (%)
C-ZnO	89.2	10.8
O-ZnO	64.1	35.9

Table S2. Fluorescence lifetime parameters obtained from the time-resolved PL spectra with triple-exponential fitting.

Sample	**B1**	**T1/ns**	**B2**	**T2/ns**	**T/ns**
C-ZnO	0.134403672	22.22541413	3.33E+03	1.207909924	1.223510674
O-ZnO	2.36E-01	19.9405721	3.32E+03	1.416499692	1.435021111
COZ-50	3.36E+03	2.172645248	1.359779344	25.62267035	2.283992012