Electronic Supplementary Material (ESI) for ChemComm.
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Electronic Supporting Information

Experimental details

1. Catalyst preparation

1.1 Materials

Reagents used throughout this thesis were purchased from Sigma Alrdrich and were used without modification or purification unless stated: Cadmium Chloride- $CdCl_2$ (99.99% trace metals basis), Oleylamine (technical grade,70%), Sulfur (99.998% trace metals basis), Molybdenum Disulfide- MoS_2 (99% 2H-MoS_2), n-Butly Lithium (1.6 M solution in hexane), Hexane (97 ≥ chromasolv for HPLC), Nitric Acid- HNO_3 (ACS reagent), Lactic Acid (85%), SWNT (carbon >90%, ≥80.0% carbon as SWNT (BET≈ 560 m^2g^{-1}), 0.7-1.4 nm diameter).The DWNTs (345 m^2g^{-1}) were produced by catalytic chemical vapor deposition (CCVD) of a H_2-CH_4 mixture at 1000˚C with CoMo-MgO catalyst.[1,2] MWNTs (369 m^2g^{-1}) were synthesized by Catalytic Chemical Vapour Deposition using a Co:Mo-MgO catalyst with an elemental composition of $Mg_{0.9}Co_{0.033}Mo_{0.067}O$. The catalyst was heated in an atmosphere containing 36% of CH_4 and 64% of H_2, at a total flow-rate of 15L/h, starting from room temperature to 1000°C at 5°/min. No dwell was applied and the gaseous atmosphere was maintained constant during all the procedure.[3] CNTs are free from amorphous carbon coating. During the extraction process, oxides (unreacted CoMo-MgO) and unprotected metal nanoparticles (Co, Mo) were dissolved by addition of aqueous HCl solution. The acidic suspension was then filtered on 0.45 μm pore-size polypropylene membranes and washed with deionized water until neutrality. The sample was freeze-dried.

1.2 Synthesis of cadmium sulphide

The synthesis of CdS spherical NPs followed the method described by Joo et. al.[4] Firstly, 604 mg of cadmium chloride (3 mmol) was dissolved in 30 mL of oleylamine with the assistance of sonication and stirring using a magnetic stirrer bar. This solution was then heated to 90˚C with constant stirring in a three-necked flask for 1 h in air. 48 mg of sulfur dissolved in 5 mL oleylamine was then injected into the mixture dropwise. The solution was then heated to 160˚C under a N_2 atmosphere and left for 6 h under vigorous stirring. After leaving to cool overnight, the nanoparticles were then collected using centrifugation (5000 rpm for 10 min) and were thoroughly washed with acetone five times to ensure all solvent and excess ligand had been removed.

1.3 Synthesis of single-layer molybdenum disulphide (s-MoS_2)

Single-layer MoS_2 (s-MoS_2) was synthesised by the Tsang group following a well-documented route of exfoliation of bulk MoS_2 with lithium intercalation.[5,6] Initially the black MoS_2 powder was soaked for 48 h in 1.6 M solution of n-butyl lithium in hexane under N_2 atmosphere. After this initial intercalation step of MoS_2 with lithium, the Li_xMoS_2 was then repeatedly washed with hexane to remove excess butyl lithium and dried under N_2 atmosphere. The powder was then sonicated in DI water for 48 h to assist exfoliation. The reaction between water and intercalated lithium forms H_2 between the layers and the gas expansion tends to separate the MoS_2 layers until the layers become completely separated and suspended in the aqueous solution. The product was filtered, washed extensively with water and ethanol and then dried under vacuum. Atomic force microscopy (AFM) image of the synthesised s-MoS_2 can be found in the reference no. 6 (summarised in Figure S5).

1.4 Acid treatment of CNTs

Following a method reported by E. Flahaut et al.,[7] initially 200 mg of raw CNTs were placed into 200 mL 3M HNO_3 solution in a 500 mL pyrex flask and sonicated for 30 min then refluxed under vigorous stirring for 24 h at 130˚C. The black suspension was then washed three times with 100 mL DI water before drying the product at 80˚C in air overnight.

1.5 Synthesis of CdS/CNT/*s*-MoS_2 nanocomposites

CdS/CNT/*s*-MoS_2 composites were synthesised using a modified CdS-graphene oxide-MoS_2 by T. Jia et al.[8] Initially, 100 mg CdS, 2 mg *s*-MoS_2 and acid treated CNTs (0.4, 2, 5 and 7mg) in 50 mL ethanol were sonicated for 4 h and then stirred at room temperature for a further 24 h. The suspensions were filtered using a 0.2 μm membrane and washed with 250 mL ethanol. The sample was then vacuum dried at 80˚C in air overnight.

2. Catalyst characterizations

2.1 Transmission electron microscopy (TEM)

TEM images were taken using a JEOL 2100 Transmission Electron Microscope at 200 kV. The sample particles were deposited on an Agar Scientific Holey carbon supported copper 400 mesh grid. TEM samples were prepared by sonicating a suitable amount of material in 1 mL ethanol for 15 minutes before drop wise adding the solution onto the copper grid.

2.2 X-ray diffraction (XRD)

Powder X-ray profiles were obtained on a PANalytical X’Pert Pro Diffractometer by mounting a glass sample slide with the pressed powdered material onto a sample slide holder inside the diffractometer. The intensity of the diffracted beams was measured as a function of the 2θ angle, usually in the range of 10-80°.

2.3 Fourier transform infrared spectroscopy (FTIR)

FTIR spectra were acquired using a Nicolet 6700 ATR-IR spectrometer with a liquid-nitrogen-cooled detector. The solid samples were pressed onto the smart golden gate-ZeSe/diamond crystal. The spectra were obtained by averaging 128 scans with a resolution of 2 cm^{-1} over the wavenumbers ranging from 1000-3500 cm^{-1}.

2.4 Raman spectroscopy

Raman spectra were recorded using a Perkin-Elmer Raman Station 400. This instrument is a bench-top spectrometer with laser excitation wavelength at 785 nm and CCD detector. Powder samples were prepared by placing the powder on a glass slide.

2.5 Ultraviolet-visible absorption spectroscopy

UV-vis absorption spectra were taken using a Varian 100 Bio UV-Visible Spectrometer in absorbance mode in the range 200-800 nm with a step interval of 1 nm. Samples were prepared by sonicating 2 mg of sample in 10 mL ethanol for 15 minutes before putting the sonicated solution into an optical glass cuvette. Ethanol was thus used as the reference.

2.6 Steady-state and time-resolved photoluminescence spectroscopy

Steady-state and time-resolved photoluminescence (PL) measurements were acquired using a time-correlated single photon counting (TCSPC) setup (FluoTime 300, PicoQuant GmbH). Samples were excited using 405nm laser pulsed at frequencies of 40MHz (for steady state measurements) and 10MHz (for time-resolved measurements). The PL was collected using a high resolution monochromator and hybrid photomultiplier detector assembly (PMA Hybrid 40, PicoQuant GmbH). Parameters describing the photoluminescence were obtained by fitting the background-corrected PL with a decay equation of emission intensity I(λ,t) at the time (t) and wavelength (λ) of the form:

$$I(\lambda,t) = I_0(\lambda,t=0)\sum a_i e^{\frac{t}{\tau_i}}$$

Where τ_i is the characteristic lifetime of the ith decay component, a_i is the subsequent decay amplitude, and $I_0(\lambda)$ is the emission intensity at time t=0. Errors in the fitting parameters were determined by examining the adjusted r-squares obtained by independently varying each fitting parameter.

For ease of comparison of lifetimes between CdS samples with different cocatalysts, the intensity weighted average lifetime is given by:

$$\tau_{avg} = \frac{\sum a_i \tau_i^2}{\sum a_i \tau_i} = \sum f_i \tau_i$$

Where f_i is the fractional contribution of each decay components and the denominator is over all amplitudes and decay times which is proportional to the total intensity.[9]

For PL and TRPL measurements, a proportion of sample was extracted from the mixture: A: 100 mg CdS; B: CdS/DWNT (100 mg CdS + 5mg DWNT); C: CdS/s-MoS_2 (100 mg CdS + 2mg s-MoS_2); D: CdS/5mg DWNT/s-MoS_2 (100 mg CdS + 5mg DWNT+ 2mg s-MoS_2); E: CdS/5mg SWNT/s-MoS_2 (100 mg CdS + 5mg SWNT+ 2 mg s-MoS_2); F: CdS/5mg MWNT/s-MoS_2 (100 mg CdS + 5mg MWNT+ 2 mg s-MoS_2)

3. Photocatalytic testing

Photocatalytic H_2 evolution experiments were performed in a 500 mL sealed Pyrex flask at ambient temperature and atmospheric pressure. The reactor was positioned 10 cm away from the 500 W UV-vis lamp. In a typical photocatalytic experiment, 20 mg catalyst was suspended in 90 mL DI water and 10 mL lactic acid and sonicated for 30 min. Prior to irradiation, the suspension was bubbled with 5 % CH_4/Ar for 15 min to remove the dissolved oxygen and to ensure the reaction was under anaerobic conditions, the CH_4 acted as an internal reference for gas chromatography calibration. Continuous magnetic stirring was applied in order to keep the photocatalyst particles suspended during the irradiation. A 20 mL sample of the generated gas was collected and analysed by Agilent 7890A gas chromatography with TCD detector.

In the Figure 1 of the main manuscript, hydrogen evolution rate for 20 mg catalysts was taken from the mixture and measured. A: CdS (100 mg); B: CdS/DWNT (100 mg CdS +0.4g DWNT); C: s-MoS_2; D: CdS/s-MoS_2 (100 mg CdS + 2 mg s-MoS_2); E: CdS/2mg DWNT/s-MoS_2 (100 mg CdS +2mg DWNT+ 2 mg s-MoS_2); F: CdS/5mg DWNT/s-MoS_2 (100 mg CdS +5mg DWNT+ 2 mg s-MoS_2); G: CdS/7mg DWNT/s-MoS_2 (100 mg CdS +7mg DWNT+ 2 mg s-MoS_2), etc.

Supporting figures and tables

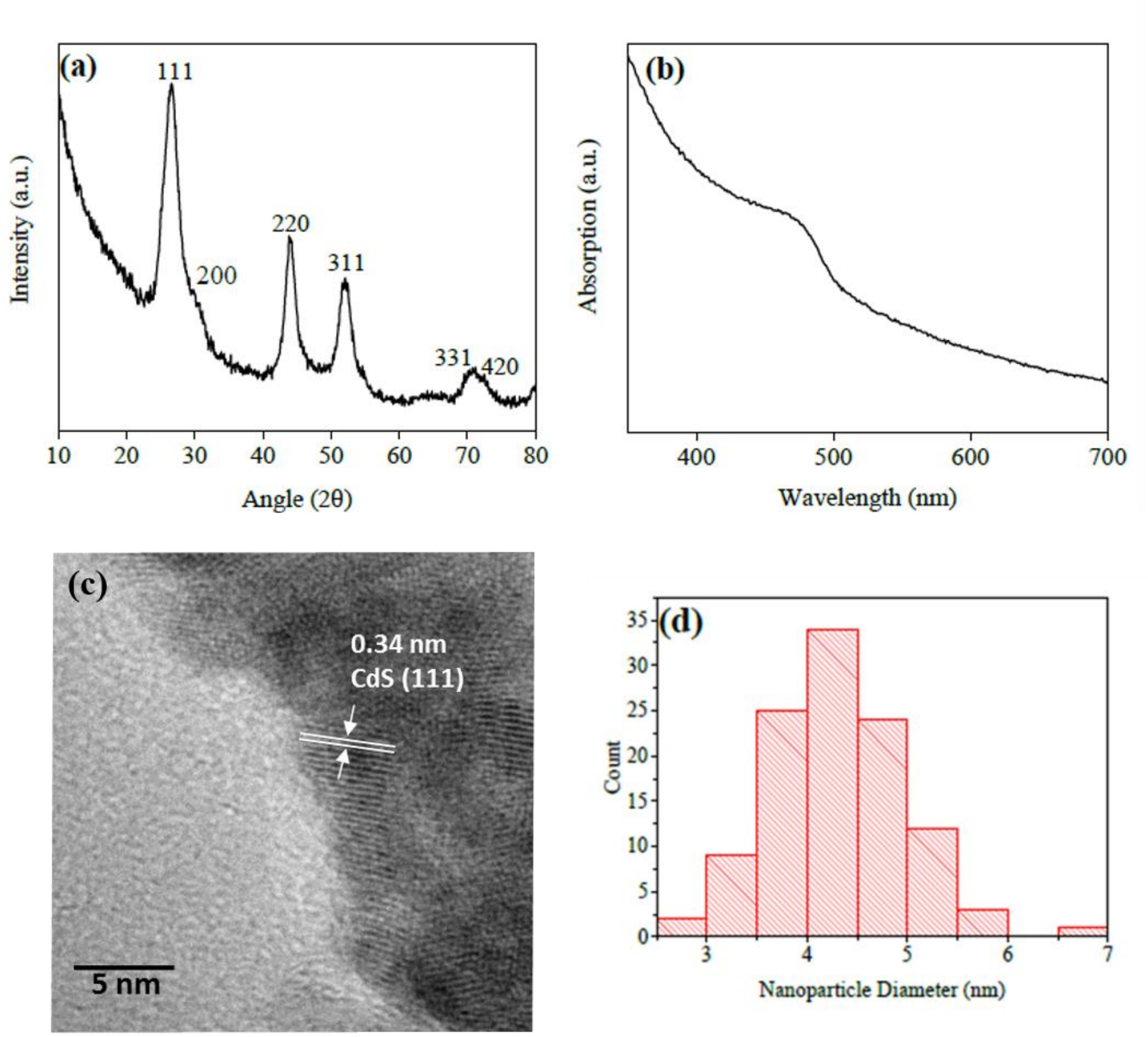

Figure S1 (a) X-ray diffraction pattern; (b) UV-visible absorption spectrum; (c) TEM image; (d) nanoparticle diameter size distribution of synthesised CdS nanoparticles.

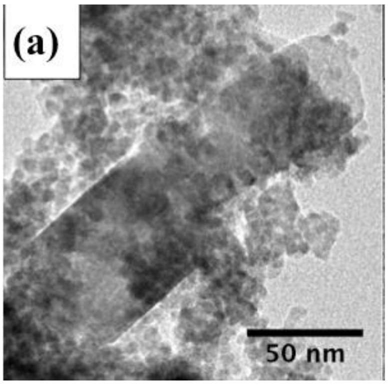

Figure S2A TEM image of CdS/*s*-MoS_2 nanocomposite, which reveals the aggregation of CdS nanoparticles on the basal planes and the edges of re-stacked *s*-MoS_2.

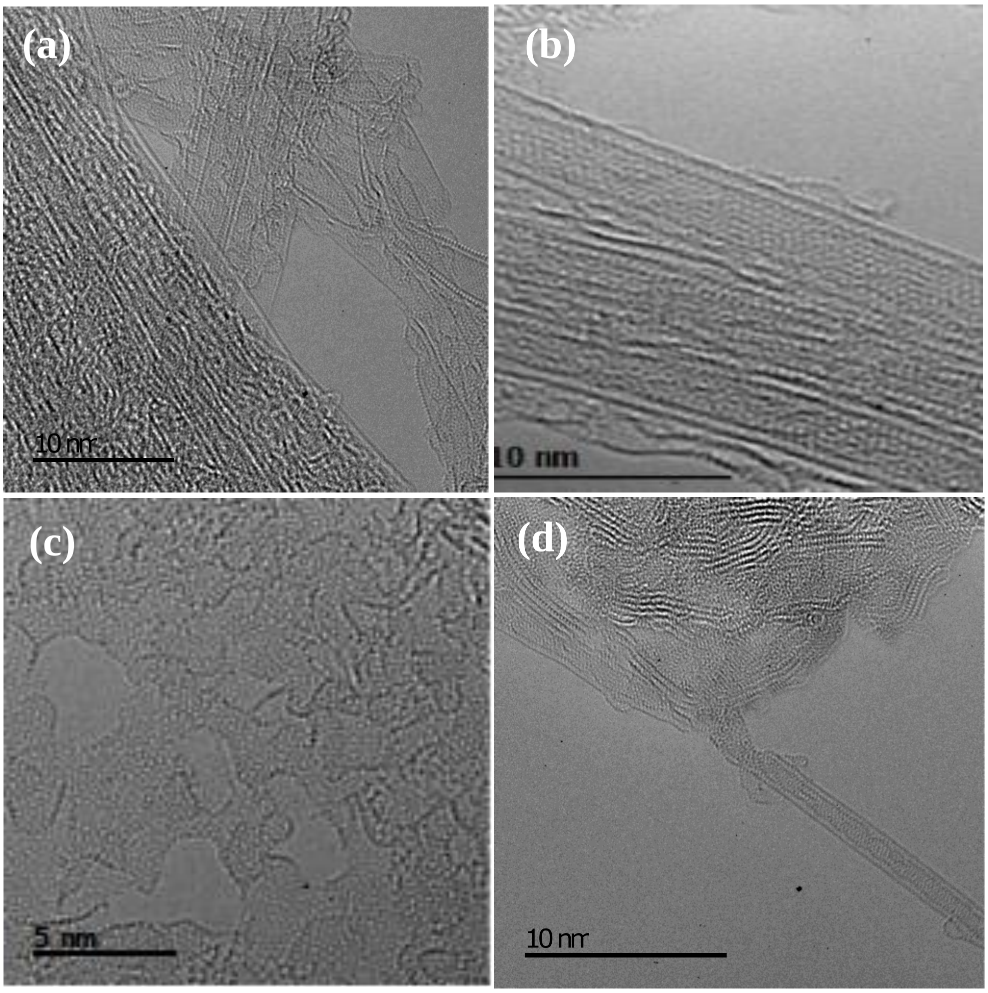

Figure S2B Typical HR-TEM images of (a) raw SWNT; (b) raw DWNT; (c) acid-treated SWNT; (d) acid-treated DWNT

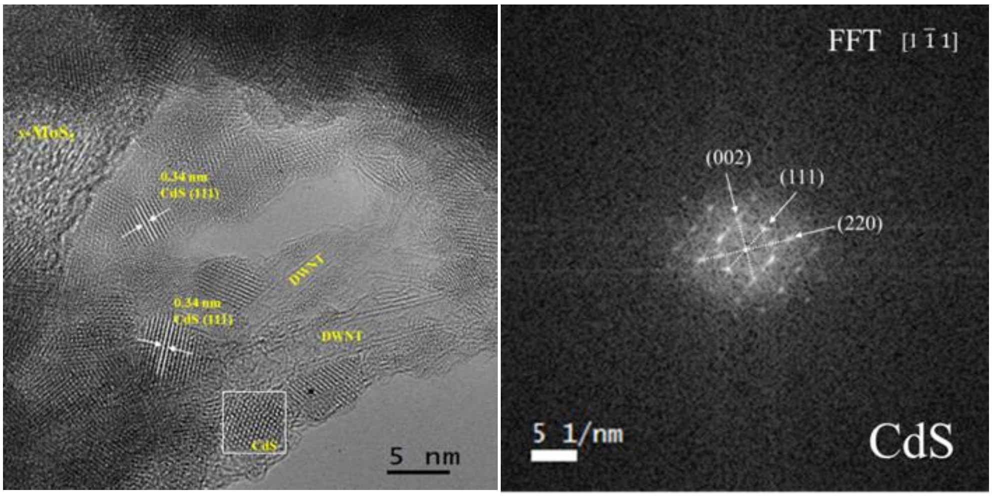

Figure S2C: Left: A typical HR-TEM image of CdS/DWNT/s-MoS_2, the marked areas rich in compound(s) were confirmed by EDX; Right: Selected area of CdS nanoparticle with corresponding fast-Fourier Transform (FFT).

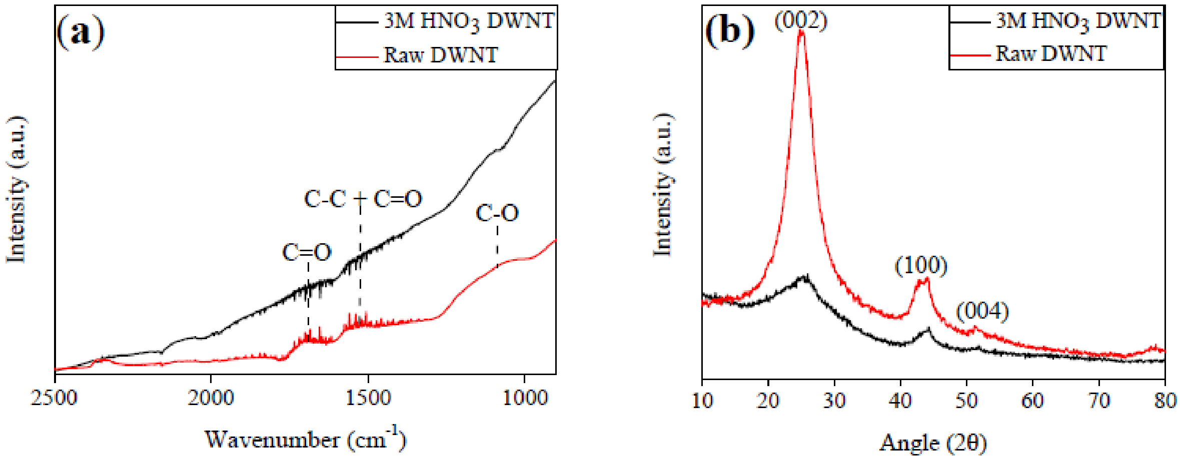

Figure S3 (a) FTIR, (b) XRD of 3M HNO_3 treated DWNT and raw DWNT.

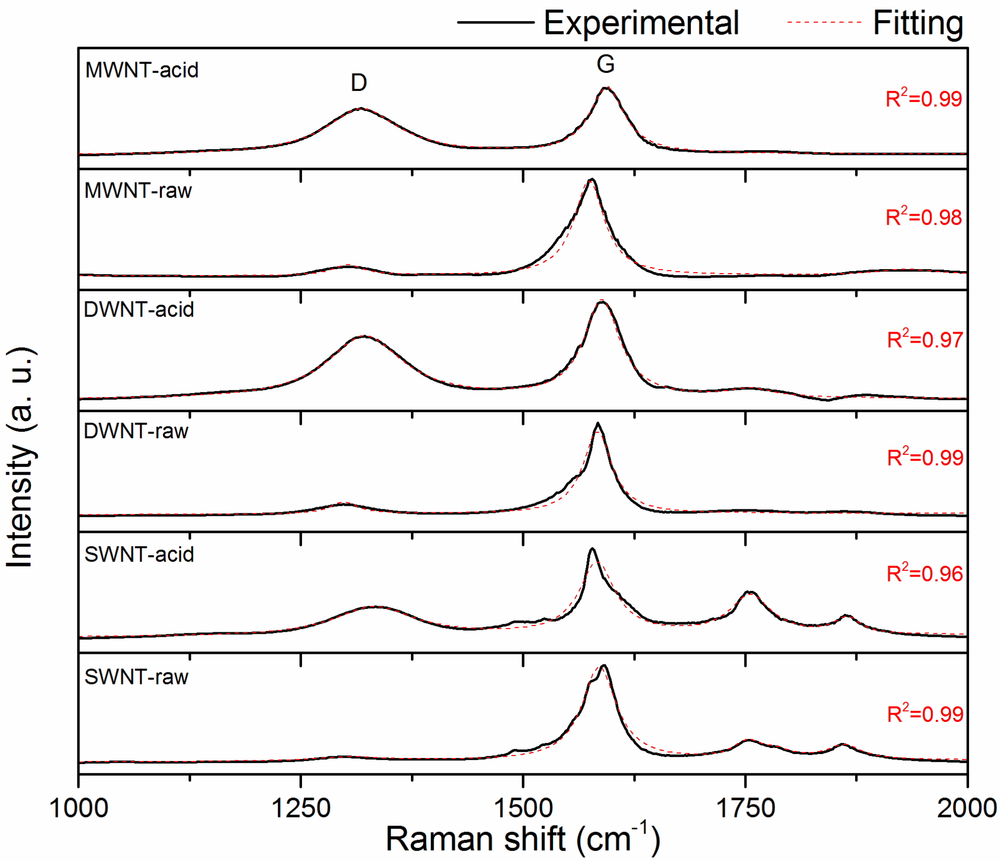

Figure S4 Raman spectra of raw CNTs and 3M HNO_3 treated CNTs.

Table S1 The A_D/A_G and I_D/I_G ratios of the raw and acid treated CNTs.

Sample	**A_D/A_G**	**I_D/I_G**
SWNT-raw	0.0261	0.0821
SWNT-Acid	1.431	0.4305
SWNT Ratio increment (acid/raw)	54.828	5.244
DWNT-raw	0.263	0.1404
DWNT-Acid	1.221	0.6894
DWNT Ratio increment (acid/raw)	4.643	4.910
MWNT-raw	0.0918	0.3490
MWNT-Acid	1.15	0.7265
MWNT Ratio increment (acid/raw)	12.527	2.082

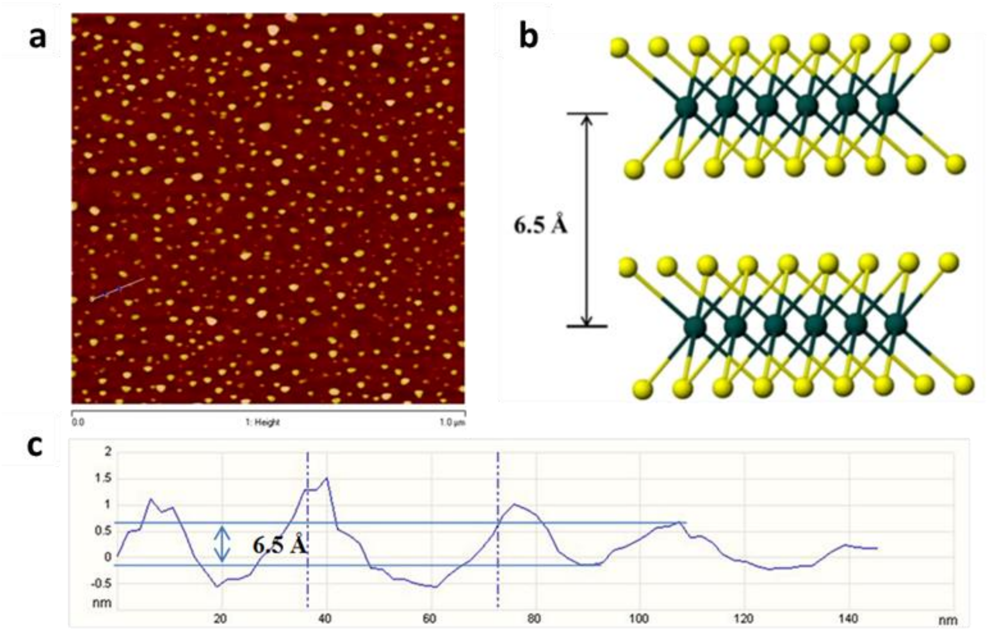

Figure S5 Atomic force microscopy (AFM) image analyses for the fresh chemically exfoliated s-MoS_2- refer to reference [6] (**a**, AFM image of spin coated s-MoS_2 and **b**, a model of 2-H MoS_2 structure perpendicular to c axis, 100 flakes is scanned with majority of heights between 0.6-0.7nm. The sample was prepared by spin-coating s-MoS_2 onto a surface of Si/SiO_2 substrate. The lateral dimension of this s-MoS_2 nanosheet is approximately 20-40 nm. **c**, It can be seen that the step heights of individual layers of 0.6-0.7 nm. This value is comparable to ca. 0.65 nm of a single layer of the S-Mo-S building block. Statistical analysis of 100 flakes produced by the lithium exfoliation method revealed that 56% of the flakes to be monolayer, 28% of two layers and 13% of three layers and so on. The average topographic height is around 1.04 nm, which agrees with typical height of a s-MoS_2 with the presence of water molecules (between 0.6 and 1.0 nm).

Photo-corrosion of CdS quantum dots on Carbon Nanotubes

It is well accepted that the competition reaction such as sulphide oxidation induced by the positive charged hole instead of carrying out the highly activated oxidation process of water molecule to oxygen and proton, can cause photo-corrosion of CdS semiconductor. However, photocatalytic hydrogen production from the reduction of proton in solution over the defined material components was the main focus of this work, we had thus tried to avoid the issue of photo-corrosion. Using a reducing agent used as the hole scavenger in aqueous solution is a well-known strategy to stabilize CdS from the photo-corrosion. In this study, lactic acid was therefore used as the sacrificial reagent to suppress the photo-corrosion of CdS with the lactic acid preferentially oxidised into pyruvic acid. Thus, in this system, we did not evaluate the extent of photo-corrosion of CdS quantum dots with or without CNTs (we did not encounter this problem by using lactic acid as the sacrificial reductant). On the other hand, the high surface area CNTs with high intrinsic electronic conductivity, are expected to reduce the local positively charge (hole) built up over the CdS quantum dots together with higher concentration of adsorbed lactic acid, that can in principle greatly reduce the extent of photo-corrosion. However, these anticipations should be carefully verified.

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