


 Cite this: *Nanoscale*, 2025, **17**, 22260

Hole scavenger concentration dependent photoreduction pathway of nitrobenzene catalyzed by CdS quantum dots

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Hole scavengers are often employed in photocatalytic reactions catalyzed by semiconductors to efficiently extract photogenerated holes, thereby suppressing charge recombination and enhancing the overall catalytic activity. Beyond improving charge separation, the type of hole scavengers can also affect the activity, selectivity, and mechanism of the reaction. Interestingly, our findings in this work reveal that not only the identity but also the amount of hole scavenger plays a significant role, indicating the reaction pathway. Specifically, in nitrobenzene reduction catalyzed by CdS quantum dots (QDs), the concentration of hole scavenger Na₂SO₃ influences the reaction pathway and the final products: low concentrations (2–8 mM) favored the direct reduction pathway and yielded phenylhydroxylamine and aniline, while high concentrations (12–24 mM) favored an indirect (coupling) pathway and produced azoxybenzene. We hypothesized that SO₄^{•-} radicals formed at high concentrations of Na₂SO₃ in the presence of dissolved oxygen is responsible for this change in reduction pathway. The existence of SO₄^{•-} radicals was validated by Electron Spin Resonance spectroscopy. Quenching of SO₄^{•-} radicals using *tert*-butyl alcohol (TBA) reverted the reaction back to the direct reduction pathway even when a high concentration of Na₂SO₃ was added, confirming the critical role of SO₄^{•-}. Density functional theory calculations revealed that the SO₄^{•-} adsorbed onto the CdS surface abstracts hydrogen from the reaction intermediates, promoting the indirect coupling reaction. In addition, photoluminescence and femtosecond transient absorption studies showed that rapid hole trapping in CdS QDs occurred within 3–4 picoseconds after excitation, and Na₂SO₃ scavenged trapped holes at a timescale of tens of nanoseconds. These findings highlight the diverse functions of hole scavengers in photocatalysis. Their quantity and the species generated after hole scavenging can direct the reaction pathways and product selectivity.

 Received 21st July 2025,
 Accepted 11th September 2025

DOI: 10.1039/d5nr03085d

rsc.li/nanoscale

Introduction

Colloidal quantum dots (QDs) are known to be efficient photocatalysts by absorbing light of proper energy and generating excited charge carriers that drive a range of chemical reactions, such as water splitting,^{1–4} CO₂ reduction,^{5–10} and decomposition of environmental pollutants.^{11,12} In photo reduction reactions catalyzed by QDs or QD-based hybrid structures, photoexcited electrons in QDs are transferred from their con-

duction band to the reactants or other components in the hybrid structures, leaving holes in the valence band.¹³ To reduce the recombination of the photoexcited electrons with holes and prevent QDs from photooxidation, hole scavengers are usually added to the reaction systems. Hole scavenger molecules donate electrons to the holes, thereby making the photoexcited electrons more available for reaction and improving the overall catalytic efficiency and stability of the system.^{14,15}

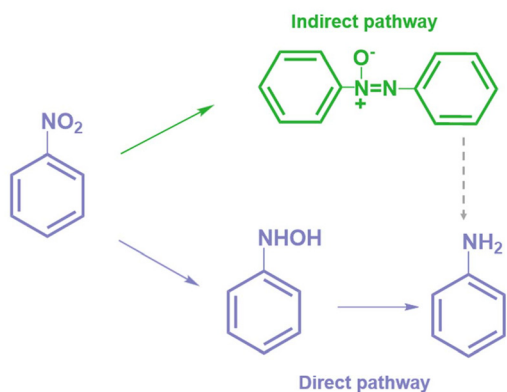
The chemical nature of the scavengers is a factor that affects the photocatalytic activity of QDs-catalyzed reactions.¹⁶ For example, Jin *et al.* reported that adding ascorbic acid to hybrid CdS/ZnS QD-Au nanoparticles led to significantly higher H₂ evolution rate compared to using methanol, Na₂S&Na₂SO₃, or triethanolamine as a hole scavenger. The improvement in H₂ evolution was ascribed to the acidic environment provided by ascorbic acid.¹⁷ Li *et al.* reported that the addition of an H₂S-saturated Na₂S&Na₂SO₃ solution to

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Scheme 1 Illustration of the reduction reaction of nitrobenzene.

hybrid CdS/PdS nanoparticles yielded a maximum H₂ production rate approximately 13.7 times higher than that achieved using triethanolamine, sodium ascorbate, methanol, or formic acid as hole scavengers, due to its higher ability in removing the holes accumulated on the surface of the catalysts.¹⁸ Hole scavengers have also been found to improve interfacial charge transfer in hybrid nanocrystal/molecular catalysts, potentially favoring photocatalytic reduction reactions.¹⁹ These reports show that the roles of hole scavengers are very complex and vary in different reaction systems.

In our recent work, we observed that in the photo-reduction of nitrobenzene catalyzed by CdS QDs, the type of hole scavengers used not only significantly influenced reaction rates, but also affected the reaction pathways and final products. When methanol, 3-mercaptopropionic acid, ascorbic acid, or ammonium formate were employed as the hole scavenger, nitrobenzene followed a “direct” reaction pathway, producing phenylhydroxylamine and aniline. However, when sodium sulfite (Na₂SO₃) was used as a hole scavenger, nitrobenzene followed the “indirect” or “coupling” reaction pathway, producing azoxybenzene.²⁰ The reaction pathway is illustrated in Scheme 1.^{21–24} To explain why Na₂SO₃ changes the selectivity of the reaction, we performed systematic studies using different concentrations (2–24 mM) of Na₂SO₃ in this work. Surprisingly, we observed that at low concentrations of Na₂SO₃ (2–8 mM), the reaction followed the direct reduction pathway; while at high Na₂SO₃ concentrations (12–24 mM), coupling product azoxybenzene was obtained. We showed that after scavenging the holes on CdS, SO₃²⁻ turned into SO₄^{•-} radicals under certain conditions, and the SO₄^{•-} on the CdS surface promoted the indirect reaction pathway and led to different reaction products.

Results and discussion

The absorption spectra of CdS QDs in water after ligand exchange with MPA exhibit features similar to previously reported spectra of CdS QDs with the first excitonic peak at 455 nm (Fig. S1a).²⁰ Furthermore, the CdS QDs were mixed with 2, 4, 8, 12, 16, and 24 mM Na₂SO₃. The absorption spectra

of the mixtures are almost identical to that of the QDs alone, suggesting that the addition of Na₂SO₃ does not alter the electronic structure or bandgap of the CdS QDs. The transmission electron microscopy (TEM) image (Fig. S1b) reveals that the QDs have an average size of approximately 6 nm, which aligns with the size calculated from the first excitonic peak.²⁵ The CdS QDs were transferred into water and used for the photocatalytic reaction of nitrobenzene following a published procedure.²⁰ Briefly, 0.35 μM CdS QDs was mixed with 2.5 mM nitrobenzene and varying amounts of Na₂SO₃ from 2–24 mM in D₂O : CD₃OD (v : v%) = 4 : 1 solvent, buffered to 9–11 pH with 0.2 M tri buffer. The estimated molar ratio of CdS : Na₂SO₃ ranges from 1 : 5.7 × 10³ to 1 : 6.9 × 10⁴. The reaction solution was purged with house N₂ gas unless otherwise noted. House N₂ gas was produced from 99.999% pure liquid N₂ but may become contaminated with air during distribution through the piping system. The cuvette was then excited with a 450–460 nm LED with a photon flux of 2.2 × 10¹⁷ photons per s per cm² for the desired reaction time and the product was analyzed by ¹H-NMR without further purification. The reference NMR spectra of nitrobenzene, nitrobenzene with CdS QDs, phenylhydroxylamine, azoxybenzene, and aniline are shown in Fig. S2. As shown in the NMR spectra of the reaction product when 16 mM Na₂SO₃ was added (Fig. 1a), the azoxybenzene (Ph-N=N(O)-Ph) peaks appeared at 7.14–7.66 ppm between 2 and 6 hours of reaction. This suggests that the reduction of nitrobenzene (Ph-NO₂) catalyzed by CdS QDs follows the “indirect” reaction pathway under this condition, consistent with our previous report. Further increasing the Na₂SO₃ concentration to 24 mM led to stronger azoxybenzene peaks persisting throughout the 6-hour reaction (Fig. S3d). Interestingly, when a low concentration of 2 mM Na₂SO₃ was added (Fig. 1b), phenylhydroxylamine (PHA) peaks appeared at 6.85–6.93 and 7.14–7.25 ppm after 1 and 2 hours of reaction. After 4 and 6 hours of reaction, additional aniline (Ph-NH₂) peaks appeared at 6.64–6.72 ppm and 7.02–7.09 ppm. These are the products of the “direct” reduction pathway. Similar results were observed for 4 mM of Na₂SO₃ (Fig. S3a) except that aniline peaks began to appear at 2 h and became more pronounced at 4 and 6 h. When 8 mM Na₂SO₃ was added (Fig. S3b), phenylhydroxylamine peaks appeared at 2 and 4 hours, and aniline peaks appeared at 6 hours. However, when Na₂SO₃ concentration was further increased to 12 mM, product from the indirect pathway, azoxybenzene, was observed at 6 hours (Fig. S3c). Thus, we conclude that the nitrobenzene reduction pathway is dependent on the hole scavenger Na₂SO₃ concentration, with the transition range falling between 8 mM and 12 mM. Below this transition range, the production of aniline is faster when increasing Na₂SO₃ concentration from 2 to 4 mM. Within the transition range, slower formation of aniline is observed at 8 mM Na₂SO₃ and the product switched to azoxybenzene at 12 mM Na₂SO₃. Above the transition concentration, a higher rate of azoxybenzene formation is observed when Na₂SO₃ concentration increases to 16 mM and 24 mM. These results show that the amount of hole scavengers can affect the reaction pathways and rates of photocatalytic reactions.



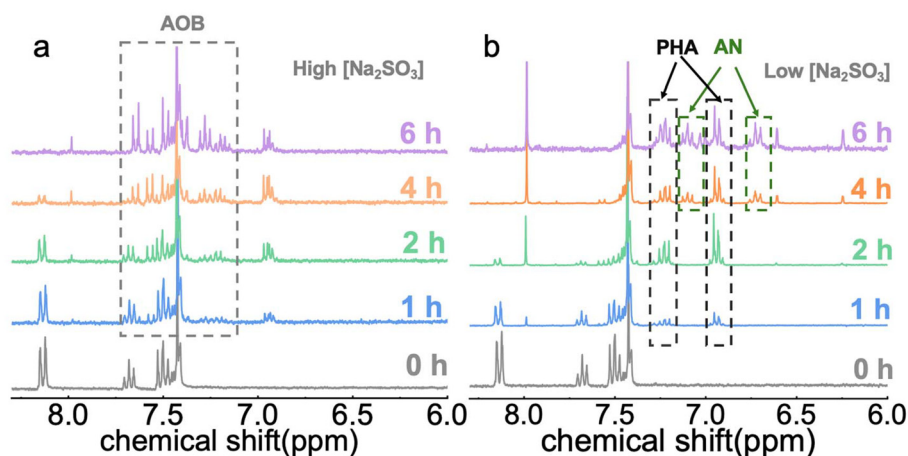
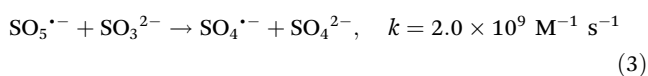
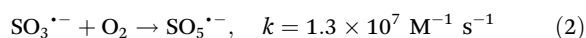
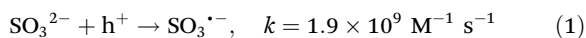


Fig. 1 ^1H -NMR results of the products during photocatalysis of nitrobenzene using CdS QDs at 0 h, 1 h, 2 h, 4 h, and 6 h with (a) high (16 mM) concentration Na_2SO_3 , (b) low (2 mM) concentration Na_2SO_3 . The reaction solutions were purged with house N_2 . AOB: azoxybenzene; PHA: phenylhydroxylamine; AN: aniline.

Based on the photocatalytic results, we hypothesize that sulfite ions (SO_3^{2-}) and their product after donating electrons to the catalysts may be involved in the reaction. As hole scavengers, SO_3^{2-} can be oxidized by the photogenerated holes in CdS QDs to form sulfite radicals ($\text{SO}_3^{\cdot-}$) via a hole-mediated oxidation process (eqn (1)), as illustrated in Fig. 2a. $\text{SO}_3^{\cdot-}$ radicals can then react with dissolved oxygen to form $\text{SO}_5^{\cdot-}$ radicals (eqn (2)); subsequently, $\text{SO}_5^{\cdot-}$ can be reduced by excess SO_3^{2-} to form $\text{SO}_4^{\cdot-}$ radicals (eqn (3)).^{26,27}



The rate constants (k) in eqn (1)–(3) are taken from Rangelova *et al.*²⁸ $\text{SO}_4^{\cdot-}$ radicals are known to abstract $-\text{H}$ from a variety of organic molecules.^{29,30} Presumably, its participation in the nitrobenzene reduction reaction could affect the reduction pathway. Note that hydroxyl radicals have also been reported to affect the reaction pathway³¹ and we do not rule out their participation in this reaction. Our observations clearly showed the importance of sulfur-containing species, and thus we focus on those in this work. To examine whether $\text{SO}_4^{\cdot-}$ formed in the reaction solution, Electron Spin Resonance (ESR) measurements of sulfur-containing radicals were performed using 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) as the spin-trap.³² The samples were prepared by mixing DMPO, CdS QDs, and 2 mM or 16 mM Na_2SO_3 in air using water as the solvent, and were illuminated under 400 nm light during the ESR measurements. The sample with 2 mM Na_2SO_3 has a very weak signal that is hard to identify. In comparison, the one with 16 mM Na_2SO_3 exhibited a clear DMPO- $\text{SO}_4^{\cdot-}$ adduct signal (Fig. 2b, bottom two spectra, and the fitted spectra are shown in Fig. S4), proving the generation

of $\text{SO}_4^{\cdot-}$ under this condition.³³ Since the formation of $\text{SO}_4^{\cdot-}$ requires O_2 , we further tested if $\text{SO}_4^{\cdot-}$ can still be detected by ESR if O_2 is excluded.²⁷ To do that, N_2 from the gas cylinder (Airgas, >99.999% pure) was flowing through the solution before and during the ESR measurements. Both 2 mM and 16 mM Na_2SO_3 -CdS QDs samples show a strong DMPO- $\text{SO}_3^{\cdot-}$ adduct signal³⁴ (Fig. 2b, top two spectra), confirming that the holes in photoexcited CdS QDs were scavenged by SO_3^{2-} , converting it to $\text{SO}_3^{\cdot-}$ (eqn (1)). Moreover, due to a lack of O_2 , eqn (2) and (3) did not proceed, thus $\text{SO}_4^{\cdot-}$ was not detected. Note that an overall weaker ESR signal for the DMPO- $\text{SO}_4^{\cdot-}$ adduct, compared to those for the DMPO- $\text{SO}_3^{\cdot-}$, is likely due to its rapid conversion to the DMPO-OH adduct, not reflecting the concentrations of the radicals.³⁵

The ESR results suggest that the purging gas affected $\text{SO}_4^{\cdot-}$ radical formation and therefore could have an impact on the nitrobenzene reduction pathway. Although all the reaction mixtures were purged with house N_2 for 5 minutes (details in SI section 1.3) prior to conducting the photocatalytic reactions presented in Fig. 1 and S3, we assume that there is still dissolved O_2 in the reaction solution due to the air in house N_2 , leading to the formation of $\text{SO}_4^{\cdot-}$. To test this assumption, we investigated if different purging gases would alter the reaction pathway of nitrobenzene reduction at a high concentration of Na_2SO_3 above the transition range, *i.e.*, 16 mM, over a 4-hour reaction. The influence of protective gas on nitrobenzene reduction product has also been reported in previous studies.³⁶ We found that under purging with house N_2 or air, the reaction follows an “indirect” pathway, as evident by the appearance of azoxybenzene peaks in the NMR spectra in Fig. 2c. However, when the reaction solution was purged with N_2 or Ar from the gas cylinder, the reaction shifts to a “direct” pathway, resulting in the formation of phenylhydroxylamine and aniline. This study confirms that the dissolved O_2 influences the reaction pathway, likely due to the formation of $\text{SO}_4^{\cdot-}$.^{27,37}



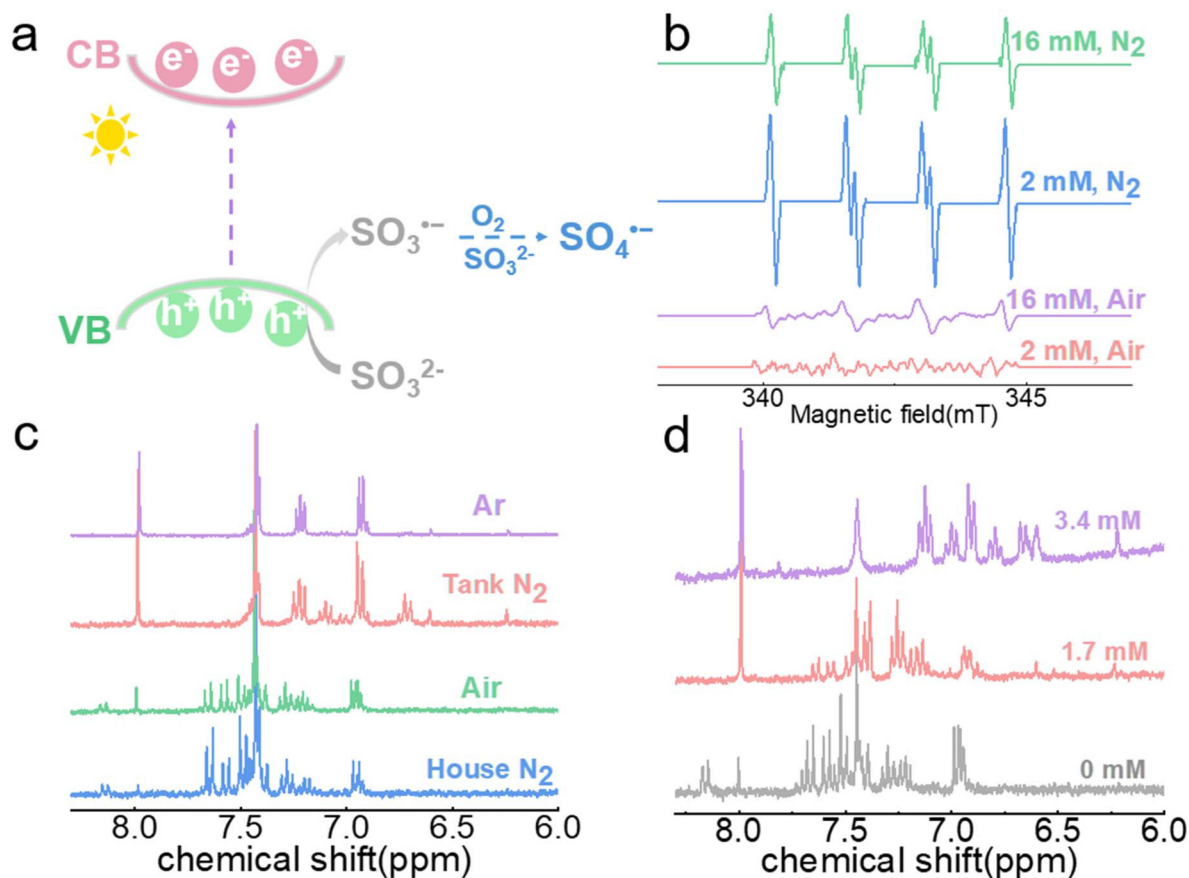


Fig. 2 (a) Schematic illustration of the potential transformation of SO_3^{2-} . (b) ESR spectra of DMPO (1.12 M), CdS QDs (0.35 μM), and Na_2SO_3 under 400 nm light taken in varying conditions: N_2 flow, 2 mM Na_2SO_3 (blue); N_2 flow, 16 mM Na_2SO_3 (green); air, 2 mM Na_2SO_3 (pink); air, 16 mM Na_2SO_3 (purple). (c) NMR spectra of the products from nitrobenzene photocatalysis using CdS QDs and 16 mM Na_2SO_3 for 4 h. The reaction solution was purged with gases: house N_2 (blue), air (green), tank N_2 (pink), and tank argon (purple). (d) NMR spectra of the products from nitrobenzene photocatalysis using CdS QDs and 16 mM Na_2SO_3 for 4 h with different concentrations of *tert*-butanol purged with house N_2 .

To further explore if $\text{SO}_4^{\bullet-}$ radicals are truly responsible for the reaction pathway, quenching experiments were carried out. Since the $\text{SO}_4^{\bullet-}$ radical is very sensitive to α -H, the rate constant (k) for its reaction with *tert*-butyl alcohol (TBA) with $\text{SO}_4^{\bullet-}$ is high ($k_{\text{TBA},\text{SO}_4^{\bullet-}} = 4.0 - 9.1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$), making TBA an effective quencher for $\text{SO}_4^{\bullet-}$ radicals.³⁸ The quenching experiments were performed by adding increasing amounts of TBA (1.7 mM, and 3.4 mM) to the photocatalytic reaction mixture with 16 mM Na_2SO_3 over a 4-hour reaction period. As observed in Fig. 2d, the addition of TBA leads to different reaction products. Without TBA, the NMR spectrum resembles that of azoxybenzene, indicating the “indirect” pathway. At 1.7 mM TBA, the spectrum changed slightly with lower intensity peaks from azoxybenzene and additional peaks at 6.85–6.93 and 7.14–7.25 ppm from phenylhydroxylamine, suggesting that both “indirect” and “direct” reactions happened; while the addition of 3.4 mM TBA switched the reaction to the “direct pathway” and produced phenylhydroxylamine and aniline. We attribute this switching to the effective quenching of $\text{SO}_4^{\bullet-}$ radicals at high concentrations of TBA. This result also demonstrated that $\text{SO}_4^{\bullet-}$ is likely the key

radical responsible for altering the reaction pathway in the CdS QDs– Na_2SO_3 system. The reaction product, pathway, and related reaction conditions are summarized in Table 1.

Hole scavengers have been reported to change the exciton dynamics and charge carrier transfer from QDs to other species in the catalytic reaction system through optical spectroscopy.^{39–42} For example, Gebre *et al.* showed that the addition of triethylamine as a hole scavenger facilitated the electron transfer rate between Cd_3P_2 QDs and *fac*- $\text{Re}(4,4'\text{-R}_2\text{-bpy})(\text{CO})_3\text{Cl}$ (where bpy = bipyridine and R = COOH) (ReC0A).¹⁹ In our work, steady-state and time-resolved photoluminescence (PL) and transient absorption (TA) spectroscopy are used to examine the interaction of Na_2SO_3 with the CdS QDs. The PL spectrum of CdS QDs has two distinct bands that are centered at 475 nm and 650 nm (Fig. 3a). The peak at 475 nm is attributed to the band-edge emission, while the broad red-shifted peak at 650 nm is assigned to trap-state emission arising from the recombination between excited electrons/holes with the holes/electrons trapped by surface defects.^{43,44} After the addition of 2 mM Na_2SO_3 , the trap-state emission is significantly reduced. Moreover, PL of



Table 1 Reaction pathways under different conditions

Purged gas	Na ₂ SO ₃ (mM)	SO ₄ ²⁻ scavenger TBA (mM)	Reaction time (hr)	Product(s)	Reaction pathway
House N ₂	2	0	6	PHA/Aniline	Direct
House N ₂	4	0	6	PHA/Aniline	Direct
House N ₂	8	0	6	PHA/Aniline	Direct
House N ₂	12	0	6	Azoxybenzene	Indirect
House N ₂	16	0	6	Azoxybenzene	Indirect
House N ₂	24	0	6	Azoxybenzene	Indirect
Air	16	0	4	Azoxybenzene	Indirect
Tank N ₂	16	0	4	PHA/Aniline	Direct
Tank Ar	16	0	4	PHA/Aniline (trace)	Direct
House N ₂	16	1.7	4	PHA/Azoxybenzene	Mixed
House N ₂	16	3.4	4	PHA/Aniline	Direct

PHA represents phenylhydroxylamine.

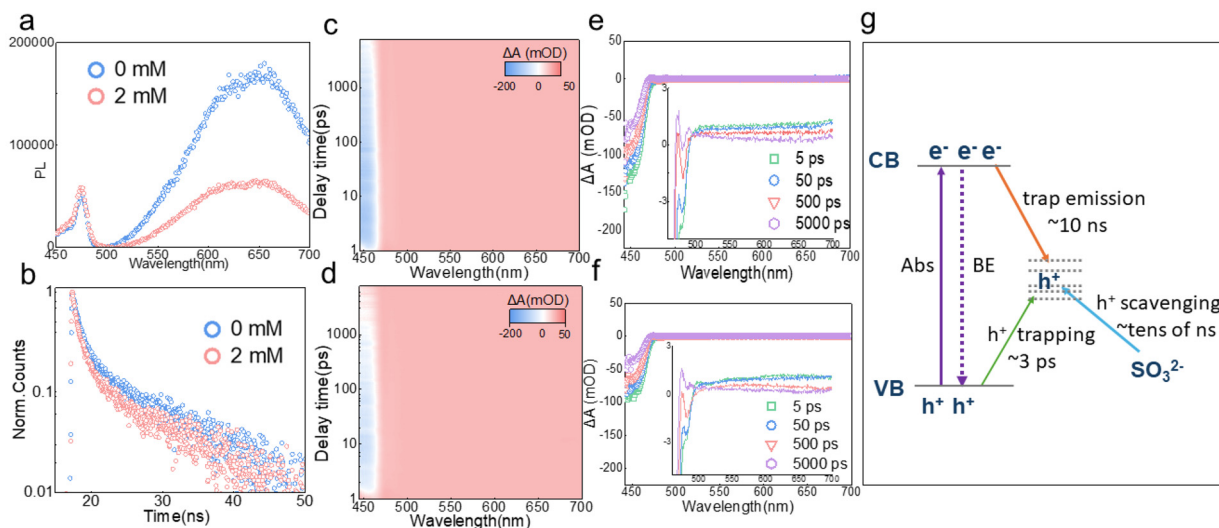


Fig. 3 (a) Photoluminescence spectra of CdS QDs with 0 or 2 mM of Na₂SO₃. (b) PL decays CdS QDs with 0 or 2 mM of Na₂SO₃ measured at 650 nm. Pseudo color TA maps of (c) CdS QDs and (d) CdS QDs with 2 mM Na₂SO₃. ΔA spectra at different time delays of (e) CdS QDs and (f) CdS QDs with 2 mM Na₂SO₃ (inset: magnified ΔA spectra from 460 nm to 700 nm). (g) Schematic illustration of the photophysical processes and timescales.

the QDs with 2 mM Na₂SO₃ measured at 650 nm showed a faster decay (weighted average lifetime 8.2 ns) compared to that of the QDs alone (weighted average lifetime of 10.5 ns), suggesting a dynamic quenching process where SO₃²⁻ ions donate electrons to the CdS QDs (Fig. 3b). Details of the lifetime determination are available in the SI. We do not rule out the possibility for SO₃²⁻ to passivate the QD surface and reduce the number of traps. Increasing the Na₂SO₃ concentration from 4 mM to 24 mM caused slight variations in both the PL intensity and decays at 650 nm, suggesting the quenching effect reaches saturation at 2 mM Na₂SO₃ (Fig. S5a). In contrast, the PL intensity and decays of the band-edge emission peaked at 475 nm only varied slightly between 0 to 24 mM Na₂SO₃, indicating that the quenching process of trap-state emission did not have much influence on the band-edge exciton recombination. The results from TA spectroscopy further support this conclusion, as detailed below.

TA spectroscopic measurements were carried out on CdS QDs mixed with varying concentrations of Na₂SO₃. Fig. 3c–f presents the two-dimensional pseudo-color TA map and ΔA spectra of CdS QDs with 0 and 2 mM Na₂SO₃. A distinct negative signal (\sim 450 nm) from ground-state exciton bleaching was observed in both samples.⁴⁵ In addition, a weak broad positive signal appears at 500–700 nm with a rise time of 3–4 ps. This signal is attributed to the photoinduced absorption of the holes trapped to the surface according to previous studies.^{46,50} The exciton bleaching kinetics of the QDs at 450 nm with 0–24 mM Na₂SO₃ are similar to each other (Fig. S8a). This result shows that a hole scavenger, Na₂SO₃, does not change the direct exciton recombination,^{49,50} consistent with that revealed by the PL decays of the QD samples at 475 nm. The hole absorption decay kinetics at 600 nm were also similar without and with Na₂SO₃ (Fig. S8b). There is a slight variation (up to 5%) in the ΔA values at 5 ps delay time for the band-edge exciton bleach signal at 452 nm and for the hole absorp-



tion signal integrated from 580 to 620 nm when Na_2SO_3 was added (Fig. S9). The addition of hole scavengers did not significantly change the TA signal or kinetics, possibly because of the following reasons. One, the CdS QDs are capped with 3-mercaptopropionic acid. The $-\text{COOH}$ groups are deprotonated under the reaction pH of 9–11, leaving the QD surface negatively charged. Therefore, the QDs could have repelled SO_3^{2-} due to electrostatic interactions, making them harder to adsorb onto the QD surface to scavenge the holes. Although the concentration of SO_3^{2-} is much higher than that of the QDs in the solution ($[\text{SO}_3^{2-}]:[\text{QD}] = 5.7 \times 10^3 - 6.9 \times 10^4:1$), the SO_3^{2-} ions on the QD surface will only be a portion. Thus, the number of holes scavenged may be too low to cause a detectable change in the overall TA signal ($\Delta A \sim 2\text{--}3$ mOD for the hole absorption band), but still yield enough sulfur-containing radicals to affect the nitrobenzene reduction. Two, it is possible that the $\text{SO}_3^{\cdot-}$ radicals stay attached to the QD surface instead of diffusing away after scavenging the holes. The assumption of the adsorption of sulfur-containing radicals (such as $\text{SO}_3^{\cdot-}$ and $\text{SO}_4^{\cdot-}$) on the QD surface is logical and reasonable, considering their role in dictating the reaction pathway of nitrobenzene reduction. Since photoreduction of nitrobenzene happens on the CdS QD surface, it is necessary for these radicals to stay on the surface to influence the reaction pathway. This assumption is further supported by the Density Functional Theory (DFT) results shown below. Third, the hole absorption signal probed by TA is from the trapped holes on the CdS QD surface as discussed above. The rise of the hole absorption signal indicates that hole trapping is fast, on the time scale of 2–3 ps. On the other hand, when 2 mM SO_3^{2-} was added to the solution, the lifetime of the trap-state emission ($\lambda_{\text{max}} \sim 650$ nm, Fig. S5) is reduced from 10.5 ns to 8.2 ns (Table S1). Assuming this reduction is because of SO_3^{2-}

scavenging the trapped holes (illustrated in Fig. 3g), we estimated the rate of hole scavenging to be $2.7 \times 10^7 \text{ s}^{-1}$, which means that hole scavenging takes tens of ns (calculation details shown in SI). This time scale is much longer than that probed by TA spectroscopy (sub-ps to ~ 8 ns); therefore, on top of a likely small number of scavengers on the surface, there was no clear change in the TA signal of the trapped holes within the time of the TA measurements.

To better understand the role of surface-adsorbed $\text{SO}_4^{\cdot-}$ in modulating the reaction pathway of nitrobenzene on CdS QDs, we conducted density functional theory (DFT) calculations focusing on the key hydrogenation step from $^*\text{PhN}$ to $^*\text{PhNH}$ (see details of these calculations in DFT methods). As shown in Fig. S11, this intermediate transformation serves as a critical branch point between the direct reduction pathway (leading to aniline) and the indirect coupling pathway (leading to azoxybenzene).²⁴ We first examined the adsorption geometries of $^*\text{PhN}$ on the CdS(111) surface. Two distinct adsorption modes were identified: a monodentate configuration in which the nitrogen of $^*\text{PhN}$ binds directly to surface sulfur (Fig. 4a), and a bidentate configuration involving dual interactions (Fig. 4d). The monodentate mode was found to be thermodynamically more stable, with an adsorption energy (ΔE_{ads}) of -2.17 eV, compared to -0.83 eV for the bidentate structure. This suggests that the monodentate configuration is likely the dominant adsorption state under reaction conditions. The reaction energy for the hydrogenation of $^*\text{PhN}$ to form $^*\text{PhNH}$ (ΔE_{PhNH}) was next evaluated for the two configurations. In the absence of $^*\text{SO}_4^{\cdot-}$, hydrogenation of $^*\text{PhN}$ was found to be favorable for both configurations, but more so for the bidentate mode (Fig. 4d, $\Delta E_{\text{PhNH}} = -2.19$ eV) than for the monodentate one (Fig. 4b, $\Delta E_{\text{PhNH}} = -1.40$ eV). This indicates that while the monodentate structure dominates the surface population,

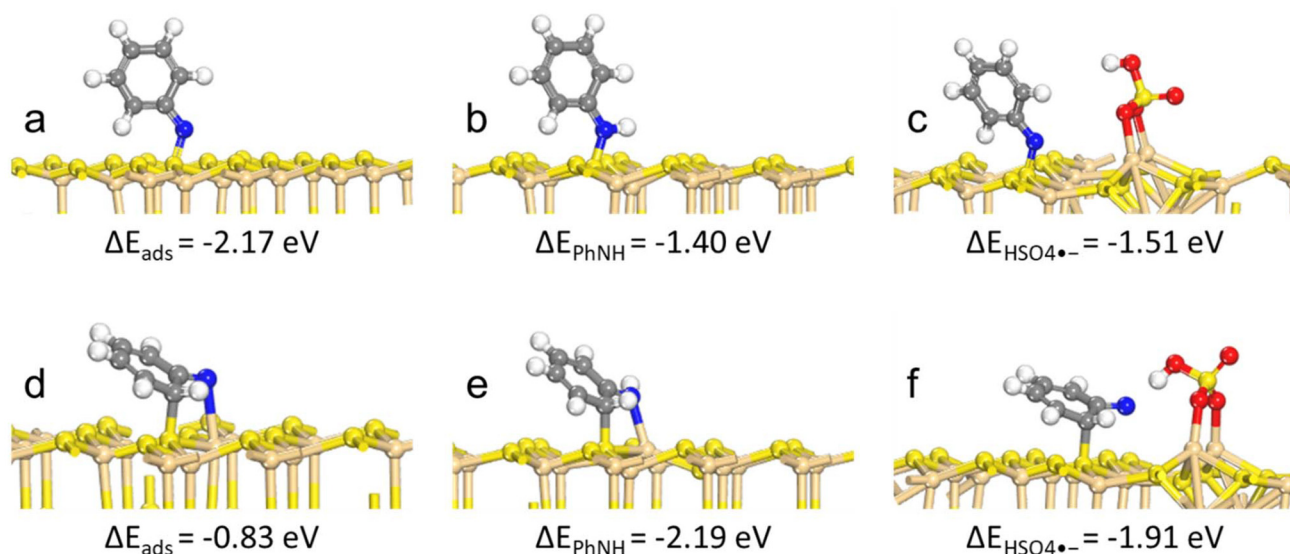


Fig. 4 (a) and (d) Adsorption configurations for $^*\text{PhN}$ on the CdS(111) surface. (b) and (e) Hydrogenation of $^*\text{PhN}$ to form $^*\text{PhNH}$ for the two configurations on the surface. (c) and (f) Hydrogenation of $^*\text{SO}_4^{\cdot-}$ to form $^*\text{HSO}_4^{\cdot-}$ for the two configurations on the surface. H, white; C, gray; N, blue; O, red; S, yellow; Cd, gold.



the bidentate species may serve as a more reactive intermediate for reduction.

We then turn to the scenario involving the presence of $^*SO_4^{\cdot-}$. For the monodentate configuration, the reaction energy for the hydrogenation of $^*SO_4^{\cdot-}$ to form $^*HSO_4^{\cdot-}$ ($\Delta E_{HSO_4^{\cdot-}}$) was found to be -1.51 eV, suggesting that $^*SO_4^{\cdot-}$ can effectively abstract hydrogen from *PhNH (Fig. 4c). A similar hydrogenation abstraction could also occur for the bidentate configuration (Fig. 4f). Here, the hydrogen bonding between $^*HSO_4^{\cdot-}$ and *PhN results in an even more favorable $\Delta E_{HSO_4^{\cdot-}}$ of -1.91 eV. Although $\Delta E_{HSO_4^{\cdot-}}$ is not more favorable than ΔE_{PhNH} in the bidentate configuration, statistically a considerable fraction of surface hydrogen can be consumed by $^*SO_4^{\cdot-}$, especially at elevated $^*SO_4^{\cdot-}$ concentrations. These results support a mechanism governed by competitive hydrogenation: in the presence of $^*SO_4^{\cdot-}$, surface hydrogen is preferentially consumed by $^*SO_4^{\cdot-}$ rather than by *PhN intermediate. This competition suppresses direct hydrogenation of *PhN to form *PhNH and instead facilitates an indirect coupling pathway. Such a shift aligns with the experimentally observed change in product distribution at higher Na_2SO_3 concentrations. Overall, the DFT calculations offer theoretical support for $SO_4^{\cdot-}$ -mediated modulation of photocatalytic selectivity.

Conclusions

In conclusion, we have shown that the concentration of hole scavenger Na_2SO_3 has a significant impact in the reaction pathways and final products of nitrobenzene reduction using CdS QDs as the catalyst. In particular, we have identified a transition from a direct reduction to indirect coupling when the concentration of Na_2SO_3 increases, even though it is always in excess compared to that of the CdS QDs. ESR spectroscopy and control experiments proved the existence of $SO_4^{\cdot-}$ radicals and revealed its critical impact in changing the reaction pathway. Steady-state and time-resolved PL, alongside fs-TA suggested that SO_3^{2-} scavenged the holes trapped on the CdS surface, turned into $SO_3^{\cdot-}$ and eventually became $SO_4^{\cdot-}$ in the presence of excess SO_3^{2-} and dissolved O_2 . DFT calculations provide theoretical support for the role of $SO_4^{\cdot-}$ in modulating photocatalytic selectivity. This study highlights the importance of the quantity of hole scavengers in photocatalytic reactions, where they are typically used in excess without careful consideration of the quantity. Our results indicate that systematically varying the scavenger concentration can influence the formation of radical intermediates during photocatalysis. Such an effect may also occur in other photocatalytic systems with similar hole dynamics and radical formation pathways.

Materials and methods

Chemicals

Sulfur powder (S, 325 mesh, 99.5%), azoxybenzene (AOB, 98%+), and benzyltrimethylammonia hydroxide 40% w/w in

methanol (Triton B) were obtained from Alfa Aesar. Methanol- d_4 (CD_3OD , 99.8%) and deuterium dioxide (D_2O , 99.9%) were purchased from Cambridge Isotope Laboratory. 2-Amino-2-hydroxymethyl-propane-1,3-diol (tris buffer, R99.8%) was purchased from Thermo Fisher Scientific. 3-Mercaptopropionic acid (3-MPA, 99%+) was purchased from Acros Organics. Nitrobenzene (NB, R99.0%), cadmium oxide (CdO, R99.99%), oleic acid (OA, 90%), diethyl ether (99.0%), sodium sulfite (Na_2SO_3 , 98%), ethyl acetate (99.7%), 1-octadecene (ODE, 99%), *N*-phenylhydroxylamine (PHA, R95.0%), aniline (R99.5%), acetone (HPLC, R99.9%), and ethanol (99.8%) were purchased from Sigma-Aldrich. 5,5-Dimethyl-1-pyrroline *N*-oxide (DMPO) was purchased from Dojindo. Nitrogen (N_2) and argon (Ar) gases were purchased from Airgas, each with a purity of 99.999%. All chemicals were used without further purification.

Photocatalytic experiments

CdS QDs were prepared using a slightly modified procedure from the previous work and the details are included in the SI.¹⁸ A total of 3 mL solution was prepared for each sample, consisting of 0.2 M (72.6 mg) tris buffer, 0/2/4/8/12/16/24 mM sodium sulfite, 2.5 mM nitrobenzene, and 0.35 μ M CdS QDs in $D_2O:CD_3OD$ ($v:v = 4:1$) solvent mixture to form a homogenous light-yellow solution. The solution was then transferred into a quartz cuvette, sealed with septa. Then, each solution was purged with protective gas (house N_2 , and N_2 or Ar from Airgas) for 5 minutes. Photocatalytic reduction reactions were carried out using a blue LED (ABI, 12 W, PAR38, 450–460 nm) for illumination over specified reaction times. Finally, a 0.6 mL sample was taken from each reaction solution without further purification and measured with NMR.

Spectroscopic instruments and characterization

Absorption spectra of the QDs were collected by an Agilent Technologies Cary-60 UV-vis spectrometer. Transmission electron microscopy (TEM) images were taken using a TechnaiT-12 microscope. 1H NMR spectra for all samples were acquired using a Bruker Avance III 300 MHz NMR spectrometer. Fluorescence was tested by a Horiba FluoroMax Plus fluorometer. PL decay was measured using the Mini-tau model of Edinburgh Instruments with a 405 nm pulsed laser, and the emission was collected between 425–475 nm and 625–675 nm. X-ray diffraction (XRD) patterns of the CdS QDs were recorded on a Bruker D2 diffractometer with Bragg-Brentano θ - 2θ geometry (30 kV and 10 mA) by using a nickel filter with a Cu $K\alpha$ radiation source.

ESR experiments

The electron spin resonance (ESR) measurements were performed at room temperature utilizing a Bruker EMXnano spectrometer equipped with an X-band frequency. The parameters for ESR tests are as follows: 9.62–9.64 GHz microwave frequency, 0.6310 mW microwave power, 9.27 s sweep time, 0.6 Gauss modulation amplitude, and 100 kHz modulation frequency. For ESR measurements, a total sample volume of



20 μL was prepared, with DMPO (1.12 M), CdS QDs (0.35 μM), and 2 mM or 16 mM Na_2SO_3 , with ultrapure water as the solvent. The sample solutions were injected into a 0.8 mm glass capillary using a volumetric syringe, and the capillary was then placed into a 5 mm gastight Suprasil ESR tube from Wilmad LabGlass. Some of the samples were degassed for 5 minutes with N_2 prior to measurements. During ESR measurements, samples were illuminated using a 100 W mercury arc lamp equipped with a mechanical shutter and a 455 nm long-pass filter, which was connected *via* a fiber optic to the spectrometer. Spin adducts were identified by comparison of hyperfine splitting values to literature.³³ Hyperfine splitting values were extracted from experimental spectra by least squares fit using the EasySpin program for Matlab.⁵¹ Details of the fitting and simulation process are described in the SI.

Femtosecond transient absorption (TA) measurements

For femtosecond TA (fsTA) measurements, 0.6 mL of solution containing 0.35 μM CdS QDs and 0/2/4/8/12/16/24 mM of Na_2SO_3 were prepared in D_2O solvent. The samples were transferred to quartz cells with a path length of 2 mm. The fsTA setup was based on Helios Fire (Ultrafast Systems) coupled to a femtosecond laser system (Coherent). The system consists of an AStrella one-box Ti: sapphire amplifier. The pulse width was 35 fs full width at half maximum at 800 nm with an energy of 5.0 mJ per pulse at a 1 kHz repetition rate. The output of the amplifier was divided by beam splitters. One beam (48% of the total power) was used as the input for an OPerA Solo optical parametric amplifier (Coherent), which provided a pump pulse in the UV-visible (UV-vis) region. The energy of the pump beam was adjusted to 0.5–1.0 μJ by a neutral density filter. Another beam (2% of the total power) was used to generate white light continuum probe pulses in the Helios spectrometer. Samples were scanned at 400 delay time points, and the integration time was set to 0.2 s. During the measurements, samples were pseudo-randomly translated to avoid photodegradation by using a translating sample holder (Ultrafast Systems). A 1024-pixel CMOS sensor was used for detection. The raw data were processed by background subtraction and chirp correction using the Surface Xplore software (Ultrafast Systems).

DFT calculations

Spin-polarized DFT calculations were performed using the Vienna *ab initio* simulation package (VASP).^{47,48} The electron exchange–correlation was represented by the functional of Perdew, Burke, and Ernzerhof (PBE) of generalized gradient approximation (GGA).⁴⁹ The ion–electron interaction was described using the projector-augmented wave (PAW) method.⁵⁰ The plane-wave cutoff was set to 400 eV, and a conjugate gradient method was applied to relax the geometry until the interatomic forces were less than 0.025 eV \AA^{-1} . The Brillouin zone was sampled using a $3 \times 3 \times 1$ Monkhorst–Pack *k*-point mesh. The experimental lattice parameter from XRD measurement (Fig. S10) of 5.91 \AA was used for CdS, and the CdS(111) surface was modeled using a 4×4 supercell with

three atomic layers. The top two atomic layers, including adsorbates, were allowed to relax, while the bottom one atomic layer was fixed during optimization. Vacuum space in the *z* direction was set to be 20 \AA to avoid unphysical interactions.

The adsorption energy of *PhN was calculated using the equation $\Delta E = E_{\text{slab+PhN}} - E_{\text{slab}} - E_{\text{PhN}}$, where $E_{\text{slab+PhN}}$, E_{slab} , and E_{PhN} represent the energies of the CdS slab with adsorbed PhN, the clean CdS slab, and the isolated PhN intermediate, respectively. The reaction energy for the hydrogenation of *PhN was determined using $\Delta E = E_{\text{slab+PhNH}} - E_{\text{slab+PhN}} - 1/2E_{\text{H}_2}$, where $E_{\text{slab+PhNH}}$ and $E_{\text{slab+PhN}}$ are the energies of the CdS slab with adsorbed PhNH and PhN, respectively. Similarly, the reaction energy for the hydrogenation of * $\text{SO}_4^{\cdot-}$ was calculated using $\Delta E = E_{\text{slab+HSO}_4^-} - E_{\text{slab+SO}_4^{\cdot-}} - 1/2E_{\text{H}_2}$, where $E_{\text{slab+HSO}_4^-}$ and $E_{\text{slab+SO}_4^{\cdot-}}$ correspond to the energies of the CdS slab with adsorbed HSO_4^- and $\text{SO}_4^{\cdot-}$, respectively.

We note that the present DFT calculations are simplified and do not capture the full complexity of the experimental system. First, the CdS(111) surface was considered in the models because our XRD data showed that the (111) facet was the dominant exposed surface. Nevertheless, other surface facets may also be present in the experimentally obtained CdS QDs and could influence adsorption configurations and reaction energetics. Second, although we analyzed the adsorption configurations of *PhN in detail, we did not perform a systematic analysis of the adsorption geometries of * $\text{SO}_4^{\cdot-}$ radicals, which may affect the accuracy of the predicted competitive hydrogenation mechanism. Third, the CdS QDs used in experiments are capped with 3-mercaptopropionic acid (3-MPA), which could modify surface energetics and adsorption behaviors. These ligands were not included in the current calculations for computational simplicity. Future work incorporating multiple surface facets, * $\text{SO}_4^{\cdot-}$ adsorption configurations, and explicit ligand effects will provide a more comprehensive understanding of the photocatalytic mechanism.

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Conflicts of interest

The authors declare no competing financial interest.

Data availability

All data generated in this study, including the raw data from DFT calculations and experiments as well as the data required to reproduce the results, will be shared. The data will be deposited in the open-access repository Figshare and made publicly available immediately after the publication of this work.



Supplementary information: experimental details, additional NMR spectra, UV-vis absorption, TEM, ESR, steady-state and time-resolved PL, TA, and XRD (PDF). See DOI: <https://doi.org/10.1039/d5nr03085d>.

Acknowledgements

This work was partially supported by the donors of ACS Petroleum Research Fund under Doctoral New Investigator Grant 67453-DNI6. G. H. served as Principal Investigator on ACS PRF 67453-DNI6 that provided support for C. B. This research used resources of the National Energy Research Scientific Computing Center, a DOE Office of Science User Facility supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231 using NERSC award BES-ERCAP0031261.

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