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Supporting Information

Interface photo-charge kinetics regulation by carbon dots for efficient hydrogen peroxide production

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Supplementary Text

S1. Calculation process of valence band (VB) determined by UPS

The valence band energy (E_{VB}) can be determined according to the following equation[1-3]:

$$E_{VB} = -\left(21.22 - \left(E_{cutoff} - E_i\right)\right)\, eV \qquad (1)$$

where 21.22 eV is the emission energy of Helium irradiation, E_{cutoff} is the cut-off binding energy, E_i is the energy difference between Femi level (E_F) and the valence band maximum (E_{vb}). The E_{cutoff} and E_i can be extrapolated from the linear part interception to x-axis.

S2. Quantum efficiency (QE) calculations.

The quantum efficiency can be evaluated from equation:

$$QE = \frac{2 \times n_{H_2O_2} \times N_A}{N} \tag{2}$$

N_A is the number of evolved H_2O_2 molecules, is avogadro number (6.02×10^{23}) and N represents the number of incident photons, which can be calculated from the following equation:

$$N = \frac{light\ intensity\ \left(W\ cm^{-2}\right)\ \times\ illumination\ area\ \left(cm^{2}\right)\ \times illu}{\frac{hc}{\lambda}} \tag{3}$$

h is plank constant (6.626×10^{-34} J·s = 4.136×10^{-15} eV·s), *c* is the speed of light (3.0×10^{8} m·s^{-1}), λ is the wavelength of light (365, 420, 535 and 635 nm). The photocatalytic systems with 20 mg catalyst and 15 mL water were irradiated for 3 h at room temperature and atmospheric pressure, without any sacrificial reagents. The irradiated area is 9.0746 cm^2.

S3. Determination of solar-to-chemical conversion (SCC) efficiency.

The free energy for H_2O_2 formation:

$$H_2O + \frac{1}{2}O_2 \rightarrow H_2O_2 \left(\Delta G = 117\ kJ\ mol^{-1}\right) \tag{4}$$

The total input energy:

$$E_{solar}\,(W) = irradiance\left(W\ cm^{-2}\right) \times\ irradiated\ area\ \left(cm^2\right) \tag{5}$$

The determination of SCC:

$$SCC\ efficiency\ (\%) = \frac{\left[\Delta G\ for\ H_2O_2\ generation\ \left(J\ mol^{-1}\right)\right] \times\ [H_2O_2\ fromed\ (mol}{[total\ input\ energy\ (W)] \times\ [reaction\ time\ (s)]} \tag{6}$$

According to equation (4), the free energy for H_2O_2 generation is 117 kJ·mol^{-1}. The irradiance of simulated solar source is 0.53 mW·cm^{-2}, while the irradiated area is 9.0746 cm^2. The reaction time is 3 h, and the amount of H_2O_2 generated in 15 mL solution with 20 mg catalyst is 4.53 μmol. On the whole, according to equation (5) and (6), SCC efficiency can be calculated to be 1.02%.

S4. The transient photovoltage (TPV) measurements.

The TPV measurements were conducted under room temperature on platinum net covered with power sample (1cm×1cm) as the working electrodes and Pt wire as the counter electrodes. The in-situ TPV were carried out under room temperature with indium-tin oxide (ITO) glass (1cm×2cm) as the working electrodes and Pt wire as the counter electrodes. The working electrodes were prepared by depositing samples (100 μL, 2 $mg \cdot mL^{-1}$, dispersion liquid: 79.5% water, 20% isopropanol and 0.5% Nafion solution(v/v), respectively) on ITO glass substrates. During the testing process, the working electrodes were kept wet with anhydrous acetonitrile (or adding H_2O, N_2, O_2 saturated). The samples were excited by a laser radiation pulse (λ=355 nm, pulse width 5 ns) from a third-harmonic Nd: YAG laser (Polaris II, New Wave Research, Inc.). The photocurrent is the ratio of the photovoltage to the internal resistance of the test systems.

S5. The measurement of electron transfer number.

The rotating disk-ring electrode (RRDE) collection experiments were carried out in N_2-purged Na_2SO_4 solution (0.1 M). 10 μL catalyst solution (5 mg mL^{-1}) was dropped onto the surface of RRDE electrode as the working electrode. The LSV was studied at room temperature with a scan rate of 50 mV s^{-1}. The $Hg/HgCl_2$ electrode and carbon rod electrode were used as reference electrode and counter electrode, respectively. The rotating speed was 1600 rpm. The electron transfer number was derived from the following equation:

$$n = \frac{4\Delta I_{disk}}{\Delta I_{disk} + \Delta I_{ring}/N} \qquad (7)$$

where ΔI_{disk} and ΔI_{ring} are the difference of disk current density and ring current density between darkness and light, respectively. As the RRDE collection efficiency, N was experimentally determined to be 0.35, and it refered to the fraction of H_2O_2 formed at the disk that was collected at the ring. According to equation (7), the n value of the water oxidation reaction was calculated to be 4.

S6. Electrochemical ORR and OER tests.

Electrochemical oxygen evolution reaction (OER) testing was conducted by linear sweep voltammetry (LSV) in 0.1M Na_2SO_4 solution. 10 μL catalyst solution (5 mg mL^{-1}) was dropped onto the surface of glassy carbon electrode as the working electrode. The $Hg/HgCl_2$ electrode and carbon rod electrode were used as the reference electrode and counter electrode, respectively. The rotating speed was varied 1600 rpm. And the test temperature will be adjusted through the water bath (288 K–338 K).

Electrochemical oxygen reduction reaction (ORR) testing was investigated by linear sweep voltammetry (LSV) in O_2-purged Na_2SO_4 solution (0.1 M). 10 μL catalyst solution (5 mg mL^{-1}) was dropped onto the surface of the RDE electrode as the working electrode. The $Hg/HgCl_2$ electrode and carbon rod electrode were used as the reference electrode and counter electrode, respectively. The rotating speed was varied 1600 rpm. And the test temperature will be adjusted through the water bath (288 K–338 K).

S7. The calculations of OER and ORR reaction rate constant.

Reaction rate constant of OER k_1:

$$j_{f1} = n_1 F k_1 e^{-E_1/RT} e^{\left(\alpha F\ \left(U_1 - U_{10}\right)\ /RT\right)} C_1^m \tag{8}$$

$$4.12 \times 10^{-7} = 4 \times 96500 \times k_1 \times e^{\frac{-24891}{8.314 \times 298}} \times e^{\frac{0.5\ \times 96500\ \times (1.23 - 1.18)}{8.314 \times 298}} \times 1$$

$$k_1 = 9.31 \times 10^{-9}$$

According to equation (8), n_1 represents electron transfer number (4). F represents Faraday constant (96500 C mol^{-1}). k_1 is the reaction rate constant of OER. E_1 represents reaction activation energy of OER (24891 J mol^{-1}). The reaction activation energy of OER is tested by LSV with different temperature (288 K–338 K). Rrepresents gas constant (8.314 J mol^{-1}k^{-1}). Trepresents Kelvin temperature at room temperature (298 K). α epresents constant term of formula (0.5). U_1 epresents reaction potential of OER (1.23 V vs. RHE). C_1^m epresents the concentration of water (1). (U_{10}, j_{f1}) is the any point data of tafel curve region of OER. The k_1 value is calculated to be 9.31×10^{-9} from the formula.

Reaction rate constant of ORR k_2:

$$j_{f2} = n_2 F k_2 e^{-E_2/RT} e^{-\alpha F\left(U_2 - U_{20}\right)/RT)} C_2^m \tag{9}$$

$$2.75 \times 10^{-7} = 2 \times 96500 \times k_2 \times e^{\frac{-19700}{8.314 \times 298}} \times e^{\frac{-0.5 \times 96500 \times (0.65 - 0.68)}{8.314 \times 298}} \times 0.21$$

$k_2 = 1.2 \times 10^{-8}$

According to equation (9), n_2 represents electron transfer number (2). F represents Faraday constant (96500 C mol^{-1}). k_2 is the reaction rate constant of OER. E_2 represents reaction activation energy of OER (19700 J mol^{-1}). The reaction activation energy of ORR is tested by LSV with different temperature (288 K–338 K). Rrepresents gas constant (8.314 J mol^{-1}k^{-1}). Trepresents Kelvin temperature at room temperature (298 K). α epresents constant term of formula (0.5). U_2 epresents reaction potential of ORR (0.68 V vs. RHE). C_2^m epresents the partial pressure of O_2 in the air (0.21). (U_{20}, j_{f2}) is the any point data of tafel curve region of ORR. The k_2 value is calculated to be 1.2×10^{-8} from the formula.

S8. Experiment of photocatalysis

First, 20 mg of catalyst was added to a 30 mL transparent glass bottle. Then add 15 mL of ultrapure water to the bottle, seal the mouth of the bottle with a rubber stopper and squeeze it with an aluminum plastic cap. Then place the mixture in the glass bottle under ultrasound dispersed uniformly in the instrument. Finally, the reaction was performed under visible light ($\lambda \geq 420$ nm) for 3h. The suspension was centrifuged to remove the photocatalyst. The H_2O_2 produced by the reaction was added with a 1mL H_2SO_4 solution (3mol L^{-1}). The acidic $KMnO_4$ reagent solution (0.01mol L^{-1}) was subjected to redox titration. When the solution became pink after the addition of $KMnO_4$ solution and the color of the solution was kept for 1 min, the concentration of $KMnO_4$ solution was used to calculate the concentration of H_2O_2.

S9. Characterization

The scanning electron microscope (SEM), transmission electron microscopy (TEM) and energy dispersive X-ray (EDX) spectroscopy were used to characterize the surface morphology and element composition of the resultant photocatalysts. The SEM and TEM images were acquired from a FEI-Quanta 200 FEG scanning electron microscope and FEI-Tecnai F20 transmission electron microscope (200 kV). The crystal structure of samples was examined by a PIXcel3D X-ray diffractometer (Empyrean, Holland Panalytical) with Cu Kα radiation ($\lambda = 0.15406$ nm). Fourier transform infrared (FTIR) spectrum was recorded on a FTIR spectrometer over the scan range of 400-4000 cm^{-1}, using a standard KBr pellet technique. Raman spectra were collected by using a HR 800 Raman spectroscope (J Y, France) with a 20 mW air-cooled argonion laser (633 nm) as the excitation source. X-ray photoelectron spectroscopy (XPS) measurements were performed by an Escalab 250Xi X-ray photo-electron spectroscope (Thermo Fisher Scientific, America) with a monochromatic Al Kα X-ray source. Ultraviolet photoelectron spectroscopy (UPS) measurements were carried out with He I (21.22 eV) as the monochromatic light source and instrumental energy resolution of 100 meV. Room temperature UV-Vis adsorption spectrum was caried out from a UV/VIS/NIR spectrophotometer (Lambda 750, Perkinelmer), the wavelength range is 300 - 800 nm. Electron spin-resonance spectroscopy (ESR) measurements were performed by an ESR spectrometer (Bruker A300). Electro-catalysis measurement was acquired from a Model CHI 760C workstation (CH Instrument, Shanghai, China).

Supplementary Figures.

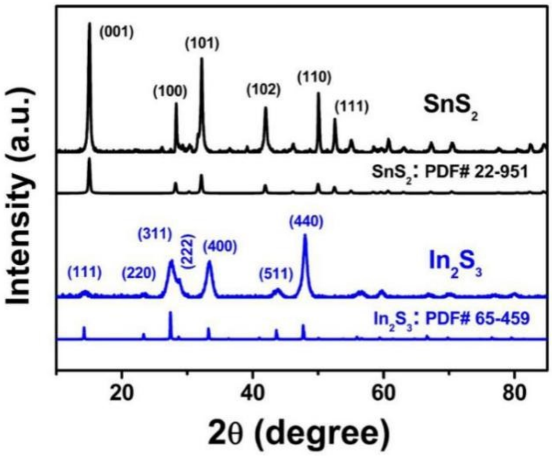

Figure S1. XRD patterns of SnS_2 (black line) and In_2S_3 (blue line).

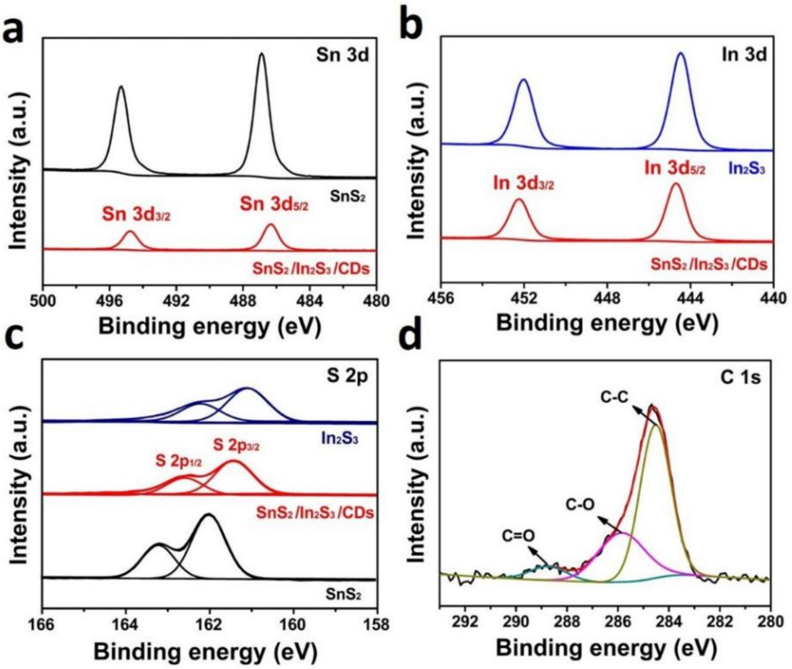

Figure S2. High-resolution XPS spectra of (a) Sn 3d (b) In 3d (c) S 2p and (d) C 1s for SnS_2/In_2S_3/CDs.

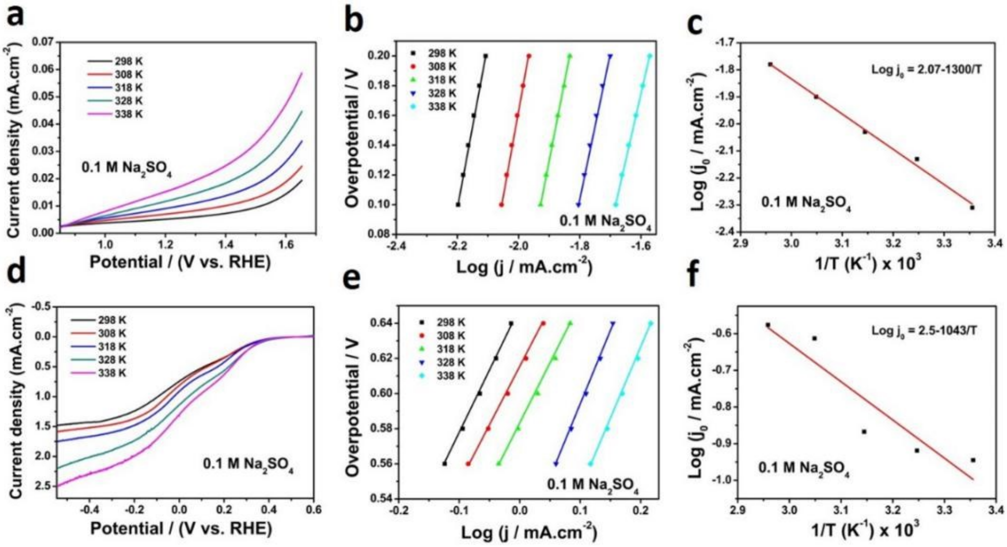

Figure S3. (a) OER performance of SnS_2/In_2S_3/CDs composite with different temperatures in 0.1 M Na_2SO_4 solution. (b) Tafel curves and (c) Arrhenius plot of SnS_2/In_2S_3/CDs for OER. (d) ORR performance of SnS_2/In_2S_3/CDs in 0.1 M Na_2SO_4 solution at different temperatures. (e) Tafel curves and (f) Arrhenius plot of SnS_2/In_2S_3/CDs for ORR.

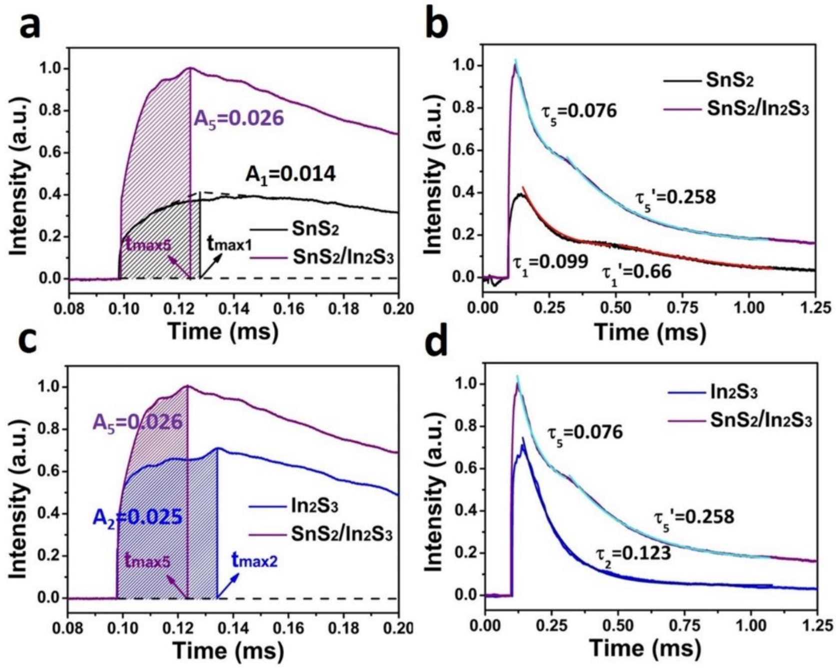

Figure S4. (a) Maximum extraction rate of charge and charge extraction process of SnS_2 and SnS_2/In_2S_3. (b) Charge recombination process of SnS_2 and SnS_2/In_2S_3. (c) Maximum extraction rate of charge and charge extraction process of In_2S_3 and SnS_2/In_2S_3. (d) Charge recombination process of In_2S_3 and SnS_2/In_2S_3.

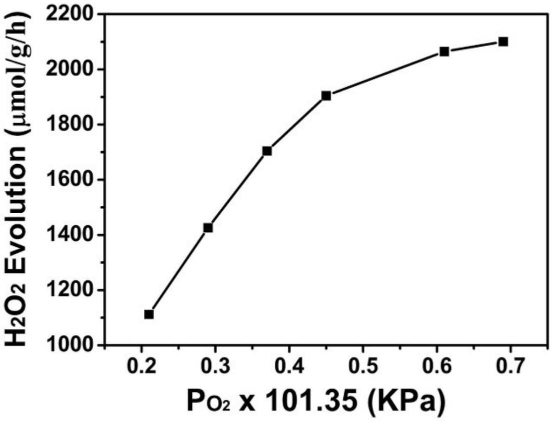

Figure S5. The relationship between the H_2O_2 production rate and P_{O_2} (the photocatalysis reaction was measured under visible light irradiation ($\lambda \geq 420$ nm) for 3 h, with the system contain 20 mg powder dispersing in 15 mL H_2O).

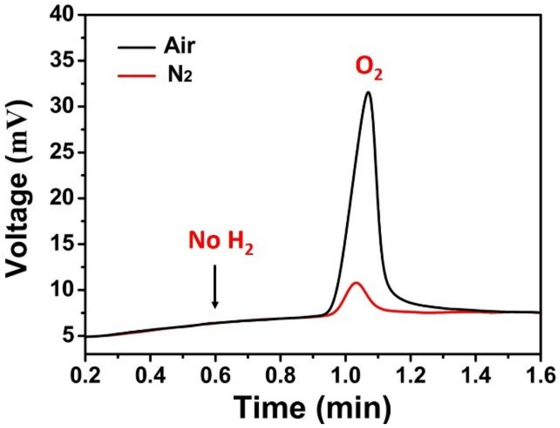

Figure S6. Detection of H_2 under Air/N_2 atmosphere by Gas chromatograph (GC-7900).

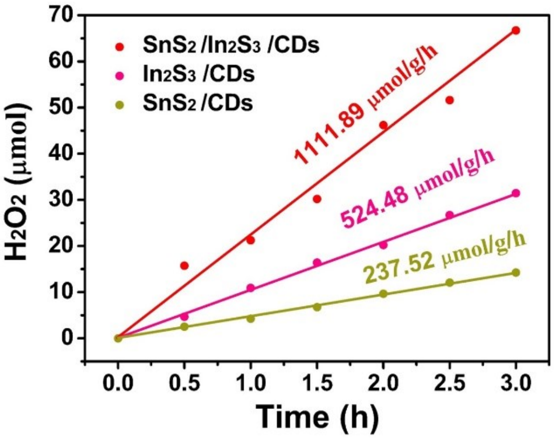

Figure S7. Evolution of H_2O_2 catalysed by SnS_2/In_2S_3/CDs, SnS_2/CDs and In_2S_3/CDs.

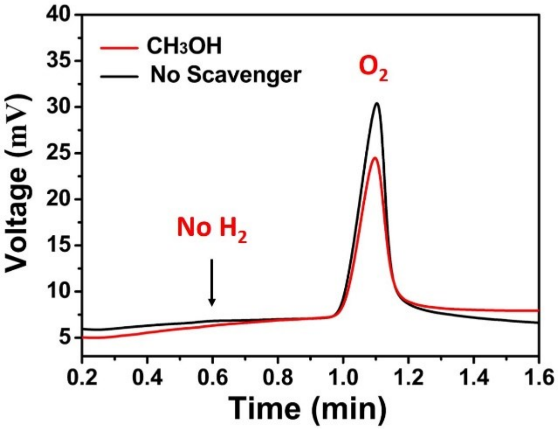

Figure S8. Detection of H_2 with no scavenger or CH_3OH solution by Gas chromatograph (GC-7900).