

## Article

# Dispersible Supertetrahedral Chalcogenide T3 Clusters: Photocatalytic Activity and Photogenerated Carrier Dynamics

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**Abstract:** Herein, we synthesized two isostructural supertetrahedral T3 cluster-based chalcogenide compounds by an ionic liquid-assisted precursor technique, namely  $[\text{Bmmim}]_6\text{In}_{10}\text{Q}_{16}\text{Cl}_4 \cdot (\text{MIm})_4$  ( $\text{Q} = \text{S}$  (**In-S**),  $\text{Q} = \text{Se}$  (**In-Se**),  $\text{Bmmim} = 1$ -butyl-2,3-dimethylimidazolium,  $\text{MIm} = 1$ -methylimidazole). The two compounds consist of a pure inorganic discrete supertetrahedral  $[\text{In}_{10}\text{Q}_{16}\text{Cl}_4]^{6-}$  T3 cluster and six charge-balancing  $[\text{Bmmim}]^+$  anions. The T3 clusters could be highly dispersed in dimethyl sulfoxide (DMSO), exposing more photocatalytic active sites, which makes the highly-dispersed **In-Se** cluster exhibit ~5 times higher photocatalytic  $\text{H}_2$  evolution activity than that of the solid-state under visible light irradiation. Comparatively, the photocatalytic performance of the highly-dispersed **In-S** cluster is only slightly higher than that of the solid state, as its inferior visible-light absorption capability limits the effective utilization of photons. More importantly, through tracking the photogenerated carriers dynamics of highly-dispersed T3 clusters by ultrafast transient absorption (TA) spectroscopy, we found that the photogenerated electrons in the **In-S** cluster would suffer a rapid internal deactivation process under illumination, whereas the photoexcited electrons in the **In-Se** cluster can be captured by its surface active centers that would effectively reduce its photo-generated carrier recombination, contributing to the significantly enhanced photocatalytic activity. This work enriches the species of highly-dispersed metal-chalcogenide nanoclusters and firstly investigates the relationship between the structures and photocatalytic performances of nanoclusters by ultrafast excited-state dynamics, which is expected to promote the development of atomically precise nano-chemistry.

**Keywords:** metal chalcogenide; nanocluster; dispersibility; photocatalytic hydrogen production; photogenerated carriers dynamics



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## 1. Introduction

The constant consumption of fossil fuels brings about multiple challenges of global warming, depletion of fossil fuels and other environmental issues due to the over-exploitation of non-renewable energy sources [1,2]. Photocatalytic hydrogen production via water splitting using renewable solar energy is a green and environmentally friendly solution to this issue [3–6]. Metal chalcogenides are popular in the field of photocatalysis because of their narrow band gap and strong light absorption [7–9]. Especially, small-sized metal chalcogenide quantum dots or nanocrystals have been considered promising photocatalytic materials due to the large specific surface area and adjustable energy levels based on shape, size and composition [10–12]; however, they face great challenges in achieving precise functional regulation at the molecular or atomic scale, which tends to limit the further exploration of the relationships between properties and structures involved in photocatalytic applications [13–15].

Discrete metal chalcogenide supertetrahedral nanoclusters (MCCs), such as  $T_n$ ,  $P_n$ , and  $C_n$ , are identified as the smallest quantum dots, which have received much attention since the 1980s benefitting from their homogeneous size, well-defined structure and semiconductor properties that are more conducive to the study of their structure–composition–property relationships [16,17]. Thus, the development of discrete MCCs has become the focus of attention, and many MCCs have been synthesized [18–21]. Nonetheless, previous reports have revealed that the photocatalytic hydrogen production activities of bulk MCCs are always very low due to the incomplete exposure of the surface active sites for MCCs in the solid state [22–24]. Therefore, the preparation of highly dispersed MCCs that can remain stable during the photocatalytic process has been expected to greatly improve their photocatalytic activity. In fact, some clusters with a chalcogenide core and an organic matter shell can be highly dispersed in common solvents [25–29], but the organic protective shell would impede the rapid transfer of photogenerated carriers in the photocatalytic process [29,30]. Therefore, due to the strong electrostatic interactions between negatively charged nanoclusters and positively charged organic templates in their crystal lattices, it is still a great challenge to develop highly dispersed discrete MCCs without covalent organic ligands.

Thus far, there are some types of dispersible discrete supertetrahedral MCCs that have been previously reported [18,20,31–34]. For instance, in 2017, Dai et al. reported a stable and dispersible Cu-In-S T5 cluster and studied the photoelectrochemical properties of its sensitized  $\text{TiO}_2$  electrode; but LiBr with strong ionic strength should be added during the dispersion of the T5 cluster to antagonize strong ionic bonds in the cluster [18]. Subsequently, Wu et al. have reported various dispersible discrete ISC-16-MInS ( $M = \text{Zn}$  and  $\text{Fe}$ ) [20], M-Ga-Sn-S ( $M = \text{Mn}$ ,  $\text{Co}$ , and  $\text{Zn}$ ) [35], and P2-CuMSnS ( $M = \text{In}$  or/and  $\text{Ga}$ ) [34] nanoclusters, and investigated their performances on photodegradation of rhodamine B dye, electrocatalytic hydrogen evolution, and intracuster photocarrier dynamics, respectively. Besides, our group has also synthesized a series of discrete T3 and T4 clusters that can be highly dispersed in the multifarious common solvents through an ionic liquid-assisted precursor method and studied their photocatalytic hydrogen production activity before and after dispersion [31–33]. Although some gratifying achievements have been made in the dispersible discrete MCCs, the relationship between the precise composition and photocatalytic activity has not been elaborated in detail. Particularly, the comprehensive understanding of photogenerated carrier dynamics of MCCs at the molecular or atomic level is crucial to clarify their photocatalytic mechanism and structure–performance relationship.

Herein, we successfully synthesized two discrete T3 clusters using the ionic liquid-assisted precursor method,  $[\text{Bmmim}]_6\text{In}_{10}\text{Q}_{16}\text{Cl}_4 \cdot (\text{MIm})_4$  ( $\text{Q} = \text{S}$  (In-S),  $\text{Q} = \text{Se}$  (In-Se)), which could be highly dispersed in dimethyl sulfoxide (DMSO), thereby exposing more reactive sites in the photocatalytic process. Among them, the highly-dispersed In-Se cluster exhibits an activity of  $23.81 \mu\text{mol h}^{-1} \text{g}^{-1}$  in the photocatalytic hydrogen production test, which is five times higher than that of the solid state, whereas the photocatalytic activity of highly-dispersed In-S cluster ( $4.66 \mu\text{mol h}^{-1} \text{g}^{-1}$ ) is barely higher than that in the solid state ( $2.34 \mu\text{mol h}^{-1} \text{g}^{-1}$ ). To comprehensively analyze the reasons for the enormous differences in photocatalytic activity of dispersed T3 clusters, we have studied the band structures, photogenerated carrier generation and separation characteristics in detail, particularly tracking the photogenerated carrier dynamics of highly-dispersed T3 clusters by using ultrafast transient absorption spectra. It is found that the excellent visible-light absorption capability, a stronger driving force for photogenerated electrons and the superior photogenerated carrier dynamics of the In-Se cluster bring about the efficient utilization of photons and a significant reduction of photogenerated carrier recombination, dedicating to the dramatically enhanced photocatalytic activity of In-Se cluster.

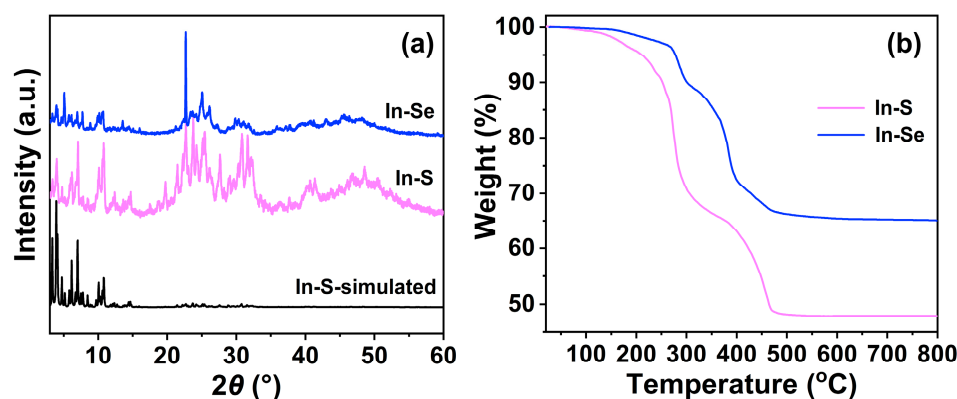
## 2. Results and Discussion

### 2.1. Crystal Structural Description

The single crystal diffraction data of **In-S** were collected on a Bruker CCD diffractometer using graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 280 K and refined by full-matrix least-squares on  $F^2$  using the SHELX-2018 program package. According to the single crystal X-ray diffraction (SCXRD) analysis, the **In-S** cluster belongs to the cubic crystal system, and the space group is  $Fd\bar{3}m$ . Due to the highly disordered  $[\text{Bmmim}]^+$  cations and lattice (MIm) molecules and the poor single-crystal quality of the **In-S** cluster, the SCXRD refinements can only unambiguously ascertain the structure of the anion  $[\text{In}_{10}\text{QCl}_4]^{6-}$  cluster, which is common for discrete  $T_n$  cluster-based compounds [32,33,36]. On the basis of the comprehensive results of SCXRD, EDS, EA, and TGA characterizations, the structural formula has been determined. The crystallographic data and the details of structural refinements for **In-S** have been listed in Table S1. The compound **In-S** consists of a discrete supertetrahedral  $[\text{In}_{10}\text{S}_{16}\text{C}_{14}]^{6-}$  T3 cluster and six charge-balancing  $[\text{Bmmim}]^+$  anions. Each asymmetry unit contains 1/2, 1/6, and 1/24 of the T3  $[\text{In}_{10}\text{S}_{16}\text{C}_{14}]^{6-}$  anions, and the bond lengths of the In-S bond are between 2.386 (5) and 2.515 (4)  $\text{\AA}$  (Figure S1), which are comparable to the reported bond lengths of the In-S-Cl T3 clusters [32,33]. The four corner sites of the **In-S** cluster are all coordinated by  $\text{Cl}^-$ , which reduces the electronegativity of the cluster, facilitating the dispersion of the cluster. In addition, we also synthesized the **In-Se** cluster, which is isostructural to the **In-S**, with the crystallographic parameters of  $a = b = c = 76.1435(10) \text{ \AA}$ ,  $\alpha = \beta = \gamma = 90^\circ$ ,  $V = 441467(10) \text{ \AA}^3$ . However, its diffraction intensity data have not been successfully collected because of the poor quality of the single crystal.

### 2.2. Crystal Structural Description

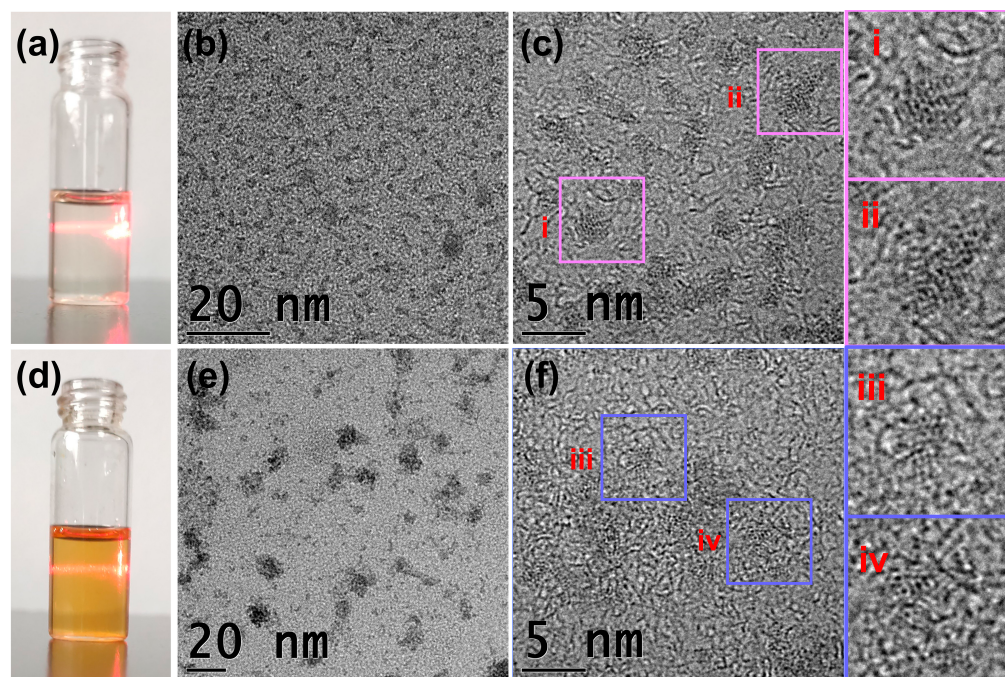
Crystals of pure phase were obtained by hand-picking for various characterization studies. The phase purity of **In-S** and **In-Se** clusters was confirmed by powder X-ray diffraction (PXRD). It can be seen that the experimental PXRD patterns of **In-S** and **In-Se** clusters are in good agreement with the simulated one of **In-S**, indicating the good phase purity and crystallinity of **In-S** and **In-Se** (Figure 1a). The thermal stability and thermal weight loss of **In-S** and **In-Se** were analyzed under an  $\text{N}_2$  atmosphere at the temperature range of 50–800  $^\circ\text{C}$ . It is found that both compounds had good stability beyond 160  $^\circ\text{C}$  and then gradually decomposed with the increase of temperature, reaching the equilibrium at  $\sim 480 \text{ }^\circ\text{C}$  (Figure 1b). The weight loss rates of **In-S** and **In-Se** clusters were 57.60% and 61.48%, corresponding to theoretical values of 53.40% and 61.36%, respectively, which was mainly attributed to the removal of organic molecules and HCl,  $\text{H}_2\text{S}$  or  $\text{H}_2\text{Se}$ .



**Figure 1.** (a) Simulated PXRD pattern of **In-S** and experimental PXRD patterns for **In-S** and **In-Se**; (b) TGA curves of **In-S** and **In-Se**.

EDS analyses of **In-S** and **In-Se** confirm the presence of In, S or Se elements in the corresponding compounds (Figures S2 and S3), and the molar ratios of In:S and In:Se are

1:1.41 and 1:1.60, respectively, which are consistent to their theoretical values of 1:1.60 and single crystal diffraction results, further verifying the molecular formula of the compounds. In addition, **In-S** and **In-Se** clusters could be well dispersed in the DMSO solution, exhibiting an obvious Tyndall effect (Figure 2a,d). The maximum dispersions were 9.55 and 10.15 mg/mL for **In-S** and **In-Se**, respectively. Transmission electron microscopy (TEM) observation reveals the excellent dispersion of obtained T3 cluster nanoparticles (Figure 2b,d), and high-resolution transmission electron microscopy (HRTEM) images further confirm the formation of T3 cluster due to the discernable lattices and triangular shape (Figure 2c,f).

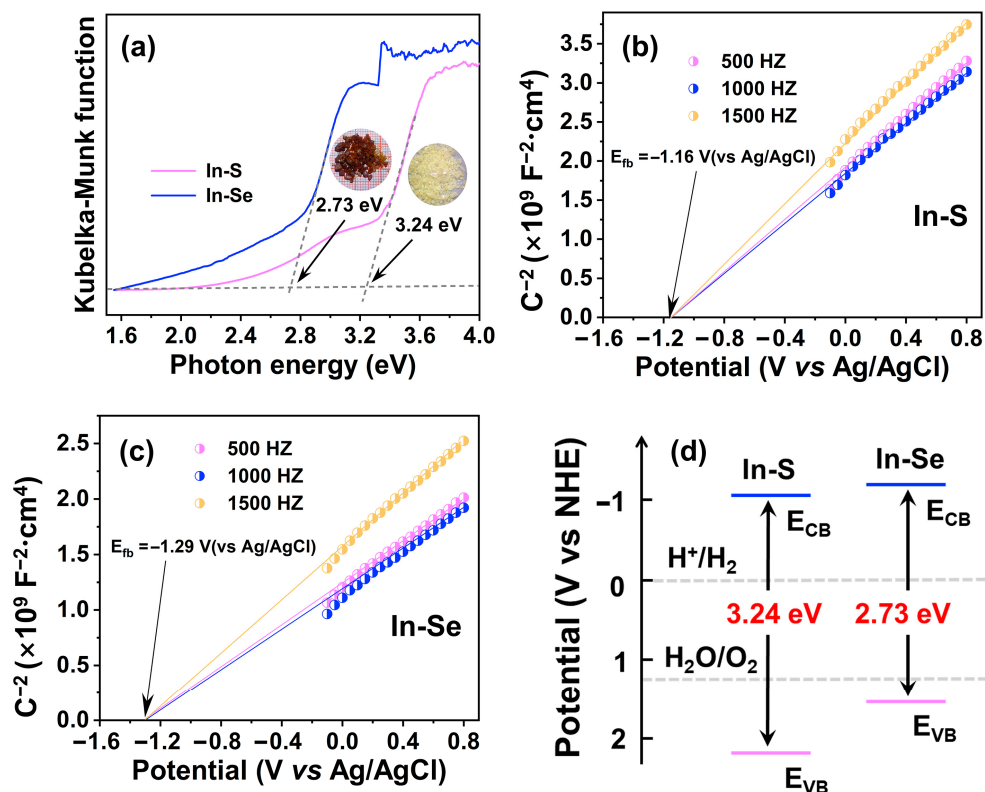


**Figure 2.** Photos of **In-S** (a) and **In-Se** (d) dispersed in the DMSO. TEM (b) and HRTEM (c) images of **In-S**; TEM (e) and HRTEM (f) images of **In-Se**. The i~ii and iii~iv are the enlarged images of corresponding areas in (c,f), respectively.

### 2.3. Energy Band Structure and Photocatalytic Properties

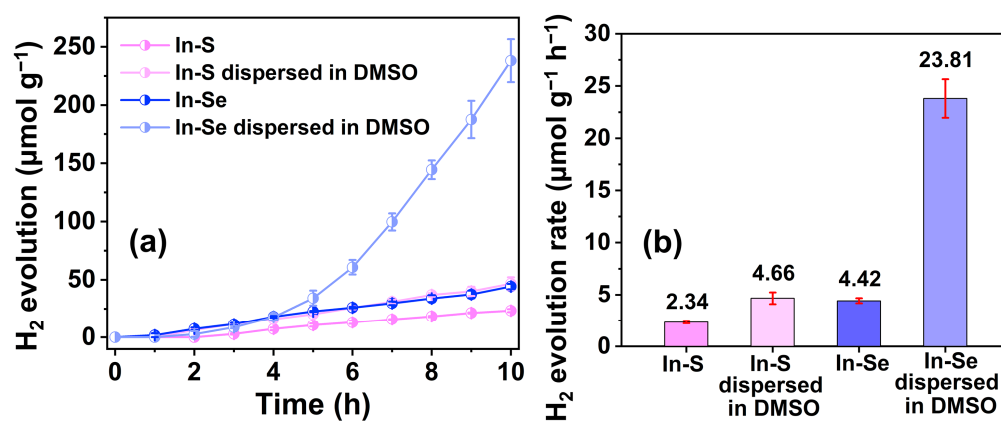
The optical absorption properties of **In-S** and **In-Se** were characterized by UV-vis diffuse reflectance spectroscopy. According to their absorption spectra, both **In-S** and **In-Se** clusters show some visible light absorption properties, implying that they could be used for visible light photocatalysis. In addition, compared to the isostructural sulfide T3 cluster **In-S**, the absorption edge of the selenide T3 cluster **In-Se** is significantly red-shifted, and the band gap values of **In-S** and **In-Se** clusters have been estimated to be 3.24 and 2.73 eV, respectively (Figure 3a). Thus, the selenide T3 cluster **In-Se** has a stronger capacity for visible light absorption, which is essential to achieve outstanding visible-light-driven photocatalytic performance. In order to further determine the positions of the conduction band (CB) and valence band (VB) edges of **In-S** and **In-Se** clusters, we characterized their Mott–Schottky curves. Their Mott–Schottky points have positive slopes, indicating that **In-S** and **In-Se** clusters are n-type semiconductors (Figure 3b,c). In general, the CB potential of an n-type semiconductor is ~0.10 V negative to the flat-band potential [37]. Therefore the CB potentials of the **In-S** and **In-Se** clusters are −1.06 and −1.19 V, respectively, relative to the NHE (normal hydrogen electrode), according to the calculations shown in Figure 3d and Table S1. In combination with their band gap values, the VB positions of **In-S** and **In-Se** clusters are calculated to be 2.18 and 1.54 V relative to NHE, respectively. Apparently, the potentials of CB and VB edges for **In-S** and **In-Se** clusters can straddle the redox potentials of  $\text{H}^+/\text{H}_2$  and  $\text{H}_2\text{O}/\text{O}_2$ , respectively, implying that these T3 clusters can be used to produce  $\text{H}_2$  by water splitting under visible light irradiation. Furthermore, the CB position of the

**In-Se** cluster is significantly higher than that of the **In-S** cluster, which provides a stronger driving force to photoexcited electrons for the  $H^+$  reduction [32]. This is another crucial factor in determining photocatalytic activity (Figure 3d).



**Figure 3.** (a) The optical absorption properties of **In-S** and **In-Se** clusters; Mott–Schottky plots of **In-S** (b) and **In-Se** clusters (c); (d) Schematic diagram of band structures for **In-S** and **In-Se** clusters.

To assess the photocatalytic  $H_2$  evolution performances of T3 clusters, the photocatalytic activity tests of **In-S** and **In-Se** before and after dispersion was carried out in the 10 vol% methanol aqueous solution under the irradiation of a 300 W Xe lamp equipped with a 420 nm cut-off filter for 10 h. The  $H_2$  generation rates of **In-S** and **In-Se** clusters were low in the initial several hours, but the activity increased gradually with the increasing illumination time. The activity remained almost constant with increasing irradiation time after the initial several hours of lag processes (Figure 4a). The average hydrogen production rates were about  $2.34 \mu\text{mol h}^{-1} \text{g}^{-1}$  for **In-S** cluster in the solid state and  $4.66 \mu\text{mol h}^{-1} \text{g}^{-1}$  in the highly-dispersed state, while they were  $4.42 \mu\text{mol h}^{-1} \text{g}^{-1}$  for **In-Se** clusters in the solid state and about  $23.81 \mu\text{mol h}^{-1} \text{g}^{-1}$  after high dispersion (Figure 4b). The photocatalytic  $H_2$  production activity of the **In-S** cluster in the highly-dispersed state is still low and only slightly higher than its performance in the solid state, mainly due to the limitation of its low visible-light absorption capability. Comparatively, the photocatalytic  $H_2$  generation activity of the **In-Se** cluster in the highly-dispersed state is about six times that in the solid state due to its intense visible light absorption and a large number of exposed surface active sites after dispersion, which is similar to the previously reported dispersible supertetrahedral  $Tn$  clusters [31–33]. Furthermore, the cycle performance of the photocatalytic  $H_2$  generation for the **In-Se** cluster was also recorded, as shown in Figure S4; it is found that the  $H_2$  generation rate of the **In-Se** cluster remained stable as the illumination time increased to 50 h, indicating that the **In-Se** cluster can be a stable catalyst for the photocatalytic  $H_2$  generation.



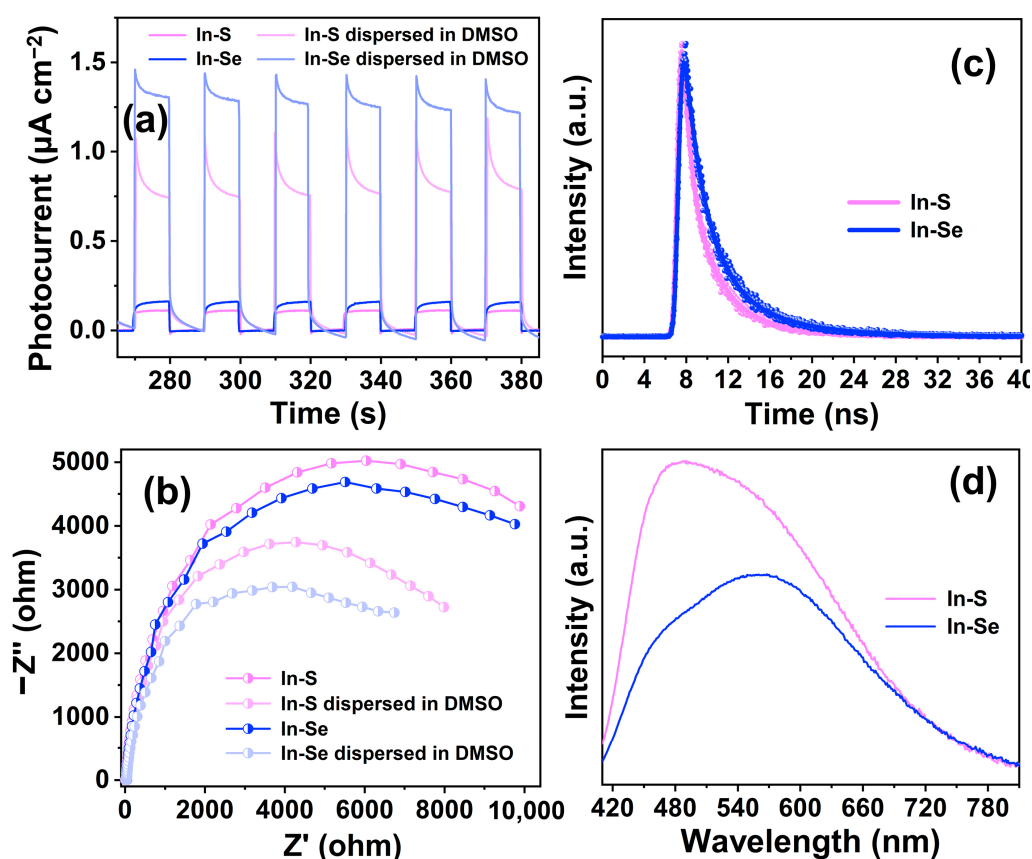
**Figure 4.** Comparison of hydrogen production (a) and photocatalytic performance (b) of **In-S** and **In-Se** clusters under visible light irradiation with the sacrificial reagent of TEOA.

#### 2.4. Photocatalytic Performance Analysis

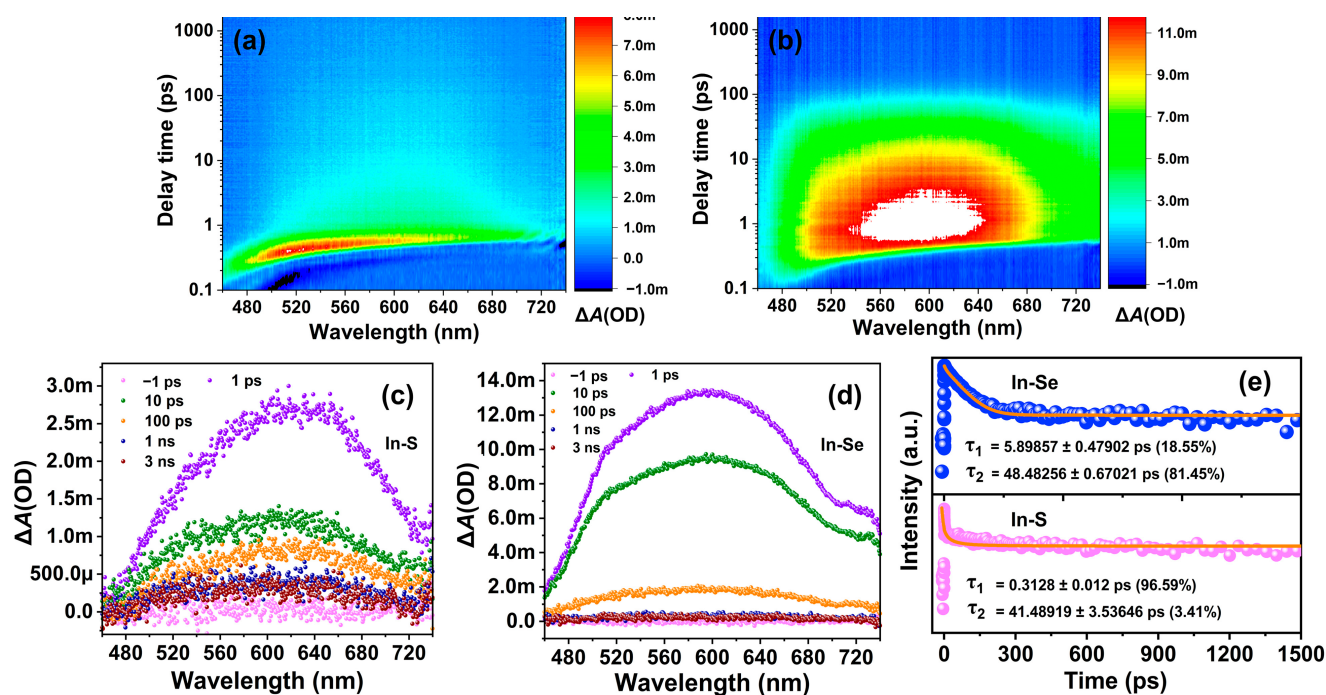
The separation efficiency of the photogenerated carriers is a vital factor influencing photocatalytic performance. In order to gain insight into the generation and transmission rates of carriers, we investigated the transient photocurrent behavior of **In-S** and **In-Se** clusters with solid and highly-dispersed states (Figure 5a). It is clearly observed that all T3 clusters exhibit a fast and consistent photocurrent response in each on/off cycle of visible light irradiation, and the photocurrent intensity of the highly-dispersed T3 clusters is obviously higher than that of the solid T3 clusters. In addition, under the same test condition, the photocurrent intensity of the selenide cluster **In-Se** is much higher than that of the sulfide cluster **In-S**. At the same time, we also tested the electrochemical impedance spectroscopy (EIS) of **In-S** and **In-Se** clusters to characterize their charge mobility (Figure 5b). The EIS Nyquist diagram of the **In-Se** cluster has a smaller semicircle radius than that of the **In-S** cluster, indicating that its charge transfer rate is faster than that of the **In-S** cluster. In addition, the fluorescence lifetimes of **In-S** and **In-Se** clusters were tested and fitted to further understand their charge transport behavior. Their fluorescence lifetime plots and fitting results (Table S2) indicate that the average lifetimes of **In-S** and **In-Se** clusters are 1.90 and 3.31 ns (Figure 5c), respectively. The longer fluorescence lifetime of the **In-Se** cluster indicates that the recombination probability of photogenerated carriers in **In-Se** clusters is lower, which improves the utilization rate of photon-generated carriers, contributing to achieving high photocatalytic activity. Compared with the **In-S** cluster, the fluorescence intensity of **In-Se** is significantly reduced (Figure 5d), which declares the significant reduction of recombination rate for the photoinduced carriers. The above results indicate that the separation and transmission of photoinduced carriers in the **In-Se** cluster is enhanced compared to that of the **In-S** cluster; the highly-dispersed T3 clusters are more favorable for the photoexcitation, generation and transport of electron-hole pairs compared to the solid states, which is consistent with their higher photocatalytic hydrogen production activity.

In order to further investigate the charge transfer dynamics during the photocatalytic process, the ultrafast transient absorption (TA) spectra of the obtained T3 clusters were executed, and the carrier behaviors were tracked in real-time. TA characterization was performed using a femtosecond ultraviolet pump with a wavelength of 365 nm and a white-light-continuum probe at the wavelength range of 460–740 nm. The pumping laser with a center wavelength of 365 nm can stimulate electrons to migrate from the VB to CB in the T3 clusters, according to the absorption spectra in Figure 3a. The TA data maps of **In-S** and **In-Se** clusters both have the characteristics of the initial signal formation and variation with the delay time as exhibited in Figure 6a,b, which verifies that the photoexcited electrons in the T3 clusters migrate to the adjacent interface states with low energy [38]. Figure 6c,d shows the TA spectra of **In-S** and **In-Se** clusters under the wavelength of 600 nm taken at the probe delays of −1, 1, 10, 100, 1000, and 3000 ps. The white-light-continuum detection

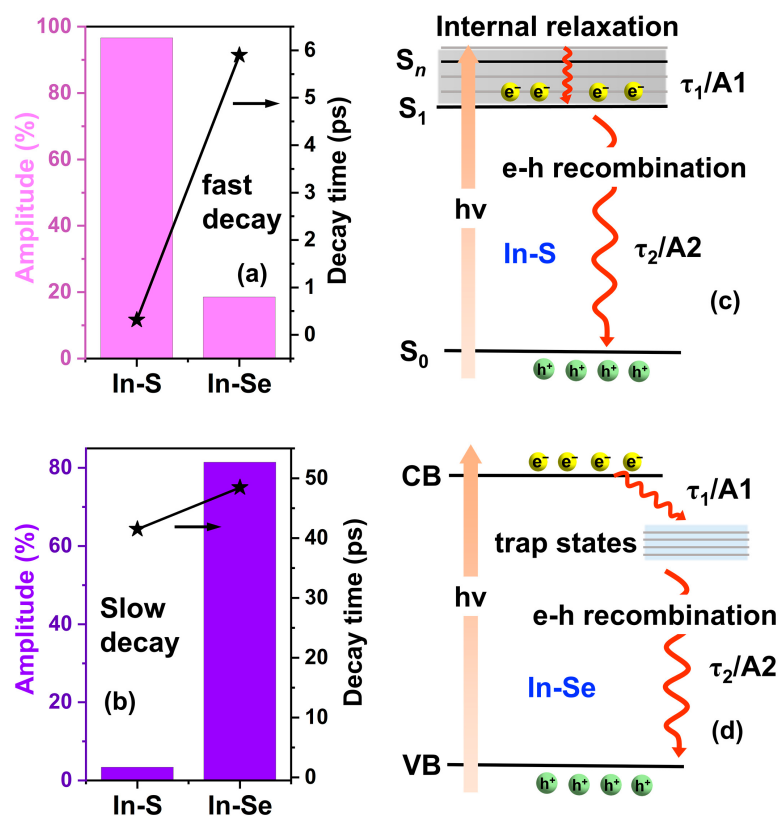
in the wavelength range of 460–780 nm shows the positive change of absorbance ( $\Delta A$ ) for **In-S** and **In-Se** clusters (Figure 6c,d), which is caused by excited state absorption (ESA). Obviously, the change of chemical composition in the T3 cluster does not bring out the essential variation of the absorption spectra, but it induces a significant difference in their TA kinetics. In addition, under the ultraviolet pump, both **In-S** and **In-Se** can generate photogenerated excitons and bring out the conspicuous ESA bands around 620 and 590 nm, respectively. Compared with that of the **In-S** cluster, the ESA bands for the **In-Se** cluster are slightly blue-shifted, which is consistent with the trend of the steady-state absorption spectra shown in Figure 5d. According to the  $\Delta A$  changes of **In-S** and **In-Se** in Figure 6c,d, we investigated the kinetic traces of **In-S** and **In-Se** probed at 600 nm. For **In-S** and **In-Se** clusters, the positive ESA signals both turned out to form immediately within  $\sim 100$  fs of the instrument response time. Bi-exponential fitting to the kinetic curves manifests two constants of decay times (Figure 6e). The fitting results towards subsequent recovery for **In-S** cluster are  $\tau_1 = (0.31280 \pm 0.01200)$  ps (96.59%) and  $\tau_2 = (41.48919 \pm 3.53646)$  ps (3.41%), with an average relaxation lifetime ( $\tau_{ave}$ ) of  $34.23679 \pm 3.22711$  ps, whereas they are  $\tau_1 = (5.89857 \pm 0.47902)$  ps (18.55%),  $\tau_2 = (48.48256 \pm 0.67021)$  ps (81.45%) and  $\tau_{ave} = 47.33438 \pm 0.64344$  ps, for **In-Se** cluster. Obviously, with the substitution of S with Se in the **In-S** cluster, the decay time constants (stars) and amplitude (bars) of  $\tau_1/A_1$  and  $\tau_2/A_2$  corresponding to the fast and slow processes, respectively, have dramatically changed, as shown in Figure 7a,b. The absolute predominance of A1 relative to A2 for the **In-S** cluster illustrates the primary process of fast relaxation.



**Figure 5.** Transient photocurrent (a) and impedance diagrams (b) for **In-S** and **In-Se** clusters; fluorescence lifetime (c) and fluorescence spectra (d) of **In-S** and **In-Se** clusters.



**Figure 6.** Transient absorption data maps of (a) In-S and (b) In-Se clusters under an excitation wavelength of 375 nm; transient absorption spectra of (c) In-S and (d) In-Se clusters at selected timescales; (e) kinetic traces for In-S and In-Se clusters probed at the wavelength of 600 nm.  $\Delta A$ , change in absorbance; OD, optical density units.



**Figure 7.** The extracted amplitudes (column) and decay times (star) of (a) fast and (b) slow decay components for In-S and In-Se clusters. Proposed relaxation diagram within (c) In-S and (d) In-Se clusters.

On the contrary, the slow relaxation process is dominant for the **In-S** cluster. According to TA observations and previous reports, the related mechanisms of photogenerated carrier dynamics in the **In-S** and **In-Se** clusters have been illustrated. For **In-S** cluster, the electrons would jump from the ground state  $S_0$  to a certain excited state  $S_n$  under the action of the laser pulse, then followed by a rapid internal deactivation process to the lowest-lying excited state  $S_1$ , corresponding to the  $\tau_1/A1$  relaxation process [39,40]; then, the excited state electrons subsequently recombine with the holes in the ground state  $S_0$ , representing the  $\tau_2/A2$  relaxation process (Figure 7c) [41,42]. Comparatively, for the **In-Se** cluster,  $\tau_1/A1$  is assigned to the photoexcited electrons that undergo a fast relaxation from CB to the surface trap states (formed by the partial surface oxidation of selenides), and  $\tau_2/A2$  is defined as the following non-radiative recombination of electron-hole pairs (Figure 7d) [34,40,43]. Therefore, the existence of surface trap states and the primary  $\tau_2$  relaxation process in the **In-Se** cluster effectively inhibit the electron-hole recombination and extend the lifetime of photogenerated electrons, rendering more electrons to participate in  $H^+$  reduction, which contributes to its excellent photocatalytic activity [11,43–45].

### 3. Materials and Methods

#### 3.1. Materials

All chemical reagents used are commercially available and can be used without further purification. Sulfur (S, 99%) was available from Kermel Chemical Reagent Co., Ltd. (Tianjin, China); selenium (Se, AR) was bought from Yingda Rare Chemical Regents Factory (Tianjin, China); indium (In, 99%) was traded from Xinlong Tellurium Technology Development Co., Ltd. (Sichuan, China); 1-butyl-2,3-dimethylimidazolium chloride ([Bmmim]Cl, 99%) was purchased from Lanzhou Institute of Chemical Physics, CAS (Gansu, China); 1,5-diazabicyclo [4,3,0]-5-nonene ( $C_7H_{12}N_2$ , 97%) and 1-methylimidazole ( $C_4H_6N_2$ , 99%) were both bought from Adamas Chem Co., Ltd. (Shanghai, China).

#### 3.2. Preparation of Catalysts

Synthesis of In-Q-ILs ( $Q = S, Se$ ) precursors. The In-Q-ILs precursors were synthesized by the ionic liquid method under nitrogen protection. Firstly, 10.0 mmol of In (1.148 g), 25 mmol of S or Se, and 18.5 mmol of ionic liquid [Bmmim]Cl (3.500 g) were mixed and added into a 50 mL of a double-pass round-bottom glass bottle, which was then placed in a magnetic stirrer, vacuumized and filled with nitrogen, keeping the reactants in a nitrogen-protected environment. The reaction was performed at 190 °C for 5 h with a magnetic stirring speed of 720 r/min. Finally, a dark-red gel was obtained.

Synthesis of In-Q ( $Q = S, Se$ ) T3 clusters. The above precursors were diluted with 5 mL of acetonitrile; then the precursor solution was divided into five by mass and mixed with 0.5 mL of 1,5-diazabicyclo [4,3,0]-5-nonene and 1 mL of 1-methylimidazole, respectively and placed in a 20 mL of Teflon reactor, which was then sealed with an autoclave and heated to 160 °C in a programmed temperature rise oven within 3 h. The reaction was then carried out at a constant temperature of 160 °C for 6 days, followed by cooling to room temperature at a rate of 0.045 °C min<sup>-1</sup>. Finally, the reaction products were washed several times with anhydrous ethanol. Yellow ( $Q = S$ ) and orange-yellow ( $Q = Se$ ) solid crystals were obtained, named [Bmmim]<sub>6</sub>In<sub>10</sub>S<sub>16</sub>Cl<sub>4</sub>·(MIm)<sub>4</sub> (**In-S**) and [Bmmim]<sub>6</sub>In<sub>10</sub>Se<sub>16</sub>Cl<sub>4</sub>·(MIm)<sub>4</sub> (**In-Se**), respectively. Elemental analyses: Calculated for ( $C_9H_{17}N_2$ )<sub>6</sub>In<sub>10</sub>S<sub>16</sub>Cl<sub>4</sub>( $C_4H_6N_2$ )<sub>4</sub> (**In-S**, formula mass: 3050.86), C 27.56%, H 4.16%, N 9.18%, S 16.82%, found, C 27.19%, H 4.47%, N 8.13%, S 16.03%; and calculated for ( $C_9H_{17}N_2$ )<sub>6</sub>In<sub>10</sub>Se<sub>16</sub>Cl<sub>4</sub>( $C_4H_6N_2$ )<sub>4</sub> (**In-Se**, formula mass: 2801.24), C 22.12%, H 3.34%, N 7.37%, found, C 20.62%, H 3.30%, N 7.05%.

#### 3.3. Characterizations

Powder X-ray diffraction (PXRD) data of the samples were collected after grinding on a Rigaku MiniFlex II powder diffractometer with a Cu target ( $\lambda = 1.54178 \text{ \AA}$ ) in the  $2\theta$  range of 3–65°. Elemental analysis (EA) data were obtained on the Element Vario EL III elemental analyzer, and C, H, and N elements of samples were analyzed. Thermogravimetric analysis

(TGA) data were obtained after testing on a NETZSCH STA 449F3 Thermogravimetric Analyzer, with approximately 10 mg of the sample selected for testing under a dry nitrogen atmosphere, the heating rate was 10 °C/min, and the test temperature range was from room temperature to 800 °C. Electron energy spectroscopy (EDX) was performed using the JEOL JSM6700F field emission scanning electron microscope with the Oxford INCA system. Transmission electron microscopy (TEM) was performed using a JSM-6700 field emission scanning electron microscope for image and data acquisition. Morphologies were characterized on a FEI Tecnai G2 F20 Transmission Electron Microscopy (TEM) in a vacuum with pressure of  $\sim 1.42 \times 10^{-4}$  Pa. Solid state optical diffuse reflectance spectra were performed at room temperature using a Shimadzu UV-2600 spectrometer in the range of 200–800 nm with a BaSO<sub>4</sub> plate as a standard (100% reflectance). The absorption spectrum was calculated from the reflection spectrum by using the Kubelka–Munk function [46]. Fluorescence emission spectra and fluorescence lifetimes were recorded on a PerkinElmer LS55 fluorescence spectrometer at room temperature. Transient absorption (TA) measurements were performed on the Helios (Ultrafast systems) spectrometers using a regeneratively amplified femtosecond Ti-sapphire laser system (Spitfire Pro-F1KXP, Spectra-Physics; frequency, 1 kHz; pulse width, 120 fs) at room temperature, and the data were analyzed through commercial software (Surface Explorer, Ultrafast Systems).

### 3.4. Photocatalytic Performance Tests

All the photocatalytic H<sub>2</sub> evolution experiments were carried out in a closed glass circulation system (CEL-SPH2N-D9) with nitrogen as the driving gas and 99.999% of argon as the carrier gas. For the solid samples, 10 mg of a solid sample, 90 mL of deionized water, 10 mL of triethanolamine (TEOA), and 33.5 µL of H<sub>2</sub>PtCl<sub>4</sub> (0.077 mol<sup>−1</sup> L<sup>−1</sup>) were first added sequentially to a 250 mL of the quartz reaction vessel, and then a rotor was added for stirring at 400 r/min. For the highly-dispersed sample, 10 mg of solid sample was added to 1 mL DMSO and completely dispersed by sonication, then the highly-dispersed sample, 90 mL of distilled water, 10 mL of TEOA and 33.5 µL of H<sub>2</sub>PtCl<sub>4</sub> (0.077 mol<sup>−1</sup> L<sup>−1</sup>) were added to a 250 mL of quartz reactor with the stirring at 400 r/min. During the photocatalytic process, TEOA, H<sub>2</sub>PtCl<sub>4</sub>, and DMSO acted as the hole sacrificial reagent, the source of cocatalyst Pt, and the solvent for the T3 cluster, respectively. Then, the system was evacuated and irradiated by a 300 W Xe lamp equipped with a cut-off filter ( $\lambda \geq 420$  nm), and the evolved hydrogen was monitored via online gas chromatography (AULTT GC-7920, molecular sieve 5A, thermal conductivity detector).

### 3.5. Electrochemical Measurements

The electrochemical experiments were carried out on a CHI660E electrochemical workstation using a three-electrode system with Indium-Tin Oxide (ITO) glass containing the target compound as the working electrode, Ag/AgCl as the reference electrode, and platinum wire as the counter electrode. Na<sub>2</sub>SO<sub>4</sub> aqueous solution (0.5 M) was used as the supporting electrolyte solution. A working electrode was prepared according to the following procedure: 5 mg of samples were dissolved in 420 µL of absolute ethanol, 50 µL of deionized water and 10 µL of D-520 Nafion dispersion with ultrasonication to obtain a uniform suspension, and then 40 µL of the suspension was deposited on a 10 × 10 mm area of a 10 × 40 mm ITO glass electrode.

## 4. Conclusions

Two pure inorganic supertetrahedral discrete T3 clusters In-Q (Q = S, Se) stabilized by the ionic liquid [Bmmim]Cl were prepared by a two-step reaction precursor technology. Notably, these T3 clusters exhibit good dispersity in DMSO, and the dispersed T3 clusters are able to expose more photocatalytic active sites. Specifically, under visible light irradiation, the photocatalytic hydrogen production activity of the highly-dispersed **In-Se** cluster is about five times higher than that of the solid **In-Se** cluster, whereas the photocatalytic activity of the highly-dispersed **In-S** cluster is barely higher than that in the solid one. The

reasons for the obvious difference of photocatalytic activity in the highly-dispersed T3 cluster under visible light irradiation have been systematically analyzed by ultrafast transient absorption spectra combined with the band structures, electrochemical characterizations, steady-state and time-resolved fluorescence techniques: (1) The inferior visible-light absorption capability of **In-S** cluster limits the effective utilization of photons; (2) the higher CB position of the **In-Se** cluster provides a more powerful driving force to photoinduced electrons for  $H^+$  reduction; (3) under illumination, the distinct photogenerated carriers dynamics results in a significant reduction of photogenerated carrier recombination rate. This work establishes the connection between the structure and photocatalytic activity of highly-dispersed discrete metal chalcogenide nanoclusters for the first time by ultrafast excited-state dynamic, which is of great significance for developing the atomically precise nano-chemistry and meanwhile will inspire more meaningful researches in the field of nanocluster chemistry.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal13081160/s1>, Figure S1: ORTEP plots of anionic clusters in compound **In-S**, displacement ellipsoids are plotted with 50% probability; Figure S2: EDS spectrum of the compound **In-S**; Figure S3: EDS spectrum of the compound **In-Se**; Figure S4: Hydrogen production of compound **In-Se** under visible light irradiation for 50 h. Table S1: Crystallographic data and refinement details for compound **In-S**; Table S2: The results of band edge position calculations for **In-S** and **In-Se**; Table S3: The best fitting parameters of fluorescence lifetime for **In-S** and **In-Se**.

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