Supporting Information

Facet-dependent generation of superoxide radical anions by

ZnO nanomaterials under simulated solar light

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Preparation of O₂⁻⁻ standard solutions

The standard O_2^{-} solutions were prepared with 12 M absolute ethanol, 15 μ M DTPA and 41 mM acetone, and were buffered to pH 12 by 1 mM borate.¹ The O_2^{-} radical was produced by exposing the standard O_2^{-} solutions to 254 nm light, and signal was detected at once by a spectrometer (USB-4000, Ocean Optics Inc.) with the absorbance at 240 nm.²

Measurement of steady-state concentrations of ¹O₂

The steady-state concentrations of ${}^{1}O_{2}$ ([${}^{1}O_{2}$]_{ss}) can be calculated according to the following reaction and equations:³

$FFA + {}^{1}O_{2} \rightarrow reaction products$	(R1)
$d[\text{FFA}]/dt = -k_{\text{FFA},102} [\text{FFA}] [^{1}\text{O}_{2}]_{\text{ss}}$	(1)
$\ln(\text{FFA}/\text{FFA}_0) = -k_{\text{FFA},1O2} [^1O_2]_{\text{ss}}t$	(2)
where $k_{\text{FFA},102} = 1.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C. ⁴	

Measurement of steady-state concentrations of HO[•]

The steady-state concentration of HO[•] ($[HO[•]]_{ss}$) can be determined according to the following reaction and equation:⁵

$$HO^{\bullet} + TA \rightarrow 2HTA$$
 (R2)

Varied concentrations of terephthalate acid (TA) were added to the ZnO suspension to trap HO[•] and produce 2HTA to explore the steady-state concentrations of HO[•].

The formation rate of 2HTA would be expressed as eq 3:

$$R_{\rm 2HTA} = d[2\rm HTA]/dt = \eta k_{\rm HO,TA} [TA] [\rm HO']_{\rm ss}$$
(3)

where η is the reaction yield, which is estimated as 0.28,⁵ k_{HO,TA} is the second-order reaction rate

constant between HO[•] and TA, which is estimated as 4.4×10^9 M⁻¹ s⁻¹.

Meanwhile, the [HO[•]]_{ss} can also be expressed as:

$$[\mathrm{HO}^{\bullet}]_{\mathrm{ss}} = R_{\mathrm{HO}}^{\bullet} / (\mathrm{S} + k_{\mathrm{HO}^{\bullet},\mathrm{TA}} [\mathrm{TA}])$$

$$\tag{4}$$

where S represents the scavenging rate constant of HO[•] by the matrix, and R_{HO}^{\bullet} is the formation rate of HO[•]. By combining equations (3) and (4), the following equation is obtained:

$$R_{2\text{HTA}} = \eta k_{\text{HO}},_{\text{TA}} [\text{TA}] \{ R_{\text{HO}}/(\text{S} + k_{\text{HO}},_{\text{TA}} [\text{TA}]) \}$$
(5)

In the absence of TA (i.e., [TA] = 0), eq 4 would be simplified as $[HO^{\bullet}]_{ss} = R_{HO}^{\bullet}/S$.

Therefore, $R_{2\text{HTA}} = \lim_{\text{TA}\to 0} (\eta k_{\text{HO}},_{\text{TA}} [\text{TA}] R_{\text{HO}} / S) = \lim_{\text{TA}\to 0} (\eta k_{\text{HO}},_{\text{TA}} [\text{TA}] [\text{HO}]_{\text{ss}}).$

The slope of the tangent to the curve at TA = 0 is $\eta k_{\text{HO}},_{\text{TA}}[\text{HO}]_{\text{ss}}$.

Therefore, $[\text{HO}^{\bullet}]_{\text{ss}} = (\text{slope}_{\text{TA}=0})/\eta k_{\text{HO}^{\bullet},\text{TA}}$.

Assignment of Raman bands

Raman spectroscopy was used to investigate the bonding structure and defect of the samples (Fig. S8). The band at 435 cm⁻¹ is assigned as the high E_2 mode of nonpolar optical phonons.⁶ The two bands at 330.5 and 380.4 cm⁻¹ are attributed to the E_{2H} - E_{2L} mode and A_{1T} mode, respectively,⁷ which belong to a typical wurtzite ZnO structure and is in good agreement with the X-ray diffraction data. However, the peak at 660 cm⁻¹ may be ascribed to disorder-activated Raman mode.⁸ The two peaks at 539 and 582 cm⁻¹are assigned the A_1 longitudinal (LO) mode and the E_1 (LO) mode, respectively. The presence of surface defects (e.g., V_o and Zn_i defects) can affect these two modes, especially the E_1 (LO) mode.⁹ The E_1 (LO) intensity of ZnO-100 is higher than that of ZnO-0001, which indicates that ZnO-100 has a higher abundance of defect.

Table S1. The XRD peak intensity ratios of different ZnO materials in Figures 1 and S4 (mean \pm SD, n = 3, p < 0.05).

Nanomaterials	$(100)/(101)^{a}$	(0002)/(101) ^b
ZnO-0001	0.64 ± 0.02	0.70 ± 0.05
ZnO-100	0.76 ± 0.04	0.45 ± 0.01

a(100)/(101) represents the intensity ratio for the (100) and (101) diffraction peaks.

^b (0002)/(101) represents the intensity ratio for the (0002) and (101) diffraction peaks.



Figure S1. XRD pattern of ZnS precursor for the synthesis of the ZnO-100 sample.



Figure S2. The spectra for the natural solar light and the solar simulator with a 290 nmcut-off filter. The natural solar irradiation spectrum was acquired at the campus of FudanUniversity,Shanghaiatnoon.



Figure S3. (a) Photochemically generated chemiluminescent signal from standard addition of superoxide (5, 20, 30, 60 and 100 nM). (b) Standard calibration curve relating the concentration of superoxide to the chemiluminescent signal.



Figure S4. XRD patterns of the ZnO materials: (a) ZnO-0001, (b) ZnO-100. The XRD measurement was performed three times for each ZnO material, using samples synthesized in three batches.



Figure S5. TEM images of ZnO materials: (a) ZnO-0001 and (b) ZnO-100.



Figure S6. The schematic diagram of predominant facets in the ZnO materials: (a) ZnO-0001 and (b) ZnO-100.



Figure S7. XPS (a) survey spectra. The C 1s peak is due to the adventitious carbon. (b) O 1s spectra, and (c) Zn 2p spectra of ZnO-0001 and ZnO-100. The Zn 2p spectra in part b show the characteristic binding energies of approximately 1021 and 1044 eV, corresponding to the Zn $2p_{3/2}$ and Zn $2p_{1/2}$ orbitals. The slightly higher Zn 2p binding energies of ZnO-100 (1021.6 and 1044.7 eV) than those of ZnO-0001 (1021.3 and 1044.4 eV) suggests the presence of Zn defects in the ZnO-100 nanosheets.¹⁰



Figure S8. TGA curves of the ZnO materials: (a) ZnO-0001, (b) ZnO-100, and the zoomin views for (c) ZnO-0001 and (d) ZnO-100. The TGA measurement was performed three times for each sample.



Figure S9. Raman spectra of ZnO-0001 and ZnO-100.



Figure S10. UPS spectra of (a) ZnO-0001 and (b) ZnO-100, with the valence band maximum energies (E_{VBM}) determined from the tangents in the main figures. The work function (Φ) is determined as the difference between the photon energy (21.2 eV) and the binding energy of the secondary cutoff edge (from the tangent in the insets). The Fermi level is deemed to be 0 eV in the spectra.



Figure S11. Band structures for different ZnO materials determined from UPS and UVvis analyses. The symbol Φ stands for work function, $E_{\rm F}$ for Fermi level, $E_{\rm CBM}$ for conduction band minimum (bottom), $E_{\rm VBM}$ for valence band maximum (top), and $E_{\rm g}$ for band gap. It is noted that the Fermi level is not located in the band gap but likely in the conduction band, as is in the case of ZnO with n-type doping.¹¹ (Note that ZnO nanomaterials are typically n-type semiconductor.)



Figure S12. Photodegradation of tetracycline by ZnO-0001 and ZnO-100 under simulated solar irradiation. Initial tetracycline concentration = 30 mg/L, ZnO concentration = 200 mg/L. Error bars represent \pm one standard deviation from the mean (n = 3).



Figure S13. Zn^{2+} leaching properties of ZnO-0001 and ZnO-100 nanomaterials at different concentrations under simulated solar irradiation. Error bars represent \pm one standard deviation from the mean (n = 3).

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