Assembling metallic 1T-MoS$_2$ nanosheets with inorganic-ligand stabilized quantum dots for exceptional solar hydrogen evolution

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Due to enhanced light harvesting, favored interfacial charge transfer and excellent proton reduction activity, the hybrid photocatalysts of metallic 1T-MoS$_2$ nanosheets and inorganic-ligand stabilized CdSe/ZnS QDs obtained via a self-assembled approach can produce H$_2$ gas with a rate of ~$155 \pm 3.5$ mol h$^{-1}$ mg$^{-1}$ under visible-light irradiation (\(\lambda = 410\) nm), an exceptional performance of solar H$_2$ evolution using MoS$_2$ as cocatalysts known to date.

Water splitting is regarded as a promising avenue to achieve solar-to-fuel conversion via photocatalytic hydrogen (H$_2$) evolution.$^1$ In this regard, platinum has shown excellent electrocatalytic and photocatalytic activities toward H$_2$ evolution. Unfortunately, the high cost and scarcity limit its large-scale application. Therefore, development of earth-abundant, low-cost and high-efficient cocatalysts to realize sustainable and large-scale H$_2$ production is in its great necessity. MoS$_2$, evidenced by experimental and theoretical results, is a very promising candidate for both electro- and photo-catalytic H$_2$ evolution.$^2$ Due to the extremely large edge-site exposure, excellent electronic conductivity and abundant new formed trap states and vacancies, metallic 1T-MoS$_2$ nanosheets have attracted special attention in recent years for photocatalytic H$_2$ production than the state-of-the-art forms of MoS$_3$.$^3$

Unlike electrocatalytic H$_2$ evolution, the use of 1T-MoS$_2$ nanosheets for photocatalytic H$_2$ production is in its infancy.$^4$ For establishing a high-efficient photocatalytic H$_2$ evolution system using 1T-MoS$_2$ nanosheets, the following aspects should be achieved: (1) excellent visible-light response and exciton generation of the light absorbers are required; (2) intact coupling between light absorbers and two-dimensional 1T-MoS$_2$ nanosheets is preferred; and (3) the energy barrier of interfacial electron transfer from light absorbers to the two-dimensional nanosheets should be greatly reduced. Among various light absorbers, colloidal semiconductor quantum dots (QDs) are regarded as the ideal candidate due to their predominant advantages in visible-light harvesting, multi-exciton generation, charge separation, and easy to surface modification.$^5$ Furthermore, modification of QDs with metal-free inorganic ligands, such as chalcogenide anions, can greatly reduce the energy barrier of interfacial charge transport, which would provide advantages for enhanced solar H$_2$ production.$^6$ Therefore, coupling 1T-MoS$_2$ nanosheets with all-inorganic QDs would be a promising approach to achieve high efficiency of solar-to-fuel conversion via solar H$_2$ evolution.

In the present work, we, for the first time, couple metallic 1T-MoS$_2$ nanosheets with all-inorganic CdSe/ZnS QDs for solar H$_2$ evolution via a self-assembled approach. Under the optimal conditions (\(\lambda = 410\) nm), the rate of H$_2$ evolution was estimated to be ~$155 \pm 3.5$ mol h$^{-1}$ mg$^{-1}$ which is an exceptional performance of solar H$_2$ evolution using MoS$_2$ as the cocatalyst. Experimental evidence indicates that the extremely high activity of solar H$_2$ production arises from the synergistic effect of the enhanced light absorbing and exciton generation of CdSe/ZnS QDs, the reduced energy barrier of interfacial charge transfer and also the abundant active sites for proton reduction of 1T-MoS$_2$ nanosheets. In virtue of these advantages, the self-assembled photocatalysts show excellent activity towards solar H$_2$ evolution.

Scheme 1 Schematic illustration of the fabrication of QDs/1T-MoS$_2$ photocatalysts via a self-assembled approach.
pattern in the inset panel of Fig. 1c showed a typical hexagonal spot pattern corresponding to 2H-MoS₂. The extra strong hexagonal spot at 30° between the hexagonal spots could be assigned to 1T-MoS₂. The coexistence of 1T-MoS₂, the regions in red circles, and 2H-MoS₂, the regions in green circles, could be further evidenced by high-resolution TEM image in Fig. 1d. Also, abundant trap sites were directly observed in TEM image as denoted by the white arrows in Fig. 1d, indicating the abundant active sites. All inorganic CdSe/ZnS QDs were obtained by a modified successive ionic layer adsorption and reaction method of growing ZnS shell on the surface CdSe cores, see detailed characterizations in Fig. S1-S3. Because of the strong electrostatic attraction between negatively charged QDs and positively charges MoS₂ nanosheets and the coordination of sulfur with molybdenum, CdSe/ZnS QDs could spontaneously assemble with 1T-MoS₂ nanosheets to form composite photocatalysts in aqueous solution. TEM image in Fig. 1e directly verified the successfully loading of QDs on the surface of 1T-MoS₂ nanosheets. The enlarged TEM images showed lattice fringes of about 3.45 Å (Fig. 1f) and 6.80 Å (Fig. 1g), which could be ascribed to the [111] plane of QDs and (002) plane of MoS₂, respectively, directly confirming the QDs on 1T-MoS₂ nanosheets.

The composite photocatalysts of QDs/1T-MoS₂ were prepared through a self-assembled process, as shown in Scheme 1. Metallic 1T-MoS₂ nanosheets were obtained via lithium intercalation of bulk-MoS₂ for one week at room temperature, see details in supporting information. The dramatically diminished intensity of (002) peak of bulk MoS₂ in X-ray diffraction (XRD) pattern indicated the destruction of long-range stacking of the layered structure into exfoliated nanosheets (Fig. 1a). The broadening of all peaks showed poor crystallinity of the obtained materials. The decreased intensity of Raman peaks at 410 cm⁻¹ and 384 cm⁻¹ also indicated the destruction of layered packing structure of bulk MoS₂. Besides, the emergence of new Raman shifts at 152 cm⁻¹, 226 cm⁻¹ and 340 cm⁻¹ could be ascribed to phonon modes of 1T-MoS₂, confirming the transformation of bulk 2H-MoS₂ to 1T-MoS₂ counterparts (Fig. 1b). Transmission electron microscopy (TEM) verified the ultrathin nature of the as-prepared 1T-MoS₂ samples (Fig. 1c). Selected area electron diffraction (SAED)
under identical condition. Control experiments indicated that QDs, 1T-MoS₂ nanosheets and sacrificial reagent were all necessary for efficient photocatalytic H₂ evolution (Fig. S4). The effect of weight percentage of 1T-MoS₂ nanosheets on the rate of H₂ production was carefully investigated. As shown in Fig. 2b, progressive increase of the weight percentage of 1T-MoS₂ from 0 to 4.8 wt% significantly improved the activity of photocatalytic H₂ production. However, further increasing the weight percentage of 1T-MoS₂ reduced the rate of H₂ evolution, which was due to the light-screening effect of excessive amount of cocatalysts. Under the optimal conditions, the assembled photocatalysts of inorganic-ligand stabilized CdSe/ZnS QDs and 1T-MoS₂ nanosheets could evolve H₂ gas with a constant rate of \( \sim 156 \pm 3.5 \text{ ~umol h}^{-1} \text{mg}^{-1} \) during 10 h irradiation (Fig. 2c). The photocatalytic activity significantly declined after a long-time irradiation. With addition of extra amount of sacrificial reagent into the system, the activity of solar H₂ evolution recovered immediately (Fig. S5). The similar rate of H₂ evolution with that of the initial stage indicated the depletion of electron donor was the major reason of declined H₂ production activity.

![Figure 3](image_url) (a) Steady-state emission quenching and (b) corresponding lifetime decay of QDs by coupling with different amounts of 1T-MoS₂ nanosheets; (c) transient photocurrent responses of bare MoS₂, bare CdSe/ZnS QDs, CdSe/ZnS QDs/1T-MoS₂ (4.8 wt%) and CdSe/ZnS QDs/bare MoS₂ (4.8 wt%) electrodes to on-off illumination (λ > 400 nm); (d) electrochemical impedance spectroscopy Nyquist plots of bare QDs, bare MoS₂ and CdSe/ZnS QDs/1T-MoS₂ (4.8 wt%) electrodes.

In order to reveal the intrinsic reasons of the exceptional photocatalytic H₂ evolution performance of this system, various experiments have been performed. As shown in Fig. S6, the obtained CdSe/ZnS QDs acquired much better light response in the realm of visible-light region. Compared with CdSe core, the band-edge emission of CdSe/ZnS QDs was dramatically enhanced along with the decrease of trap-state emission, which would inhibit exciton trapping at trap states (Fig. S7). As shown in Fig. 3a, the emission intensity of CdSe/ZnS QDs was dramatically quenched by coupling with 1T-MoS₂ nanosheets, suggesting that the recombination of photogenerated electron-hole pairs was efficiently inhibited. Also, the emission lifetime of CdSe/ZnS QDs decayed from \( \sim 20 \) to \( \sim 9.0 \) ns upon assembling with 1T-MoS₂ nanosheets (Fig. 3b), indicating the well interfacial electron transfer from QDs to 1T-MoS₂ nanosheets.

Photoelectrochemical measurements provided more information on the process of facile interfacial charge transfer. As shown in Fig. 3c, the photocurrent transient responses of QDs/1T-MoS₂ (4.8 wt%) electrode were much higher than those of QDs, bare MoS₂ and QDs/bare MoS₂ counterparts under the same conditions. The much smaller arc radius of electrochemical impedance spectroscopy (EIS) Nyquist plot of QDs/1T-MoS₂ (4.8 wt%) electrode than those of bare QDs and bare MoS₂ implied the faster interfacial electron transfer (Fig. 3d). The favored interfacial electron transfer from inorganic-ligand stabilized QDs to cocatalysts of 1T-MoS₂ was also directly confirmed by solar H₂ evolution experiments, as shown in Fig. 2d. When the surface ligands of CdSe/ZnS QDs were replaced by organic counterparts, such as 3-mercaptopropionic acid, the rate of photocatalytic H₂ evolution decreased to \( \sim 68 \text{ ~umol h}^{-1} \), which was only one sixth of the inorganic ligands stabilized counterparts (\( \sim 400 \text{ ~umol h}^{-1} \)) under identical conditions.

Besides, the abundant trap states and edge sites of the obtained 1T-MoS₂ contributed a lot to the remarkable solar H₂ production performance. It had been reported that both S-vacancy and Mo-edge of MoS₂ demonstrated a close-to-zero Gibbs free energy change,\(^6\) thus promoting the processes of proton adsorption and reduction at active sites of 1T-MoS₂ nanosheets (Fig. S8). Taken all together, we can conclude that the enhanced visible-light response, the facilitated interfacial charge transfer, and the excellent proton reduction ability of metallic 1T-MoS₂ nanosheets enable this system to show exceptional activity of solar H₂ evolution.

In summary, we have firstly coupled 1T-MoS₂ nanosheets with inorganic-ligands stabilized CdSe/ZnS QDs via a self-assembling approach for solar-to-fuel conversion application. The obtained assembled photocatalysts is able to evolve H₂ gas with a rate of \( \sim 156 \pm 3.5 \text{ ~umol h}^{-1} \text{mg}^{-1} \) under the optimum conditions. The unprecedented activity of solar H₂ evolution is a result of enhanced light harvesting, the facilitated interfacial charge transfer and excellent proton reduction ability of vacancy-rich 1T-MoS₂ nanosheets. It is anticipated that this research line can lead to the fabrication of smarter, cheaper and more robust artificial photocatalysts for solar H₂ evolution, which is actively undergoing in our research group.

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Notes and references


