Supplementary Information

Unraveling the role of superoxide radicals in CdS quantum dot instability

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Experimental section

Materials

Cadmium oxide (CdO, 99.99%), oleylamine (OAm, 90%), 1-octadecene (ODE, 90%), oleic acid (OA, 90%), and NaOH (96%) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Hydrophilic mercaptopropionic acid (MPA), acetone, *n*-hexane, and methanol were obtained from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used directly without further purification.

The synthesis of Oil-soluble CdS quantum dots (CdS-O QDs)

Oil-soluble CdS quantum dots (CdS-O QDs) were synthesized via a solvothermal process.[1] Typically, a solution containing 0.5136 g of CdO, 7.5 mL of oleic acid (OA), and 7.5 mL of 1-octadecene (ODE) was heated to 100 °C while stirring for 30 minutes under a nitrogen atmosphere to remove oxygen and water from the system. The temperature was then increased to 230 °C and maintained for 5 minutes to form a colorless Cd precursor solution, which was subsequently cooled to 60 °C. Next, sulfur powders (0.128 g) were dissolved in 5 mL of oleylamine (OAm) to create an S-OAm solution, which was then added to the Cd precursor. This mixture was stirred under nitrogen for 20 minutes before rapidly heating to 260 °C, where it was held for 5 minutes. After cooling to room temperature, the product was washed multiple times with acetone to remove any unreacted materials, yielding oil-soluble CdS-O quantum dots. The prepared CdS-O QDs are then re-dispersed in 20 mL of n-hexane for further use.

The synthesis of water-soluble CdS QDs (CdS-MPA)

To convert the CdS-O QDs to water-soluble CdS-MPA, the hydrophobic surfactants (OA and/or OAm) were replaced with MPA following standard procedures. Firstly, 0.5 mL of MPA was added to 5 mL of methanol. Then, a NaOH solution (40 wt%) was added dropwise to adjust the pH to 13. This solution was mixed with 20 mL of the CdS-O dispersion and stirred for 3 hours. Finally, the CdS-MPA were precipitated by adding excess acetone as an antisolvent. The final products were washed with acetone and water three times each and re-dispersed into water.

Characterizations

The morphology and microstructure were examined using transmission electron microscopy (TEM; Talos F200S, USA). The ultraviolet–visible diffuse reflectance absorption spectra were obtained on a UV–vis spectrophotometer (UV–2600, Shimadzu, Japan). Fourier transform infrared (FTIR) spectra were recorded using a Nicolet iS50 spectrometer (Thermo Scientific, USA). X–ray diffractometry (Shimadzu XRD–6100) with Cu Kα radiation was used to determine the crystal phases. The electron paramagnetic resonance (EPR)

measurements were conducted on an EPR spectrometer (Bruker MEX-nano, Bruker, DEU). Specifically, the as-prepared samples were dispersed into the mixture solution (0.5 mL aqueous dispersion for DMPO-·OH and 0.5 mL methanol dispersion for DMPO-·O_2^-) with 10 uL of DMPO (5, 5-dimethyl-1-pyrrolidine N-oxide (DMPO)) and then irradiated with visible light. X–ray photoelectron spectroscopy (XPS) analysis was conducted with a Thermo Scientific ESCALA 210 system (USA) using 300 W Al Kα radiation. Binding energies were calibrated using the C 1s peak at 284.8 eV from adventitious carbon.

Photocatalytic H_2O_2 production

The photocatalytic H_2O_2 production was evaluated in a typical procedure. A catalyst (20 mg) was added to 20 mL of ultrapure water in a 100 mL quartz reactor. Before illumination, oxygen (air or nitrogen) was bubbled into the flask, and the mixture was continually stirred for 30 mins in the dark to achieve equilibrium between absorption and desorption. A 5 W LED lamp (400-800 nm, perfect light, China) served as a light source to initiate photocatalytic reactions. At regular intervals (every hour), 1 mL of the solution was sampled and filtered using a 0.22 μm microporous filter to remove any solid residues. The concentration of H_2O_2 was determined by iodimetry. To this end, the obtained 1 mL of solution was added to 1 mL of 0.1 mol L^{-1} potassium hydrogen phthalate ($C_8H_5KO_4$) solution, followed by the addition of 1 mL of 0.4 mol L^{-1} potassium iodide (KI) solution, and let stand for 30 minutes. The absorbance of the mixed solution at 350 nm was measured by UV–vis spectroscopy (UV–1240, Shimadzu, Japan), from which the production of H_2O_2 was evaluated.

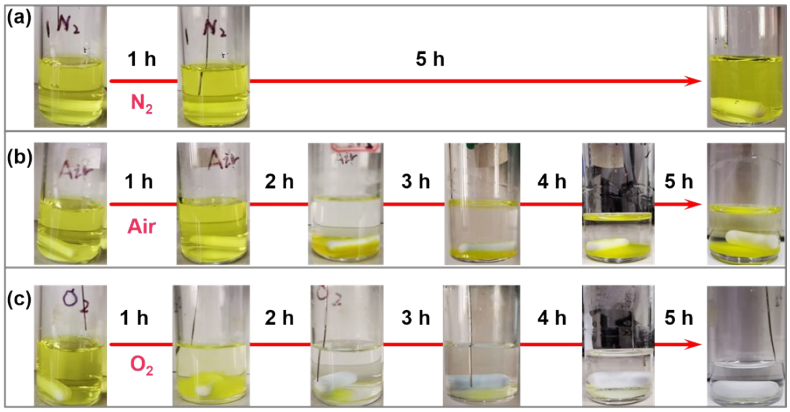

Fig. S1. Images showing the changes in CdS-MPA under different illumination durations in (a) nitrogen, (b) air, and (c) oxygen atmospheres.

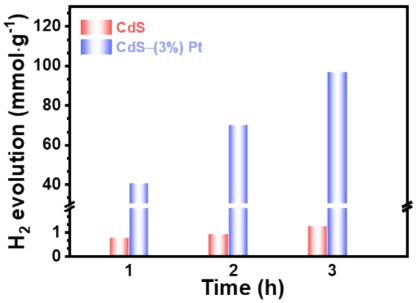

Fig. S2 The H_2 production rates of CdS-MPA QDs and CdS-MPA QDs (with 3% Pt) in a 25 mL ascorbic acid (1 mM) solution with 5 mg of catalyst under light irradiation.

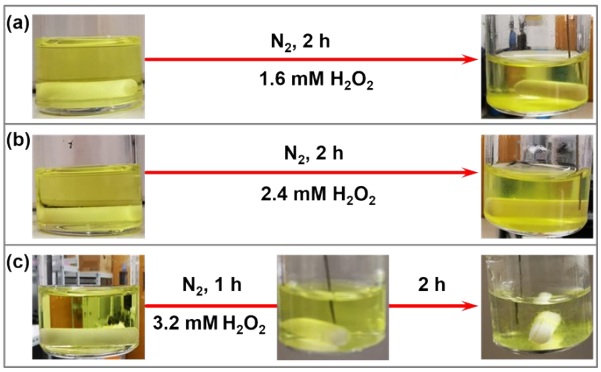

Fig. S3. Images showing the effect of hydrogen peroxide concentration on the corrosion of CdS-MPA QDs under nitrogen: (a) 1.6 mM, (b) 2.4 mM, and (c) 3.2 mM.

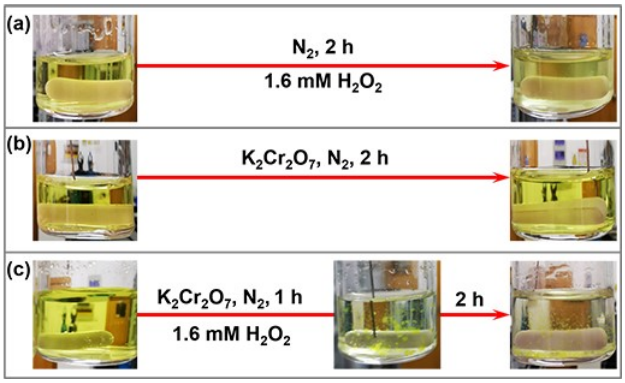

Fig. S4. Effect of electron trapping agent ($K_2Cr_2O_7$) on the corrosion of CdS-MPA QDs under nitrogen.

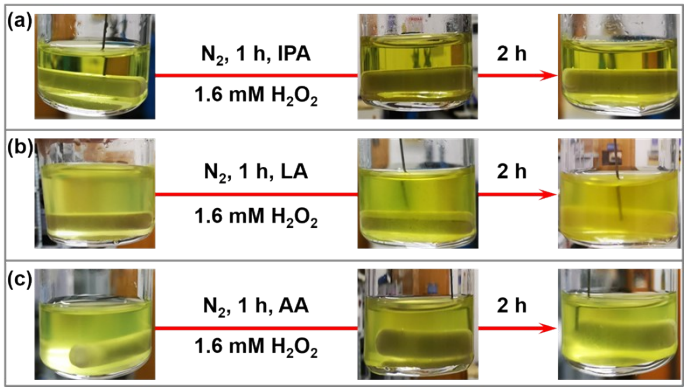

Fig. S5. Effect of hole trapping agents (IPA: isopropanol, LA: lactic acid, AA: ascorbic acid) on the corrosion of CdS-MPA QDs under nitrogen.

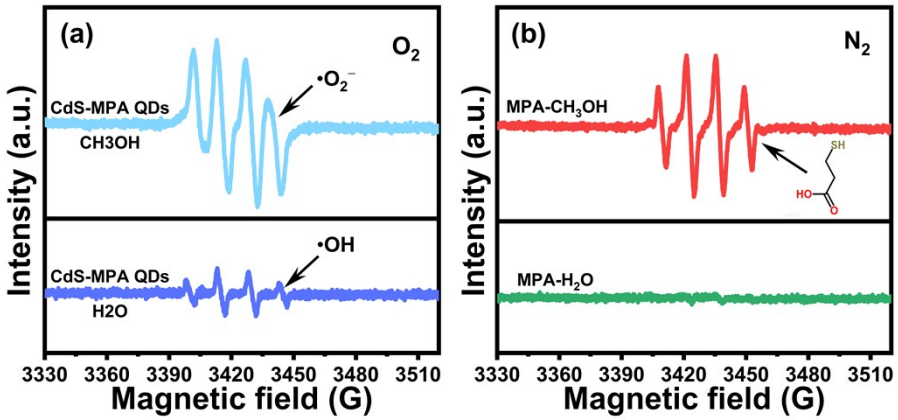

Fig. S6. (a) EPR spectra of CdS-MPA QDs for $\cdot O_2^-$ in methanol and ·OH in water under O_2 conditions, and (b) EPR spectra of MPA in methanol or in water under N_2 conditions.

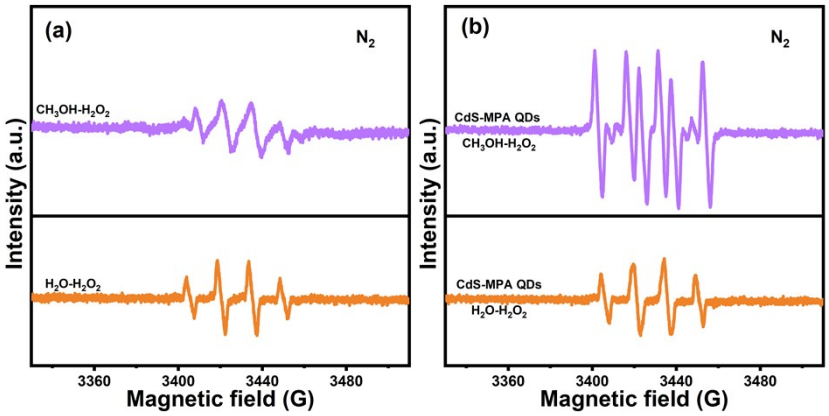

Fig. S7. DMPO spin-trapping EPR spectra for (a) $\cdot O_2^-$ in methanol and ·OH in water in the absence of a catalyst, and (b) $\cdot O_2^-$ in methanol and ·OH in water of CdS-MPA QDs.

References

1. 1. X. Xiang, B. Zhu, J. Zhang, C. Jiang, T. Chen, H. Yu, J. Yu and L. Wang, *Appl. Catal., B*, 2023, **324**, 122301.