Electronic Supplementary Material (ESI) for Nanoscale.

SUPPLEMENTARY INFORMATION

Colloidal tandem cell for photocatalytic hydrogen generation

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CdS SNC synthesis. CdS SNCs were synthesized in octadecene following the method of Yu and Peng.[1] Typically, a 18-g mixture of CdO (0.0576 g), oleic acid (0.382 - 3.82 g), and octadecene (90%, technological grade) was heated in a 50-mL three-necked flask to 300 °C under N_2 until the solution became clear and colourless. A solution of sulphur (7.2 mg, 0.15 mmol) dissolved in octadecene (9.0 g) was swiftly injected into the reaction system and the mixture was cooled to 250 °C for the growth of CdS nanocrystals. The size of the CdS SNCs was controlled by the concentration of oleic acid and the crystal growth time, and monitored by UV-Vis absorbance (Shimadzu SolidSpec-3700DUV).[2] When the desired size (2.8, 3.1, 3.7 or 4.6 nm) was achieved, the system was cooled to room temperature to stop the reaction and treated with a mixture of hexane and ethanol (1 : 2, v/v) to afford a yellowish precipitate which was separated by centrifugation. Centrifugation and decantation were repeated to remove any unreacted precursors, giving the final product as a monodisperse sample stored in chloroform.

Phase transfer of CdS SNCs and Pt deposition. Following the method of Tamang et al.[3] CdS quantum dots (QDs) were transferred into water by surface treatment with D,L-cysteine hydrochloride resulting in optically clear solutions with an optical density of 1.5 at their first excitonic absorption peak. For Pt photodeposition, 10 mL of OD 1.5 stock solution of CdS SNCs (pH 9), 0.15 mL 50 mM chloroplatinic acid hexahydrate, 65 mg ascorbic acid, 650 mg triethanolamine, and 10 mL H_2O were mixed in a beaker. The mixture was stirred under continuous bubbling with argon and UV excitation (~3.5-4 mW/cm^2 at 366 nm) from a standard UV lamp for 20 min. After completing the reaction, solutions were purified by three centrifugation cycles on Millipore 5,000 mwco filters, and the resulting precipitate is re-dissolved in distilled water giving a clear yellowish solution of Pt-decorated CdS QDs with OD 0.6.

Photocatalytic reactions. Single-cell hydrogen generation experiments were carried out in a set-up comprising a 5 cm long cylindrical gas-tight quartz cuvette with two gas outlets, which is filled with 7 mL solution (containing 3.5 mL Pt/CdS, 0.02 M Na_2SO_3 and 0.05 M triethanolamine, pH 9) leaving a remaining 11.2 mL volume of Ar in which the evolving hydrogen escapes. The reaction mixture is de-aerated under magnetic stirring and bubbling with Ar for 30 min before illumination. The samples were excited in the spectral range between 350-480 nm using the filtered output of a 450 W Xe lamp to provide a beam with 1 cm^2 excitation area and an excitation power of ~50 mW/cm^2. For the tandem cell, two identical quartz cuvette were positioned behind each other and index matching fluid was applied in between the quartz windows to minimize reflection losses. In all measurements, the OD of the SNC suspensions in each 5 cm quartz cuvette was kept at 1.5 at their first excitonic absorption peak, with amount of Pt-decorated CdS in a range of 26 ~ 53 mg/L for the four sizes. 300 µL aliquots of the gas mixture evolving over the illuminated solution are taken at regular time intervals and analysed by gas chromatography (Bruker-430-GC) equipped with a thermal conductivity detector.

EQE and IQE. The external quantum efficiency for hydrogen generation is determined as the ratio of 2x number of hydrogen molecules evolved/number of incident photons. The incident power is measured with a thermal power sensor (Thorlabs S302C). The spectrum of the incident light was measured using an Ocean optics USB4000 spectrometer. For an irradiation area of 1.0 cm^2 and an irradiation power of 50 mW (approx. 602 µmol/h photons@400nm), H_2 production rates of up to 44.7 µmol/h which corresponds to 14.7% external quantum efficiency are obtained. For internal quantum efficiency measurements, the number of incident photons is replaced by the number of absorbed photons as estimated from the incident spectrum and extinction spectrum of the SNCs. Alternative measures (e.g. formation rate and turn-over-frequency) are determined as well showing specific efficiency of hydrogen generation normalised to amount of catalyst.

Photocatalyst characterisation. The chemical composition of the Pt/CdS catalyst was determined with an Inductively Coupled Plasma – Optical Emission Spectrometry (Spectro Ciros ICP-OES). ICP-OES samples were prepared directly from colloidal sample solutions. X-ray photoelectron spectroscopy (XPS) was applied to determine the energy band diagram. XPS was performed in ultrahigh vacuum using a PSP Vacuum Technology electron energy analyser (integrating angle ±10°) and a Specs monochromated dual anode x-ray source. The base pressure of the system was less than 2×10^{-10} mbar, with hydrogen as the main residual gas in the chamber. The XPS measurements were carried out with a Al K_α source (hv=1486.7 eV). The spectrometer was calibrated using the Ag $3d_{5/2}$ core level at 368.2 eV as standard and operated at an overall resolution that allowed the determination of band edge position with an accuracy of 30 meV. XPS samples were prepared by drop-casting from colloidal nanocrystal suspensions onto clean silicon wafers. Valence band edges of the samples were determined by linear extrapolation of the leading edge of the XPS spectra at low binding energies and taking the intercept with the energy axis as the band edge. The matching of the Cd 3d peaks for samples of identical CdS nanocrystal size allowed determination of the position of the valence band edge with respect to the Fermi level. The valence band edges of Pt-containing samples were set as reference with a binding energy of 0. The morphology of the photocatalyst was characterised with a JEOL JEM-3010 TEM operating at a 300 kV accelerating voltage.

Additional TEM characterisation

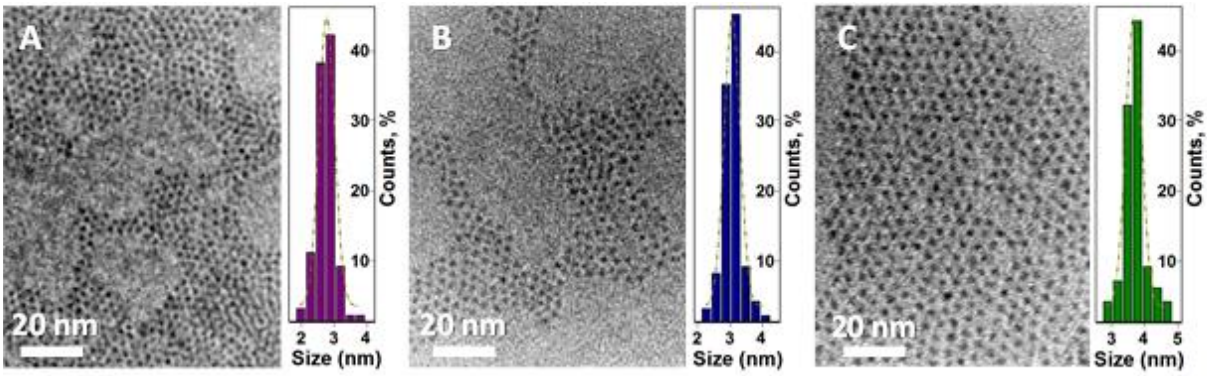

Figure S1 TEM images of A) 2.8nm, B) 3.1 nm and C) 3.7 nm diameter CdS nanospheres along with the size distribution (centred at around 2.8 nm, 3.2 nm and 3.8 nm, respectively) as determined from TEM images.

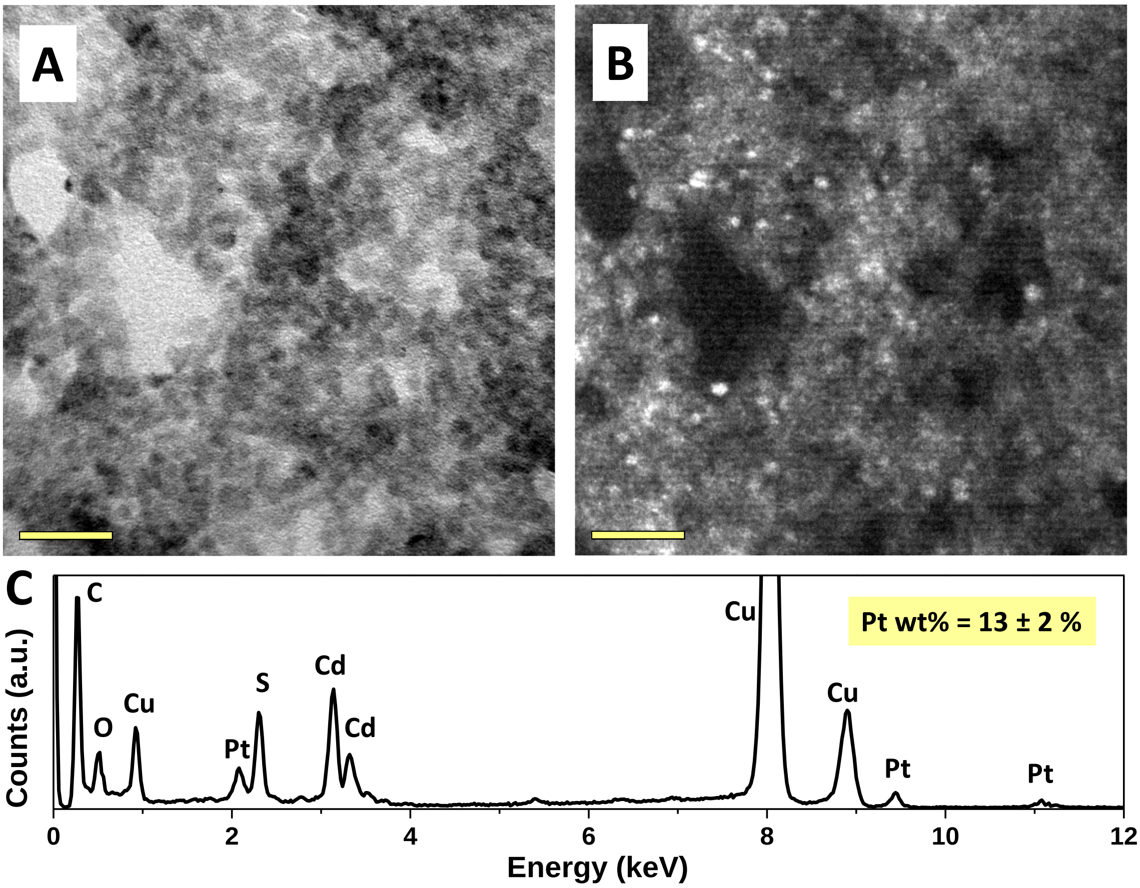

Figure S2. TEM analysis of the Pt-decorated 4.6 nm diameter SNC sample. A) bright-field image; B) High-angle annular dark-field image; and C) energy dispersive spectrum. 13 ± 2 wt% of Pt was identified by energy dispersive spectroscopy in agreement with the inductively coupled plasma results. The majority of Pt was dispersed well as sub-nm clusters along with a minority of slightly bigger particles of up to ~ 2 nm in size.

ICP-OES characterisation

Samples/nm	Pt, W% (ICP-OES)	Pt, atom/nm^2
2.8	16.3	1.3
3.1	16.3	1.5
3.7	16.3	1.8
4.6	16.3	2.2

Table S1. Amount of Pt in the Pt-decorated CdS nanospheres expressed in weight-% and atom density on the nanosphere surface as determined form inductively coupled plasma optical emission spectrometry (ICP-OES).

Additional XPS data

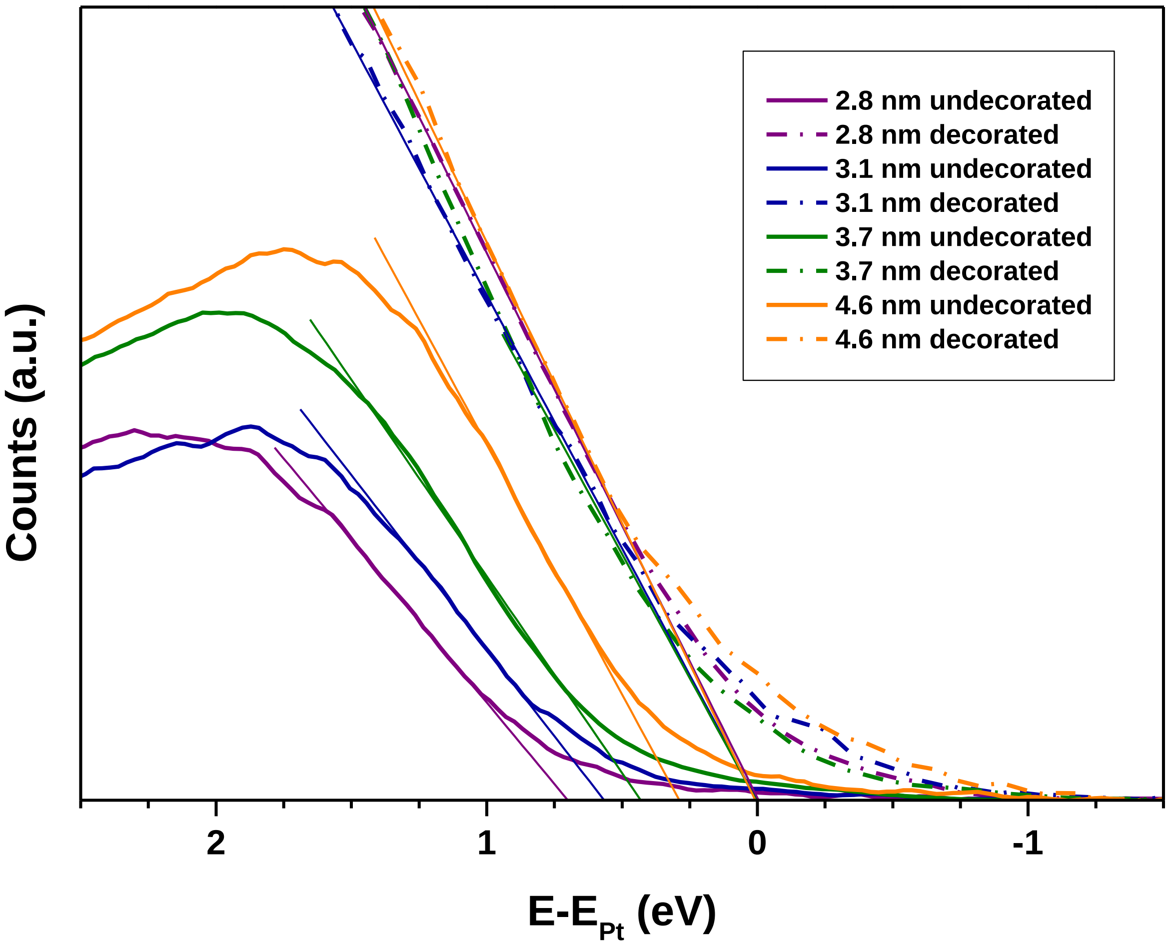

Figure S3. XPS spectra for the valence band edges of Pt-decorated SNCs and undecorated SNCs with linear fits extrapolating the valence band edge positions.

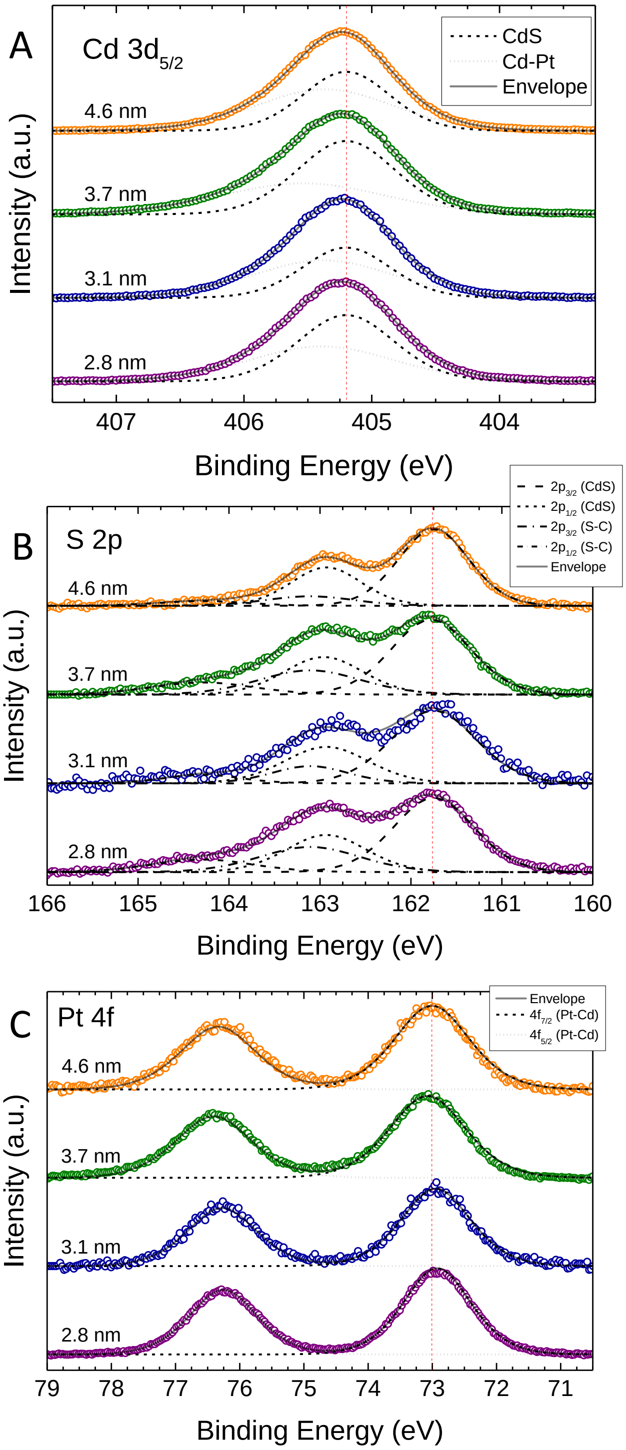

Figure S4. XPS core level spectra as function of SNC size for Pt-decorated CdS nanospheres: A) Cd 3d level, B) S 2p level, and C) Pt 4f level.

The Cd $3d_{5/2}$ spectra show the presence of two Cd environments in all sizes of SNC. The components at 405.2 eV are assigned to CdS. The second component at 405.4 eV is assigned to a platinum bonded cadmium environment. It is noted that the second component is absent in samples containing no Pt. The S 2p spectra show two species of sulphur in all sizes of SNC, each of which is well resolved into its spin-orbit components. The main doublet, with a S $2p_{3/2}$ peak binding energy of 161.8 eV is assigned to CdS. The second doublet is attributed to organically bonded sulphur, commonly present in materials containing sulphur and consistent with the organic ligands present on the SNCs. The Cd $3d_{5/2}$ and S $2p_{3/2}$ binding energies found here for CdS are in agreement with previous measurements of CdS nanomaterials.[4–6] The Pt 4f spectra show a single, well resolved doublet for each size of SNC with a Pt $4f_{7/2}$ binding energy of 73.0 eV. These doublets are assigned to the platinum clusters, bonded to the cadmium. The platinum is shown to be non-metallic in nature because of the symmetrical peak shapes and the increase in binding energy from the known value of 71.0 eV for metallic Pt.[7] Due to the very good agreement between the elemental binding energies of all sizes of SNC, it is concluded that the VBM shifts seen between the crystal sizes are purely electronic and no chemical structure changes are taking place.

Illumination conditions

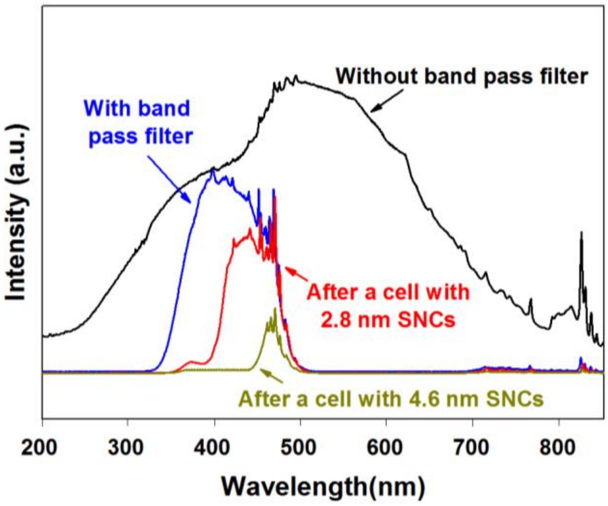

Figure S5. Spectra of illumination light source used for photocatalytic experiments (Xenon lamp + water filter) with and without band pass filter, and spectra after the first cells with different SNCs sizes.

References

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