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Importance of the structural integrity of a carbon conjugated mediator for photocatalytic hydrogen generation from water over a CdS–carbon nanotube–MoS₂ composite†

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Incorporation of CdS quantum dots is shown to significantly promote photocatalytic hydrogen production from water over single-layer MoS₂ in a remote manner via their dispersions on a carbon nanotube as a nanocomposite: the hydrogen evolution rate is found to be critically dependent on the content and structural integrity of the carbon nanotube such that the double-walled carbon nanotube shows superior H₂ production to a single-walled carbon nanotube because the inner carbon tubules survive from the structural damage during functionalization.

The depletion of fossil fuel reserves and the undeniable environmental harm caused by their overconsumption make photocatalytic H₂ production from water attractive as a future renewable energy source.^{1,2} Typically, photocatalytic splitting of water requires semiconductors to capture a photon with energy equal to or greater than their band gap energy. The photons are absorbed by a semiconductor nanocrystal, causing the generation of photo-excited electrons and holes in the conduction and valence bands, respectively. The excited electron-hole pairs, known as excitons, are then subjected to two main competitive deactivation routes, namely exciton recombination and exciton separation followed by chemical reactions. The former route is undesirable in photocatalysis, since this only emits heat or light with no chemical process involved, whereas the latter is important for photocatalytic reduction of water to hydrogen gas.

Nanosize CdS is a quantum dot material for efficient capture and emission of photons due to its characteristic band edges and band gap.^{3,4} However, it displays very poor photocatalytic

activity due to rapid exciton recombination.^{5,6} On the other hand, molybdenum disulfide (MoS₂) is not an intrinsically active semiconductor to capture photons in photo-catalysis but its conduction band (−0.12 eV vs. NHE) and valence band (1.78 eV vs. NHE) render it suitable for electrochemical water-splitting.⁷ It has been reported that an intimate CdS/MoS₂ mixture can catalyze photocatalytic H₂ evolution efficiently.⁸ In addition, CdS supported on carbon materials is also proven to suppress charge recombination and provide active adsorption sites, which leads to the enhancement of photocatalytic activity.^{9–13} Furthermore, the use of graphene to support CdS quantum dots and single layer MoS₂ (s-MoS₂) appears to give a higher hydrogen evolution rate.⁷ The functional roles of each component in these composite mixtures and their synergistic effect(s) for photocatalytic H₂ evolution are not yet clear. It is believed that by elucidating such material interactions, a rational design of composite materials for more efficient photocatalytic conversion into chemicals could be developed.

Here we report the systematic study of correlation of the photocatalytic H₂ activity with the structural and electronic properties of CdS and s-MoS₂ and interactions with surface functionalized single, double and multi-walled carbon nanotubes (SWNTs, DWNTs and MWNTs) (see the ESI†) in composites using a range of characterization techniques including XRD, TEM, SAED and Raman. In particular, the time-resolved photoluminescence (TRPL) technique is invoked to investigate the lifetime of excitons with reference to activity measured for this type of composite. It is found that the exciton recombination that readily takes place on CdS upon light activation can be effectively quenched when it is mixed with carbon nanotubes (CNTs) due to rapid transfer of the photo-excited electrons to the carbon structure before the proton reduction from water for the hydrogen production over s-MoS₂. Thus, the light capturing sites (CdS) can be separated from hydrogen production sites (s-MoS₂) via CNTs as electronic mediators. A higher hydrogen production rate is achieved over the two finely dispersed phases on the CNT than without the carbon structure due to its higher electron

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conductivity and storage capacity.^{14,15} It is also found that typical acid functionalization of CNTs for the immobilization of CdS and MoS₂ can lead to destruction of surface graphitic conjugation, affecting the essential process of electron transfer, which will lead to poor activity. As a result, DWNTs with intact inner carbon tubules act as optimal electron mediators for photocatalytic hydrogen production.

The powder XRD pattern of synthesised CdS quantum dots according to the literature is shown in Fig. S1(a) (ESI[†]), which confirms the CdS cubic structure. The Scherrer equation revealed an average particle size of 4.76 nm. This suggests small but uniform CdS nanoparticle size. The UV-visible absorption of CdS presented in Fig. S1(b) (ESI[†]) features an absorption hump at 472 nm corresponding to a reported band gap of 2.63 eV.^{3,4} The TEM image also reveals typical 4.32 nm CdS nanoparticles and their size distribution is shown in Fig. S1(c) and (d) (ESI[†]). Single layer MoS₂ has also been synthesised (see the ESI[†]). Fig. S2 (ESI[†]) clearly shows that CdS nanoparticles tend to aggregate on the basal and edge regions of the restacked s-MoS₂ sheets with more than one monolayer thickness. The severe aggregation of CdS and s-MoS₂ at the material interface indicates a poor dispersion of these components for light capture and charge (exciton) separation. It was envisaged that dispersion of CdS and s-MoS₂ on high surface area CNTs may overcome the problems. Typical HNO₃ acid pre-treatment on CNTs has been applied for the removal of contaminants (such as amorphous carbon and catalyst particles) and also functionalization of the outer carbon structure with terminal carboxyl and hydroxyl groups for the immobilization and dispersion of a solid phase in the composite.¹⁶ A detailed selection of acid treatments was reviewed, which revealed that most of the treatments can not only effectively remove contaminants but also cause shortening of tube length and functionalize the carbon surface.¹⁷ Among various acids and concentrations applied, 3 M HNO₃ was regarded as the optimum concentration and served as a compromise between the yield of the functional groups created on CNTs and the chemical damage to the CNT structure. Therefore, the 3 M HNO₃ treatment was chosen for the CNT pre-treatment. The photocatalytic hydrogen production activity of the composite samples with lactic acid as the sacrificial reagent was measured. Fig. 1(a) shows that CdS or CdS/DWNTs are totally inert for the hydrogen production, implying that CdS and the CdS/DWNT interface cannot provide sites for proton reduction despite the well-known light capture ability for exciton production over the CdS and DWNT phases. In contrast, when s-MoS₂ is used, a significant quantity of H₂ is produced (137 $\mu\text{mol h}^{-1} \text{g}^{-1}$). Furthermore, the CdS/s-MoS₂ composite produces 1380 $\mu\text{mol h}^{-1} \text{g}^{-1}$ H₂, which is clearly greater than CdS or s-MoS₂ alone.⁷ There is a further increase in the amount of evolved H₂ gas when DWNTs are added to the CdS/s-MoS₂ (see E, F, G).

With an increased amount of DWNTs added, a maximum of H₂ gas is evolved (5728 $\mu\text{mol h}^{-1} \text{g}^{-1}$) at a 5 mg DWNT content. However, further increase in the amount of DWNTs could impair the photocatalytic H₂ production, presumably due to masking of active sites, *i.e.* the shielding effect,⁴ when 7 mg of DWNTs is used. Upon comparing different forms of CNTs

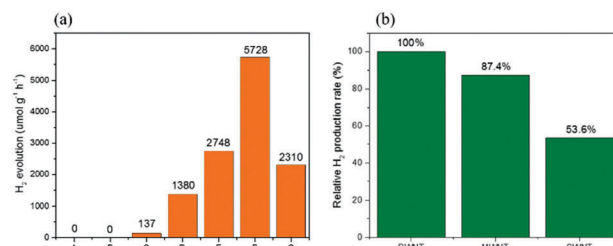


Fig. 1 (a) Hydrogen evolution rate for 20 mg of catalysts extracted from (A) CdS, (B) CdS/DWNT, (C) s-MoS₂, (D) CdS/s-MoS₂, (E) CdS/2 mg DWNT/s-MoS₂, (F) CdS/5 mg DWNT/s-MoS₂, and (G) CdS/7 mg DWNT/s-MoS₂. (b) Hydrogen evolution rate for 5 mg of DWNTs; MWNTs and SWNTs to support CdS and s-MoS₂.

(SWNTs, DWNTs and MWNTs) with the same loading, see Fig. 1(b), the DWNT composite gives the best activity on a per gram basis. Noticeably, the SWNT composite gives only half a H₂ production rate compared to the DWNT. As a result, the functional roles for each component particularly the nature and quality of CNTs as supports with respect to hydrogen production activity were investigated through careful material characterisation studies. To explore the charge (exciton) dynamics within the synthesised composites, the samples were examined using static and time-resolved photoluminescence spectroscopy (PL and TRPL). The steady-state PL spectra at an excitation wavelength of 405 nm shown in Fig. 2a contain anticipated strong emission from CdS quantum dots centred at 750 nm by recombination of excitons from the trap-state. However, CdS quantum dots when mixed with either CNTs or s-MoS₂ or CNT/s-MoS₂ exhibit much smaller trap-state peaks compared with CdS alone, suggesting that the radiative recombination of excitons in CdS is minimised. CNTs appear to be more effective in quenching the PL than MoS₂ on the same weight basis but the CdS/DWNT/s-MoS₂ mixture is the most effective. Fig. 2b shows the effectiveness

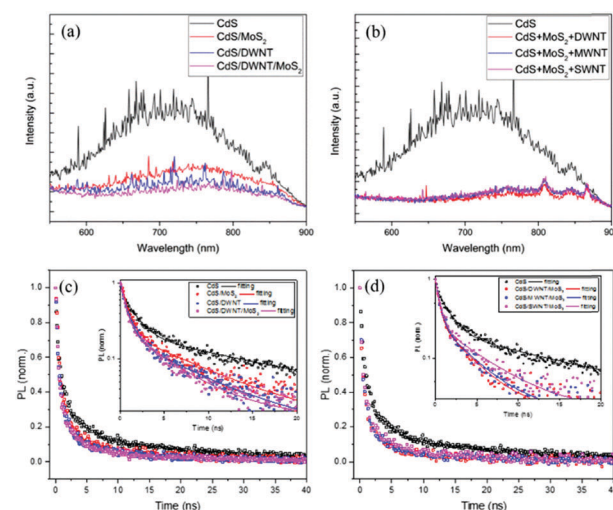


Fig. 2 Steady state PL, excitation 405 nm, for (a) CdS samples with different components and (b) CdS and CdS/CNT/s-MoS₂ samples. Time-resolved PL with decay monitored at 750 nm, excitation 405 nm, for (c) CdS samples with different components and (d) CdS and CdS/CNT/s-MoS₂ with different natures of CNTs.



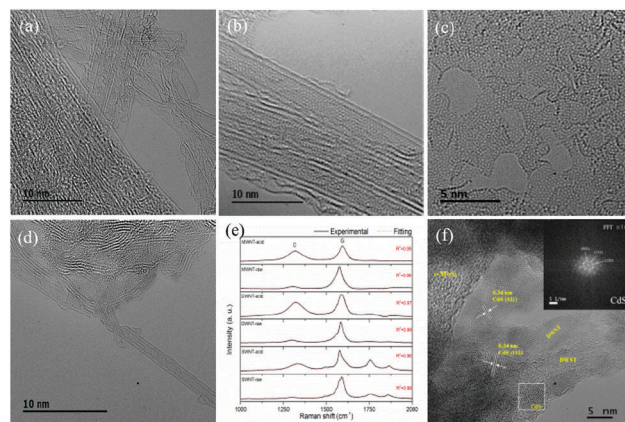
Table 1 The fractional contribution (f_i) and lifetime (τ_i) of each decay component & average lifetime (τ_{avg}) for various samples

Material	f_1 (%)	τ_1 (ns)	f_2 (%)	τ_2 (ns)	τ_{avg} (ns)
CdS	20.8	1.45	79.2	16.03	13.00
CdS/MoS ₂	27.3	0.74	72.7	7.82	5.88
CdS/DWNT	30.9	0.79	69.1	6.83	4.97
CdS/DWNT/MoS ₂	28.4	0.64	71.6	3.96	3.02
CdS/MWNT/MoS ₂	33.9	0.89	66.1	4.72	3.42
CdS/SWNT/MoS ₂	26.8	0.79	73.2	5.90	4.53

of DWNTs, MWNTs and SWNTs in quenching the trap-state emission PL. From TRPL (Fig. 2c and d), an average lifetime (τ) for exciton recombination for each sample was derived and is shown in Table 1. The pristine CdS demonstrates an average lifetime of 13.00 ns; upon mixing with s-MoS₂ and DWNTs, the photo-generated carriers are indeed significantly quenched, where the DWNTs again show better quenching ability compared to s-MoS₂. This indicates that the collection/extraction of photo-excited electrons from CdS to s-MoS₂ *via* DWNTs is more efficient than that of CdS/s-MoS₂, presumably due to the electron storage and mobility of DWNTs. Among all the samples, CdS/DWNT/s-MoS₂ displays the lowest τ (3.02 ns). Similar to the static PL, SWNTs (4.53 ns) are less effective than MWNTs (3.42 ns) and DWNTs (3.02 ns) in quenching the exciton emission. As MoS₂ is only the component to provide active sites for proton reduction to hydrogen (see Fig. 1), it is likely that the photoelectrons generated by CdS upon light excitation are quickly taken up by the CNTs before passing to s-MoS₂. Apparently, the nature of CNTs appears to be critical for efficient transport and storage of photoelectrons from the CdS phase.

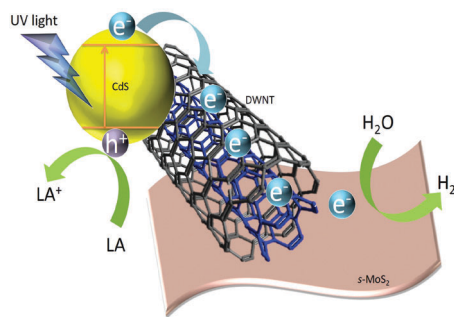
It is well known that the electronic properties of carbon nanotubes are crucially dependent on the diameter and chirality due to their distorted conjugated atomic tubular structure with partial overlap of Pz orbitals, whereas the electronic properties of MWNTs are quite complex, as each layer in the MWNTs can have different chiralities. Furthermore, MWNTs show considerably lower electronic conductivity than those of SWNTs or DWNTs because the interactions between the layers within MWNTs were found to disturb the electrical current along the tube axis.¹⁵

The morphology of DWNTs is very close to SWNTs, but the inner carbon tubes may provide detainment of the conjugation atomic pathway from aggressive mechanical or chemical damage to the outer tube surface.¹⁷ High-resolution TEM (HR-TEM) images (Fig. 3a and b) thus show the raw single and double-walled CNTs with the tubular graphene feature for the SWNT and DWNT, respectively. After 3 M HNO₃ treatment, the majority of SWNTs are converted into carbon sheets and amorphous carbon (the area of serious destruction of SWNTs to amorphous carbon is shown in Fig. 3c). But many of the DWNTs retain their partially destructed tubular structure with amorphous carbon fragments (Fig. 3d). Thus, the more fragile nature of SWNTs leading to opening, unfolding and destruction to carbon fragments is particularly noted. Fig. S3 (a) (ESI[†]) shows the formation of new peaks of C=O stretching at 1691 cm⁻¹, C=C and C=O at 1571 cm⁻¹ and C-O stretching at 1064 cm⁻¹ for the acid treated CNTs by FTIR spectroscopy. To quantify the global structural

**Fig. 3** HR-TEM images of (a) raw SWNTs, (b) raw DWNTs, (c) acid-treated SWNTs, and (d) acid-treated DWNTs. (e) Raman spectra of raw CNTs and 3 M HNO₃ treated CNTs. (f) CdS/DWNT/s-MoS₂ (sheets) with inset of fast-Fourier transform (FFT) of CdS. The enlarged images are found in Fig. S2 (ESI[†]).

change of the samples before and after the same acid treatment, Raman spectra of raw and HNO₃-treated CNTs are shown in Fig. 3e. The band located around 1315 cm⁻¹ is assigned to the D-band which is commonly associated with the disordered, sp³-hybridised carbon arising from defects and impurities, while the band located around 1580 cm⁻¹ is assigned to the G-band which is associated with the crystalline graphitic structures.¹⁸ The intensity ratio of the D-band to the G-band is commonly used to quantify the degree of disorder in a graphene structure.¹⁹ Generally, HNO₃-treated CNTs showed larger D-band to G-band ratios, indicating the destruction of the graphene structure of CNTs during the acid treatment. Notably, the I_D/I_G ratio increases to 5.2 times in the SWNT, followed by 4.9 times in the DWNT and 2.1 times in the MWNT sample. The increase of the D-band ratio in SWNTs suggests that SWNTs indeed have undergone more serious damage after identical acid treatment (particularly on surfaces), which we believe impairs their charge transfer ability (larger τ shown in Table 1), hence resulting in lower H₂ activity compared to DWNTs (see Fig. 1b). Fig. 3f shows that the image of the CdS/DWNT/s-MoS₂ composite, in which the regions of CdS nanoparticles and s-MoS₂ sheets dispersed on the partial tubular carbon structure can be differentiated through the corresponding lattice fringe distances and fast-Fourier transform (FFT) (inset of Fig. 3f). The intimate contact between CdS, s-MoS₂ and carbon nanotubes are clearly evidenced, which suggests that the CNTs remarkably decrease the aggregation of CdS and s-MoS₂ as they spread uniformly in the nanocomposite for superior H₂ activity compared to that without the carbon support. This indicates the future design of efficient photoactive composites for separation and optimization of light capture nanomaterials from catalytic hydrogen production materials *via* electron conductive mediators in a remote way. It is also clear from this study that the crucial maintenance of the integrity of the graphitic tubular structure and the intactness of the conjugation of inner tubes are imperatively important for the charge transport and storage from the light capture CdS phase to hydrogen production sites on s-MoS₂ for optimal photo-catalysis.





Scheme 1 Photocatalytic production of hydrogen from water over CdS–carbon nanotube (CNT)–MoS₂ is found critically dependent on the content and nature of the nanotube used. Time resolved photo-luminescence indicates that the surface graphitic structure of the CNT is vulnerable to damage, halting the essential electron transfer for H₂ formation. Thus, the DWNT exhibits superior H₂ activity to the SWNT because of the structural integrity of the inner tubule.

In summary, photocatalytic hydrogen evolution activity through water splitting is greatly enhanced by the incorporation of carbon nanotubes and single-layered MoS₂ nano-sheets as cocatalysts into the CdS system. CdS/DWNT/s-MoS₂ with the optimal amount of DWNTs (mass ratio of CdS:DWNT:s-MoS₂ = 100:5:2) can provide a high hydrogen evolution rate of 5728 $\mu\text{mol g}^{-1} \text{h}^{-1}$, and the unique roles of intact carbon nanotubes as electron mediators are for the first time identified by this present systematic TRPL study, as summarized in Scheme 1. In addition, a DWNT shows the best performance compared to other forms of CNTs, due to its robust double-walled structure, which can provide protection for the inner tube from surface damage during functionalization/handling, while a SWNT inevitably suffers from destruction of conjugation. This study depicts the importance of fabrication of intimate heterojunctions demonstrating the benefits of nano-ensembles of functional units for light

capture, carrier transfer and catalysis in synergy for efficient photo-production of hydrogen from water.

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