Inorganic ligands-mediated hole attraction and surface structural reorganization in InP/ZnS QD photocatalysts studied via ultrafast visible and midinfrared spectroscopies

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ABSTRACT Photoinduced carrier dynamical processes dominate the optical excitation properties of photocatalysts and further determine the photocatalytic performance. In addition, as the electrons generally possess a faster transfer rate than holes, hole transfer and accumulation are critical, and they play the key efficiency-limiting step during the photocatalytic process. Therefore, a comprehensive understanding of the dynamics of photogenerated holes and their determining factors in the photocatalytic system is highly essential to rationalize the full catalytic mechanism and develop highly efficient photocatalysts, which have not yet been revealed. In this work, the photoinduced charge carrier dynamics in InP/ZnS quantum dots (QDs) capped with long-chain L-typed ligands (oleylamine) and inorganic ligands (sulfide ion (S\textsuperscript{2−})) were explored. Time-resolved photoluminescence and femtosecond transient-absorption spectroscopy unambiguously confirmed the ultrafast hole transfer from the InP core to S\textsuperscript{2−} ligands. Moreover, by probing the bleach of vibrational stretching of the ligands with transient midinfrared absorption spectroscopy, the hole transfer time was determined to be 4.2 ps. The injected holes are long-lived at the S\textsuperscript{2−} ligands (>4.5 ns), and they can remove electrostatically attached surfactants to compensate for the spatial charge redistribution. Finally, compared with other inorganic ligands such as Cl\textsuperscript{−} and PO\textsubscript{4}\textsuperscript{3−}, S\textsuperscript{2−} balances the ionic radii and charge redistribution. In this work, the ultrafast hole transfer was determined to be 4.2 ps. The injected holes are long-lived at the S\textsuperscript{2−} ligands (>4.5 ns), and they can remove electrostatically attached surfactants to compensate for the spatial charge redistribution. Finally, compared with other inorganic ligands such as Cl\textsuperscript{−} and PO\textsubscript{4}\textsuperscript{3−}, S\textsuperscript{2−} balances the ionic radii and charge redistribution.

Keywords: InP/ZnS QD photocatalysts, surface ligands, ultrafast visible spectroscopies, midinfrared spectroscopies, hole transfer

INTRODUCTION Photocatalytic hydrogen evolution (PHE) has aroused broad interest because of the increasing demand for clean and sustainable energy sources [1–3]. However, the catalytic performance of most state-of-the-art photocatalysts is hindered by some photophysical bottlenecks among which the inefficient charge carrier separation after photoexcitation is frequently reported [4–7]. For addressing this issue, numerous important studies have focused on electron collection, which directly triggers proton reduction for H\textsubscript{2} evolution [8,9]. However, as the electrons generally possess a faster transfer rate than holes, the hole transfer is critical for the whole catalytic process, and the severe charge recombination caused by hole accumulation is a key efficiency-limiting step for photocatalytic H\textsubscript{2} evolution in many cases [10–12]. Therefore, a comprehensive understanding of the dynamics of photogenerated holes and their determining factors in the photocatalytic system is highly essential to rationalize the full catalytic mechanism and develop highly efficient photocatalysts.

Recent studies suggest that the surface chemistry engineering of various photocatalysts plays a role in controlling the photoinduced dynamics of electrons and holes. For example, surface ligands engineering can significantly modulate the charge carrier transfer in semiconductor colloidal quantum dots (QDs) [13–19]. Surface ligands of QDs usually anchor to the surface uncoordinated atoms and passivate the surface trap states, avoiding the random recombination of charge carriers and ensuring the sufficiently long excited-state lifetime to drive proton reduction [20–22]. Furthermore, when the molecular orbitals of surface ligands fall into the bandgap of the QDs, they could act as donors or acceptors to selectively induce photogenerated charge carrier transfer in QDs [23–33]. Nevertheless, surface ligands can also form dielectric energy barriers against the crystalline core of QDs to prevent photogenerated charges from tunneling toward the outside environment randomly [23]. Therefore, optimizing such photophysical tradeoff remains a highly demanding task to comprehensively understand charge carrier transfer dynamics and finally develop efficient QD photocatalysts. Moreover, compared with conventional organic/inorganic surface ligands (such as oleylamine (OLA), carboxyl,
mercaptop, hydroxyl, and amino group) for QDs, inorganic chalcogenide ligands usually possess lone pair electrons, and they can selectively capture photogenerated holes by Coulombic attraction, which provides a perfect hole sacrificial agent to induce hydrogen generation [26,34–37]. For example, Ohmori et al. [37] found that S²⁻ in the solution could capture holes to enhance photocatalytic performance. Furthermore, we revealed that the S²⁻ ligands can serve as a hole-trap state to capture holes and drastically improve the PHE efficiency of InP/ZnS QDs and CdSe QDs [33,38]. However, the assumed inorganic ligands-mediated hole attraction has not been rigorously verified. The detailed pathways of hole transfer could also be different from that of QDs with conventional organic ligands, as the anchoring of those inorganic surface ligands relies on the electrostatic forces rather than covalent bonds. Therefore, an in-depth investigation of photoinduced hole dynamics of QDs capped with inorganic ligands is essential to manifest their superior photocatalytic performance. It is also crucial for the rational design of advanced photocatalysts.

Therefore, InP/ZnS QDs with different surface ligands (OLA, Cl⁻, S²⁻, and PO₄³⁻) were targeted as a benchmark system. The photoinduced hole transfer dynamics from QDs to surface ligands has been initially explored via the complementary studies of time-resolved photoluminescence (TRPL), femtosecond (fs) transient visible absorption (fs-TA), and fs-time resolved infrared (fs-TRIR) absorption spectroscopies. TRPL and fs-TA probe the population of excited states at InP QDs, whereas fs-TRIR confirms the population of transferred holes at surface ligands concurrently. We have demonstrated that the holes would transfer to the surface S²⁻ ligand within 4.2 ps, form a charge transfer state (CTS) with a lifetime of 900 ps, and stay at the ligands for more than 4.5 ns. This ligands-mediated hole transfer substantially retards the recombination of electron-hole pairs. In addition, fs-TRIR reveals for the first time the structural reorganization of surface ligands after hole injection induced by the decoupling of counterions and the redistribution of surface electrostatic force at ultra-long timescale. Such a phenomenon only occurs with the S²⁻ ligands because of the large electrostatic driving force to dissociate the CTS; thus, the H₂ evolution efficiency from H₂S splitting has been enhanced 3.74 and 11.3 times than those of other inorganic ligands (e.g., Cl⁻ and PO₄³⁻). Our results indicate that S²⁻ surface ligands-mediated hole scavenging during the photocatalytic activity is combined with the fast charge transfer and slow structural dynamics of the surface ligands, which unveils the importance of dynamics over hole transfer in artificial photosynthesis.

EXPERIMENTAL SECTION

Sample preparation
All the InP and InP/ZnS QDs were synthesized by hot injection methods identical to our previous published work, and the detailed synthesis procedures can be found in the references [20,34]. The S²⁻ capping agents were attached to QDs by the ligand exchange process with details described in the reference [34].

Time-resolved visible spectroscopies
The fs-TA measurements were performed using a standard femtosecond pump-probe setup. Spitfire Pro regenerative amplifier seeded by Mai Tai SP femtosecond oscillator generates the laser pulses with 800 nm wavelength and 80 fs pulse-length under 1 kHz repetition rate (all techniques from Spectra-Physics). TRPL measurements were carried out via a time-correlated single photon counting setup (TCSPC) utilizing a pulsed diode laser. Moreover, TA data were analyzed by the singular value decomposition (SVD).

Photocatalytic H₂ generation from H₂S
The photocatalytic H₂ generation from saturated H₂S over InP/ZnS QDs with different surface ligands was achieved via a homemade off-line system. Firstly, H₂S gas was bubbled into a three-neck flask containing 50 mL DI water with Na₂S (0.1 mol L⁻¹) and Na₂SO₃ as the hole sacrificial agents to obtain H₂S absorbent. Secondly, 1 mg QDs together with 5 mL H₂S absorbent were added into the Pyrex tube. Before reaction, the Pyrex tube was de-aerated with Ar gas for 15 min to remove impurity air and then injected with 0.5 mL CH₄ as the standard reference gas for quantitative analysis. At last, monochromatic light-emitting diode light (440 nm, 84 mW cm⁻²) was used as the light source to illuminate InP QDs and gas chromatograph (TM GC-2010 Plus, China, Ar carrier gas, molecular sieve 5 Å, TCD detector) was used to monitor the amount of evolved H₂.

RESULTS AND DISCUSSION

Photocatalytic H₂ evolution of InP/ZnS QDs capped with different ligands
In our work, photocatalytic H₂ evolution from H₂S absorbent aqueous solution with Na₂S/Na₂SO₃ as the hole sacrificial agent was selected as a reference reaction to elucidate the role of surface ligands in photocatalytic reaction. Millions of tons of H₂S (>4 × 10⁷ t) are widely produced from oil and gas extraction every year with high-density hydrogen energy [39,40]. As shown in Fig. 1a, evident photocatalytic activities only occur in QDs with PO₄³⁻, Cl⁻, and S²⁻ ligands under light illumination. The negligible activity in InP/ZnS capped with OLA ligands (namely InP/ZnS-OLA) should be attributed to the electrical barrier effect of insulator carbon chains. In addition, InP/ZnS capped with S²⁻ ligands (namely InP/ZnS-S) exhibits the highest H₂ evolution efficiency (213.6 μmol mg⁻¹) in 10 h and the highest apparent quantum yield (AQY, 19.3% at 440 nm, the detailed calculation can be seen in the Supplementary information). Moreover, as shown in Fig. 1b, the H₂ evolution of InP/ZnS-S is stable up to 10 h, whereas the catalytic reaction ceases after 3 h in a sample capped with phosphate (PO₄³⁻) and chloride ion (Cl⁻) ligands (namely, InP/ZnS-PO₄ and InP/ZnS-Cl, respectively). In the following section, we will rationalize the superior photocatalytic performance of QDs capped with S²⁻ by investigating the excited-state dynamics, particularly the photoinduced hole transfer, which has been dominated by the surface ligands in the QD system [40–42].
Structure and steady-state spectroscopies

QDs capped with S\(^{2-}\) exhibited the highest H\(_2\) evolution efficiency and catalytic stability among all QDs. Accordingly, we conducted detailed photophysical studies on this sample using QDs capped with conventional organic OLA as the control reference. A series of InP/ZnS QDs with different ZnS growth times (0–120 min) were synthesized following the hot injection protocols, and inorganic S\(^{2-}\) ligands were introduced to replace the original organic OLA ligands attached on the QD surface as evidenced by Fourier transform infrared (FT-IR) spectra (Fig. S1). Those samples were then named by InP-OLA, InP/ZnS-OLA, InP/ZnS-OLA (30 min), InP/ZnS-OLA (60 min), InP/ZnS-OLA (120 min) for OLA-capped QDs, while InP-S, InP/ZnS-S (30 min), InP/ZnS-S (60 min), InP/ZnS-S (120 min) for S\(^{2-}\)-capped QDs. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images (Fig. S2) of QD samples with OLA and S\(^{2-}\) ligands exhibited homogeneous particles with an average size of 2–3 nm. Lattice spacing was calculated to be 0.33 nm following literature data along (111) facets of InP [20,34]. Moreover, energy dispersive X-ray spectroscopy (EDX) analysis (Table S1) revealed the gradually increased elemental composition of zinc and sulfur after introducing the ZnS layer on InP QDs. Powder X-ray diffraction (PXRD) patterns (Fig. S3) also confirmed the retention of the intrinsic zinc blende structure in QDs during the ZnS growth and ligand exchange. However, no clear heterojunction boundary between ZnS and InP was observed from the HRTEM images (Fig. S2), implying a potential gradient or alloy structures for our InP/ZnS QDs [20,34,38,43,44]. Fig. 2 illustrates the steady-state absorption and PL spectra of the as-prepared neat InP and InP/ZnS QDs with a typical absorption (emission) peak located at 525 nm (580 nm), which should be ascribed to the absorption and emission of 1S excitons, respectively [34,45–48]. The unchanged absorption band edges and emission peaks during the ZnS layer growth and S\(^{2-}\) ligand exchange exclude the direct contribution of the ZnS layer or the S\(^{2-}\) ligand to the optical transition. On the contrary, the PL quantum yield (PLQY) of InP QDs is modulated by ZnS growth and ligand exchange.
exchange. The PLQY of OLA-capped QDs significantly increases from 7.5% to 55% with the increase of ZnS growing time because of the passivation of surface trap states [34,47–51]. Nevertheless, the PLQY of QDs capped with $S^{2-}$ shrunk drastically below 2% and became less dependent on ZnS growth, which indicated that $S^{2-}$ ligands introduced an extra nonradiative charge carrier recombination channel [35,36,52,53]. For rationalizing additional quenching, we first characterized the electronic structures of InP/ZnS QDs to demonstrate the possible depopulation pathway of the excited species. The valence band maximum (VBM) position could be confirmed by the X-ray photoelectron spectroscopy (XPS) valance band spectra of QDs (Fig. S4), while the conduction band minimum (CBM) was further determined by adding up the optical band gap extracted from the absorption spectra (Fig. 2), which is consistent with other reports [48]. The energy level of $S^{2-}$ ligands at $-0.48$ eV vs. normal hydrogen electrode (NHE) calculated by electrochemistry is higher than the VBM of InP, providing sufficient driving force for photoinduced hole injection [30]. The lone pair electrons of $S^{2-}$ ligands have Coulombic attraction with the photogenerated holes at the VBM of the InP, reducing the potential barrier of the ZnS layer and consequently making the hole transfer more thermodynamically feasible [51,54–57].

### fs-TA absorption and TRPL spectroscopy

We first measured the fs-TA for all the as-prepared InP QDs and InP/ZnS QDs to elucidate photophysics and charge transfer dynamics (Figs S5 and S6). The typical TA spectra of InP/ZnS QD (30 min) samples capped with OLA and $S^{2-}$ ligands show a characteristic band-edge ground-state bleaching (GSB) signal at approximately 530 nm (Fig. 3a, c), which is attributed to the state filling of 1S exciton states [34,50,58–60]. The SVD fitting of fs-TA data generates four excited-state decay components (Fig. 3b, d and Table 1). The fast components with lifetime ($\tau_1$) of 0.2–0.4 ps for QDs capped with OLA and $S^{2-}$ ligands are fingerprints of the cooling of hot electrons from a higher vibration level to CBM (blue curves), which are featured as the negative GSB signal at a higher energy level than band-edge bleach. The board positive bands from 500 to 600 nm represent the population of the band-edge state resulting from hot-carrier cooling. The subpicosecond lifetimes (0.2–0.4 ps) also resemble the conventional hot-carrier cooling time in semiconductor QDs [45,46]. The slowest component with a lifetime longer than the TA time-delay ($\tau > 10$ ns) of OLA-capped QDs (Fig. 3b) exhibits a typical Gaussian GSB band. It overlapped perfectly with the ground-state absorption band edge (depicted as GSA). In addition, such a long lifetime is consistent with the PL lifetime shown in Fig. 4. This finding should be ascribed to the radiative recombination of electrons and holes at the band edge [56]. Compared with component $\tau_4$, the other two components $\tau_2$ (5.8 ps) and $\tau_3$ (1.24 ns) show slightly blue-shifted GSB with an additional positive band at the red side of the bleach. In component $\tau_2$, such positive band is narrower from 590 to 610 nm. It reflects a typical biexciton Stark effect in QDs after pump excitation, which can be mimicked by the differential spectrum between ground-state absorption and a red-shifted (20 nm) version of it (dashed green line in Fig. 3b) [47,61,62]. Moreover, we found that the PLQY and the lifetime of $\tau_2$ component in InP/ZnS samples increase synchronously with the increase of ZnS growing time, whereas lifetimes ($\tau_1$, $\tau_3$, and $\tau_4$) of other components remain constant (Table 1). This finding indicates that the $\tau_2$ component should be more surface-related. In this scenario, the $\tau_2$ component can be attributed to the fast-surface trapping of the photo-excited electrons in some of the QDs, whereas the remaining pool of QDs does not show this trapping channel. Component $\tau_3$ (1.24 ns) shows a pronounced and broad

![Figure 3](image-url)  
**Figure 3** Transient-absorption spectra and respective SVD fittings of InP/ZnS QDs (30 min) samples capped with (a, b) OLA and (c, d) $S^{2-}$ ligands; lifetimes of $\tau_2$ (e) and $\tau_4$ (f) components vs. ZnS growing time of InP/ZnS QDs capped with OLA and $S^{2-}$ ligands.
positive absorption band from 560 to 900 nm. Different possibilities are identified to interpret this component: (1) Auger recombination, (2) electron depopulation, or (3) hole depopulation in QDs. Considering that the average excitation density per QD \( N \ll 1 \), the possibility of Auger recombination can be excluded (for detailed calculation, see the Supplementary information and Fig. S7). On the contrary, TA signals are not sensitive to the hole dynamics in strongly confined QDs, where the close-packed states and flat band distribution make the state filling at VB less detectable in GSB \[58,59,63\]. Therefore, component \( \tau_3 \) can only be attributed to excited electron depopulation. The SVD components of QDs capped with \( S_2^- \) are summarized in Fig. 3d. The spectral feature and lifetime for \( \tau_1 \) and \( \tau_2 \) are similar to those in OLA-capped QDs, manifesting the same processes (i.e., hot-carrier cooling and surface electron trapping). The \( \tau_3 \) component of QDs capped with \( S_2^- \) still represents electron depopulation but with a shorter lifetime. The \( \tau_4 \) component exhibits extra featureless positive absorption from 580 to 900 nm in addition to the GSB of the band-edge excitation.

We also conducted TRPL measurement of all samples using TCSPC to obtain an insight into the excited-state dynamics, where the decay dynamics of excited electrons and holes can be retraced \[36\]. The PL kinetics can also be well fitted using a multiexponential decay equation \[57,64\]:

\[
f(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} + \ldots + A_N e^{-t/\tau_N},
\]

where \( \tau \) is the lifetime of the different components, \( N \) is the number of components in charge recombination, and \( A \) is the contribution ratio of each component to the total decay. Fig. 3a, b illustrate the PL decay dynamics of QDs capped with OLA and \( S_2^- \) excited at 438 nm. The PL lifetimes of QDs capped with OLA increase with ZnS addition, and the PL decays can be globally fitted by using three components with analogous lifetime sets \( (\tau_1, \tau_2, \text{and } \tau_3) \) but with varying amplitude (Table 2). Component \( \tau_1 \) in TRPL exhibits the identical lifetime as TA decay component \( \tau_3 \) (1.2 ns), reflecting the same electron depopulation. The gradual shrinkage in the amplitude of component \( \tau_1 \) with the increment of ZnS addition follows the trend of PLQY (Fig. 1b). This finding indicates that such electron depopulation is also a primary nonradiative process that quenches the emission of QDs \[36\]. As the surface passivation by ZnS strongly determines the PLQY, such electron depopulation should also be related to surface trapping but should be originated differently from the fast ps timescale electron trapping described by TA decay component \( \tau_2 \). Therefore, components \( \tau_2 \) and \( \tau_3 \) with long lifetimes can be assigned to all radiative recombination of photo-generated species. When the surface of QDs is replaced with \( S_2^- \) ligands, the PL kinetics remains the same regardless of ZnS coating (Fig. 3). We can fit the kinetics by one fast component with a lifetime of 0.8 ns \( (\tau_1) \) and one slow component with a lifetime of approximately 10 ns \( (\tau_2) \). The fast component resembles the lifetime of \( \tau_3 \) in TA dynamics, which should be attributed to the abovementioned electron depopulation in QDs. Moreover, such a process dominates the PL kinetics, and it is insensitive to surface passivation, indicating that it is irrelevant to any surface trapping.

**fs-TRIR absorption spectroscopy**

to date, the possible hole transfer to the \( S_2^- \) ligands still cannot

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**Table 1 SVD fitting lifetime of each component of all InP and InP/ZnS QDs**

| Sample                  | \( \tau_1 \) (ps) | \( \tau_2 \) (ps) | \( \tau_3 \) (ns) | \( \tau_4 \) (ns) |
|-------------------------|-------------------|-------------------|-------------------|-------------------|
| InP-OLA                 | 0.4               | 4.5               | 0.9               | >10               |
| InP/ZnS-OLA (30 min)    | 0.3               | 5.7               | 1.2               | >10               |
| InP/ZnS-OLA (60 min)    | 0.2               | 8.7               | 1.1               | >10               |
| InP/ZnS-OLA (120 min)   | 0.2               | 12.8              | 1.2               | >10               |
| InP-S                   | 0.2               | 4.9               | 0.9               | >10               |
| InP/ZnS-S (30 min)      | 0.1               | 7.0               | 0.8               | >10               |
| InP/ZnS-S (60 min)      | 0.2               | 9.0               | 0.8               | >10               |
| InP/ZnS-S (120 min)     | 0.2               | 10.4              | 0.9               | >10               |

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**Figure 4** TCSPC kinetics of InP/ZnS QDs (30 min) with (a) OLA and (b) \( S_2^- \) ligands, respectively.
be confirmed merely by probing the excited-state depopulation in QDs. Therefore, time-resolved mid-IR spectroscopy was used. It can monitor the transient change of vibrational modes in the molecules during radical species formation after external charging \([65,66]\). In general, \(S^2^-\) or other inorganic ionic ligands can bond to the surface of QDs either by electrostatic attraction with uncoordinated surface atoms (e.g., Zn) or X-type bonding. The surface residual charges are responsible for the dispersion of the QDs in the polar solvent \([65]\). On the contrary, the surface charges can also be balanced by protonated free amines in the solution to form bounded ion pairs \([67–70]\). Based on our synthesis methods, sulfur was dissolved into \(N\)-methylformamide (NMF) to link with InP/ZnS QDs, and it finally formed \(S^2^-\) ligands coated on the surface of QDs. Therefore, \(S^2^-\) ions should also electrostatically adsorb NMF via their protonated amino groups (Fig. 5a). Steady-state FTIR clearly shows the extra peak in QDs capped with \(S^2^-\) corresponding to the vibration modes of the attached NMF (Fig. 5b and Fig. S1) \([67]\). This finding indicates an electrostatically balanced bilayer on the surface of our QDs (Fig. 5a). If a hole is injected into the \(S^2^-\) ligands, the extra donated charge would break the electrostatic balance and change the vibration strength of adsorbed NMF (Fig. 5a).

### Table 2 TRPL lifetimes and the respective amplitudes of all InP and InP/ZnS QDs

| Sample                  | \(\tau_1\) (ns) | \(\tau_2\) (ns) | \(\tau_3\) (ns) |
|-------------------------|-----------------|-----------------|-----------------|
| InP-OLA                 | 1.2 (81%)       | 20 (14%)        | 135 (5%)        |
| InP/ZnS-OLA (30 min)    | 1.2 (18%)       | 25 (54%)        | 105 (28%)       |
| InP/ZnS-OLA (60 min)    | 1.2 (10%)       | 25 (53%)        | 107 (37%)       |
| InP/ZnS-OLA (120 min)   | 1.2 (19%)       | 25 (50%)        | 114 (31%)       |
| InP-S                   | 0.8 (86%)       | 10 (14%)        | –               |
| InP/ZnS-S (30 min)      | 0.8 (94%)       | 14 (6%)         | –               |
| InP/ZnS-S (60 min)      | 0.8 (92%)       | 11 (8%)         | –               |
| InP/ZnS-S (120 min)     | 0.8 (88%)       | 11 (12%)        | –               |

Figure 5  (a) Schematic illustration of hole transfer; (b) FTIR and corresponding TRIR spectra under different decay times of InP/ZnS-S QDs (inset is schematic of vibration mode); (c) TRIR kinetic traces at different probe wavelengths and (d) differential kinetic trace up to 4500 ps delay after photoexcitation of InP/ZnS QD sample capped with \(S^2^-\) ligands (30 min).
Consequently, the characteristic C=O stretching band of NMF can be utilized to identify the hole injection process. Here we used the IR laser pulse as a probe to measure fs-TRIR spectra with wavelengths covering the C=O stretching band (i.e., 5100–6200 nm or 1610–1960 cm$^{-1}$) and trace the corresponding kinetics. As shown in Fig. 5b and Fig. S8b, the TRIR spectra of QDs capped with S$_{2}^{2-}$ initially show a typical derivative transient signal with a negative peak at 5950 nm (i.e., 1695 cm$^{-1}$) and a positive peak at 5650 nm (i.e., 1770 cm$^{-1}$) up to 600 ps. At longer delay times, a negative bleaching band at 5950 nm dominates the transient derivative signal, demonstrating the blue shift of the C=O stretching band, because the population of extra holes in the S$_{2}^{2-}$ ligands diminishes the Coulombic interaction toward NMF, thereby enhancing the vibrational motion of the C=O bonds. In addition, a featureless positive signal all over the wavelength region at early time scale can be observed, corresponding to the intraband transition of photogenerated free C=O bonds. In addition, a featureless positive signal all over the wavelength region at early time scale can be observed, corresponding to the intraband transition of photogenerated free charge carriers [63]. In our case, the photoexcited electron-hole pairs in InP QDs formed excitons spontaneously because of the strong quantum confinement. The hole transfer to the S$_{2}^{2-}$ ligands leads to the dissociation of an exciton and consequently releases free electrons in the conduction band of QDs. On the contrary, the excited species in OLA-capped QDs is purely exciton; therefore, no clear transient signal could be observed in TRIR (Fig. S8). Furthermore, we compared the kinetic traces at 5500 and 5950 nm (Fig. 5c), where the former represents the pure dynamics of free charges as the decay returns to zero at a long delay time and the latter is a combination between the absorption of free charges and bleaching of C=O stretching. The differential kinetic trace (Fig. 5d and Fig. S9) could reveal the pure kinetics of the C=O stretching mode bleaching. It displayed an ultrafast increase within 4.2 ps, followed by a flat plateau up to 900 ps, and ended with a slow rise of the kinetics at long time delay. The ultrafast component should represent the initial hole injection from VB of the QDs to the S$_{2}^{2-}$ ligands. The second period of 900 ps flat plateau shares a similar lifetime to that of the middle component observed in TA and PL decays. One of the possible interpretations of the process is the geminate recombination between excited electrons in the CB of QDs and injected holes in the S$_{2}^{2-}$ ligands. However, we observe fast quenching in PL decay corresponding to the hole injection time (i.e., 5 ps), whereas the following geminate recombination should be invisible after the quenching of emission. Alternatively, we attributed this process to the formation and dissociation of an intermediate CTS that consists of the injected holes in S$_{2}^{2-}$ and left-over electrons in the CB of QDs with strong Coulombic interaction. We observed the same CTS in our previous studies for CdSe QDs after photoinduced electron injection to the ZnO acceptors [39]. Within this model, the injected holes can hop back and forth between the S$_{2}^{2-}$ ligands and the VB of the QDs and exhibit an equilibrium hole population at the ligands. Consequently, the TRIR kinetics remains constant. On the contrary, as the hole, which can hop back, can also recombine with the electrons radiatively, the PL emission would only be completely quenched after the dissociation of such a CTS state. Therefore, the time-resolved quenching in PL decay is equal to the CTS dissociation time extracted in TRIR and fs-TA in this study (i.e., 900 ps).

After the CTS dissociation, a slow increase of the C=O bleach could be observed in TRIR kinetics. As the electronic states should be constant after hole injection and CTS dissociation, the following modification on the vibration mode of the surface ligands can only be induced by the slow structural dynamics of the ligands. Besides direct evidence from structural characterization, we can still provide some possible scenarios. First, the existence of an extra hole at the S$_{2}^{2-}$ ligands would significantly diminish its electrostatic attraction to NMF and lead to the detachment of one or even both anchored NMF (Fig. 5a). This scenario may cause the spatial reorientation of surface ligands to minimize the surface energy and neutralize the electrostatic charges. This process would change the local C=O stretching strength in NMF but in a slower manner compared with the electronic dynamics [66,71–73]. Second, the spectral feature of TA component $\tau_{2}$ in OLA-capped QDs is the same as that of the abovementioned component with a lifetime of 800 ps in QDs capped with S$_{2}^{2-}$. This scenario indicates a similar excited-state scheme between the two cases; that is, the hole is depopulated from the VB with electrons staying at the CB. As no hole injection to the ligands is expected in OLA-capped QDs, the only possibility is the trapping of holes from the surface hole traps. Here the 1.2 ns lifetime refers to the nonradiative recombination between electrons and trapped holes on the surface.

Fig. 6 summarizes all the photoinduced processes in the two types of QDs with different surface ligands. In OLA-capped QDs, one portion of the QDs (pool A) undergoes fast-surface electron trapping after excitation within 4–10 ps. By contrast, the other portion of the QDs (pool B) undergoes hole trapping, followed by the geminate recombination with excited electron within 1.2 ns. Electron and hole trapping represent the main nonradiative loss of the excited states, which can be efficiently diminished by surface passivation via ZnS. The radiative recombination in QDs, except for trapping, exhibits a lifetime longer than 10 ns. In QDs capped with S$_{2}^{2-}$, the hole injection entirely suppresses hole trapping to the surface S$_{2}^{2-}$ ligands within the picosecond timescale. The injected holes are still bounded with residual electrons in the QDs to form the intermediate CTS state within 0.8–0.9 ns dissociation time. After CTS dissociation, the injected holes can stay long at the S$_{2}^{2-}$ ligands, facilitating the photocatalytic reaction. However, they will trigger the removal of electrostatic adsorption surfactant NMF and lead to the slow geometrical reorganization of the surface ligands, which modify the vibration mode of the counterions in the colloidal solution.

The abovementioned analysis of charge transfer dynamics indicates that surface-anchored S$_{2}^{2-}$ ligands efficiently dissociate the CTS state, which improves photogenerated hole transfer, thereby achieving excellent photocatalytic H$_2$ evolution efficiency compared with InP/ZnS QDs capped with OLA ligands. Moreover, as shown in Fig. 1a, other InP/ZnS QDs capped with inorganic surface ligands exhibited good photocatalytic H$_2$ evolution efficiency. Thus, we measured the TRIR of InP/ZnS QDs capped with various inorganic ligands, including Cl$^{-}$, PO$_{4}^{3-}$, and S$_{2}^{2-}$, to rationalize the relationship between hole injection dynamics of different inorganic ligands and photocatalytic performance systematically. Photoinduced bleaches of C=O vibration in NMF have been observed in all the three samples, indicating the abovementioned hole injection to the surface ligands (for detailed TRIR spectra, see Figs S10 and S11). The deferential TRIR kinetics shown in Fig. 7 illustrated faster hole injection to the Cl$^{-}$ and PO$_{4}^{3-}$ ligands (<1 ps) compared with S$_{2}^{2-}$. However, no NMF removal processes are observed as
Figure 6  Schematic illustration of the photophysical pathways of different components after photoexcitation of QDs capped with (a) OLA and (b) S$^{2-}$.

Figure 7  TRIR differential kinetic trace (6000–5580 nm) of QDs capped with various ligands (i.e., OLA, Cl$^{-}$, PO$_4^{3-}$, and S$^{2-}$) and corresponding schematic of the hole injection dynamics.
the bleaches constantly delay over time, which can be attributed to the backward recombination of injected holes with the residual electrons in QDs. The absence of NMF removal probably indicates that the injected holes are still bonded in the CTS states without dissociation. The underlying reason needs further exploration, but we can provide some assumptions here. The overall Coulombic energy between injected holes and electrons at QDs dominates the dissociation of CTS states, which is screened by the electrostatic force created from the surface ligands. Such electrostatic force is increased with the net charges of the surface ligands (i.e., PO$_4^{3-}$ > S$_2^{2-}$ > Cl$^{-}$) and decreased with their ionic radii (i.e., PO$_4^{3-}$ (238 pm) < S$_2^{2-}$ (184 pm) < Cl$^{-}$ (181 pm)). S$_2^{2-}$ ligands can be optimal in those two tradeoff factors and may possess the largest electrostatic force to dissociate the CTS states. Consequently, photogenerated electrons are free to diffuse to the surface reduction sites, whereas NMF removal would ensure the direct intact between the catalysts and reagents in the photocatalytic reaction; thus, InP/ZnS-S exhibits excellent H$_2$ evolution performance.

Based on the abovementioned observation, we can rationalize the underlying mechanism behind the superior photocatalytic performance of QDs capped with S$_2^{2-}$: (1) the S$_2^{2-}$ ligands function as an intermediate state to direct the hole transfer toward the surface of the QDs, thereby diminishing charge recombination and facilitating the reduction of proton hydrogen; (2) thorough hole transfer and surface structure reorganization ensure the efficient hole scavenging in the medium and prevent the spatial charge accumulation, which is the main origin of photodegradation during the catalytic reaction [74–76]; (3) photocatalytic H$_2$ evolution from H$_2$S splitting in our system occurs under sulfur-rich aqueous condition; therefore, the S$_2^{2-}$ ligand is more stable than other inorganic ligands. These mechanisms should account for the superior photocatalytic performance of QDs capped with the S$_2^{2-}$ ligands to QDs with other inorganic ligands [34].

**CONCLUSION**

We systematically explored the photogenerated charge carrier dynamics of InP/ZnS QD photocatalysts with different surface ligands by TRPL, ultrafast fs-TA, and TRIR spectroscopies. Complementary studies from TRPL and fs-TA unambiguously confirmed ultrafast hole transfer from InP QDs to surface S$_2^{2-}$ ligands. TRIR further characterized the hole transfer time to be 4.2 ps and identified the formation of CTS after hole injection with the dissociation time of 0.8–0.9 ns. The injected holes were long lived at the S$_2^{2-}$ ligands (>4.5 ns), and they removed the electrostatically attached surfactants on the ligands. Those observations rationalized the enhanced photocatalytic performance in InP/ZnS QDs capped with S$_2^{2-}$ compared with QDs capped with other inorganic and organic ligands. Furthermore, our results demonstrated a dynamically modified surface chemistry during the photocatalytic reaction associated with the charge transfer to the surface ligands. We hypothesized that our understanding of the role of surface ligands in the photocatalytic process of colloidal QDs opens a new avenue for designing and engineering QD-based photocatalysts.

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Author contributions Zhou Y and Zheng K conceived the research and designed the experiments. Liu Y designed the synthesis. Liu Y, Xie Z and Zhao Q performed the synthesis. Abdellah M performed ultrafast mid-IR spectroscopy. Lin W performed ultrafast visible spectroscopy. Liu Y and Meng J performed the TEM and HRTEM characterizations. Liu Y wrote the manuscript with support from Zhou Y and Zheng K. Yu S, Pan Q, Zhang F and Pullerits T revised the manuscript. All authors discussed the results and commented on the manuscript.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

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通过瞬态可见和瞬态中红外光谱研究InP/ZnS QDs无机配体诱导的表面空穴转移和构型调整过程

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摘要 光生载流子动力学过程可以显著影响材料光催化活性。通常, 光生电子的转移速率远高于光生空穴的, 致使空穴的转移和累积成为影响光催化效率的关键因素。因此, 深入探究光生空穴转移过程和动力学可以极大地帮助我们认识和理解光催化机理, 但该工作鲜有人关注研究。本工作中, 时间分辨中红外光谱 (TRIR) 和飞秒瞬态可见吸收光谱 (TRPL) 显示空穴会在InP/ZnS QDs表面的S−配体转移至表面S5−配体。此外, 瞬态中红外光谱 (TRIR) 中S5−配体伸缩振动信号表明该空穴转移时间为4.2 ps。转移至S5−配体的空穴具有明显的长寿命特征 (>4.5 ns) 并且会导致表面活性产物的电荷分离和构型重组。最后, 通过与其他无机配体(Cl−、PO43−)比较, 我们发现S5−配体具有最合适的离子半径和净电荷, 因此带有该配体的InP/ZnS量子点(InP/ZnS QDs)光催化剂具有最高的光解硫化氢产氢性能 (213.6 μmol mg−1)。本文的研究结果为理解InP QDs光催化过程和机理提供了有价值的见解。