

## Electronic Supplementary

# Insight into Band Positions and Inter-particle Electron Transfer Dynamics between CdS Nanoclusters and Spatially Isolated TiO<sub>2</sub> Dispersed in Cubic MCM-48 Mesoporous Materials: A Highly Efficient System for Photocatalytic Hydrogen Evolution under Visible Light Illumination

*Rui Peng<sup>†</sup>, Cuikun Lin<sup>†</sup>, Jonas Baltrusaitis<sup>§</sup>, Chia-Ming Wu<sup>†</sup>, Nada M. Dimitrijević<sup>‡</sup>,  
Tijana Rajh<sup>‡</sup>, Stanley May<sup>†</sup>, and Ranjit T. Koodali<sup>\*†</sup>*

## Experimental

### Materials

Tetraethyl orthosilicate (TEOS, 98%), methanol, and chloroform (99.8%) were obtained from Acros. Cetyltrimethylammonium bromide (CTAB, 98%) and (3-mercaptopropyl) trimethoxysilane were purchased from Alfa Aesar. Ammonium hydroxide, HPLC grade methanol, cadmium acetate dihydrate, and thiourea were obtained from Fisher Scientific. Ethanol was produced by Pharmo-AAPER. Deionized water was used throughout this study. All the chemicals were used without further purification unless otherwise noted.

### Synthesis

Pure siliceous MCM-48 (Si-MCM-48) and Ti-MCM-48 mesoporous materials were prepared as described below. Subsequently, CdS nanoparticles were encapsulated inside the parent Si-MCM-48 and Ti-MCM-48 mesoporous materials through a two-step modification method.

*Synthesis of Si-MCM-48.* 1.2 g (3.3 mmol) of the surfactant, CTAB was added to 50 mL deionized water under vigorous stirring. After CTAB was completely dissolved, 25 mL ethanol was poured into the clear solution. 6 mL of aqueous  $\text{NH}_3$  (0.09 mol) was added to the surfactant solution and then 1.8 mL (8 mmol) of the TEOS was added immediately. After stirring at 300 rpm for 4 h, Si-MCM-48 was recovered by filtration, washed with distilled water, and dried in oven at 80 - 90 °C overnight. The dried powder was then ground finely and calcined at 550 °C for 6 hours in static air at a heating rate of 3 °C  $\text{min}^{-1}$  to remove the template.

*Synthesis of Ti-MCM-48.* The synthesis of Ti-MCM-48 was carried out in a similar manner as described for Si-MCM-48 with the exception that titanium (IV) isopropoxide was

added after TEOS. The samples with Si/Ti ratios of 200, 50, and 25 in the gel were named Ti-MCM-48-01, Ti-MCM-48-21 and Ti-MCM-48-31 respectively. The final Si/Ti ratios in the final product are calculated to be 189, 47, and 20 respectively (to be moved to SI).

The X-ray diffractometer was operated at 40 kV and 40 mA with a step width of  $0.02^\circ$  and the scan rate used was  $0.24^\circ/\text{min}$ . During the nitrogen physisorption studies, samples were dried in an air oven overnight and degassed at  $100^\circ\text{C}$  extensively prior to the adsorption measurements. The surface area was determined using the Brunauer-Emmett-Teller (BET) method in the relative pressure range of  $(P/P_0) = 0.05$  to  $0.30$ . The pore sizes were calculated by applying the Barrett-Joyner-Halenda (BJH) equation to the desorption isotherm. The pore volume was calculated from the amount of nitrogen adsorbed at the highest relative pressure  $(P/P_0) = 0.98$ . In the AAS analysis, the working current used was 4 mA working current and the wavelength of excitation was 228.8 nm. About 5 mg of the sample was accurately weighed and then digested with known volume of conc.  $\text{HNO}_3$  for 30 min. In our experience this was sufficient for dissolution of CdS from the mesoporous matrix. The resulting suspension was then centrifuged and the filtrate was diluted to 25 mL. The concentration of the  $\text{Cd}^{2+}$  ions in the filtrate was determined from a calibration plot made previously. TEM samples were prepared by first sonicating a dispersion consisting of CdS-Ti-MCM-48 sample in ethanol and then carefully placing a drop of the sonicated dispersion on a carbon-coated copper grid (mesh size = 200). This was allowed to air dry overnight before transferring to the vacuum chamber of the TEM instrument. Image acquisition was performed with a Gatan Orius bottom-mount, 14-bit, 11-megapixel CCD camera. An Oxford Inca energy-dispersive silicon-drift X-ray spectrometer was used for compositional analysis and mapping at high count rates. For the XPS analysis, samples were pressed into indium foil and mounted onto a copper stub. These samples were then

transferred to the analysis chamber for the XPS scan. The X-ray was operated using 15 mA emission current and 15 kV accelerating voltage. Survey scans were collected from energy range 1200 to -5 eV with 1 eV step size. High resolution spectra were acquired in the region of interest using a 20 to 40 eV energy window with 0.1 eV step size. To perform the photoluminescence test, the samples were finely ground with an appropriate amount of KBr and then pressed into pellets prior to photoluminescence experiments. All spectra were corrected for instrument response in terms of relative photon flux per wavelength interval. In the EPR studies, samples were dispersed in water/glycerol (1:1) solution and purged with argon. A 300-W Xe UV lamp (ILC) with 400 nm cut off and water as IR filters was used as the light source. Samples were illuminated at 77 K, and EPR spectra were recorded at 5 K immediately after illumination. The  $g$  factors were calibrated for homogeneity and accuracy by comparison to a coal standard,  $g = 2.00285 \pm 0.00005$ .

Table S1. Summary of photocatalytic hydrogen evolution rate of fresh and recycled samples.

Sample	Hydrogen evolution rate of fresh	Hydrogen evolution rate of recycling run 1	Hydrogen evolution rate of recycling run 2
--------	-------------------------------------	---	---

	(mmol/h/g catalyst)	(mmol/h/g catalyst)	(mmol/h/g catalyst)
CdS-Ti-MCM-48-01- MPTMS-25	0.26	0.25	0.23
CdS-Ti-MCM-48-21- MPTMS-25	0.51	0.48	0.46
CdS-Ti-MCM-48-31- MPTMS-25	0.73	0.69	0.65

Table S2. Textural properties of fresh and spent CdS-Ti-MCM-48-31-MPTMS-25 samples.

Photocatalyst	Si/CdS (mol) <sup>a</sup>	Si/CdS (mol) <sup>b</sup>	Surface Area (m <sup>2</sup> g <sup>-1</sup> ) <sup>c</sup>	Pore Volume (cm <sup>3</sup> g <sup>-1</sup> ) <sup>d</sup>	Pore Diameter (Å) <sup>e</sup>
CdS-Ti-MCM-48-31-MPTMS-25	25	35	1005	0.63	16.9

CdS-Ti-MCM-48-31-MPTMS-25- spent	25	39	1088	0.69	17.0
-------------------------------------	----	----	------	------	------

<sup>a</sup> Molar ratio in the gel.

<sup>b</sup> Molar ratio in the product measured by the AAS study.

<sup>c</sup> Determined by applying the Brunauer-Emmett-Teller (BET) equation to a relative pressure ( $P/P_0$ ) range of 0.05–0.30 to the adsorption isotherm.

<sup>d</sup> Calculated from the amount of nitrogen adsorbed at the highest relative pressure ( $P/P_0$ ) ~ 0.98.

<sup>e</sup> Calculated from the Barrett-Joyner-Halenda (BJH) equation using the desorption isotherm.

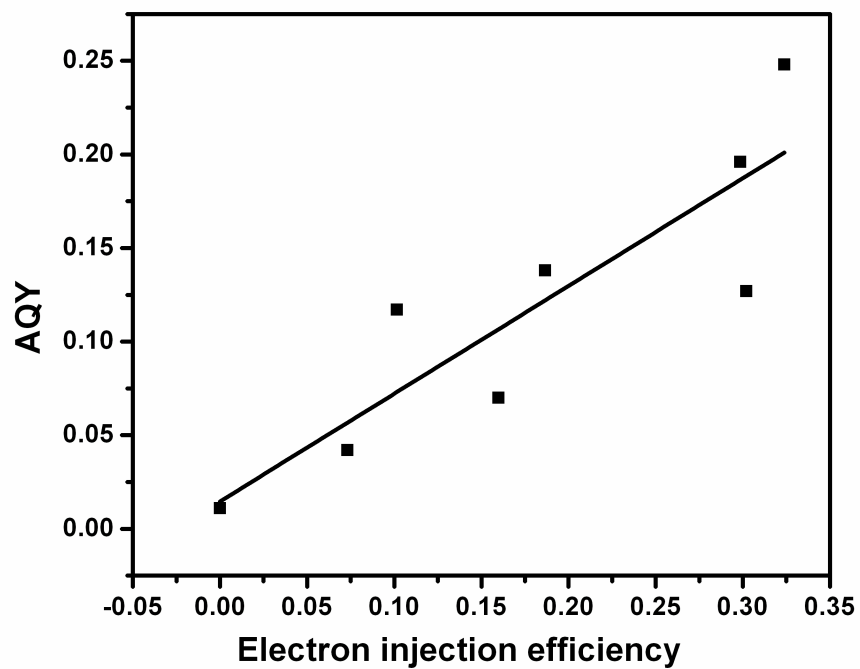


Figure S1. Correlation of the electron injection efficiencies with photocatalytic apparent quantum yields (AQY) in all studied samples.

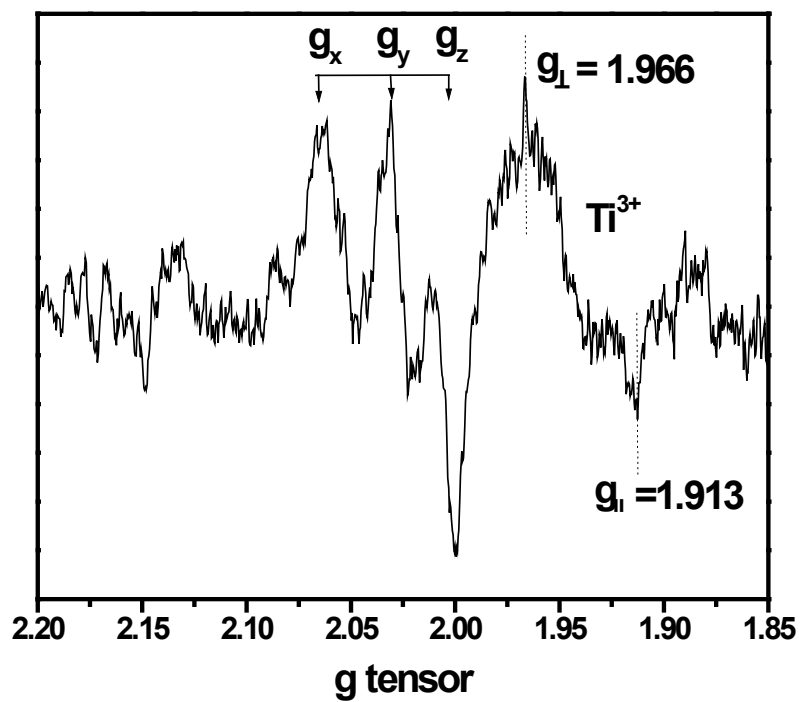


Figure S2. EPR spectra of CdS-Ti-MCM-48-31-MPTMS-25 sample measured at 5 K in dark after illumination at 77 K with a light  $\lambda > 400$  nm.



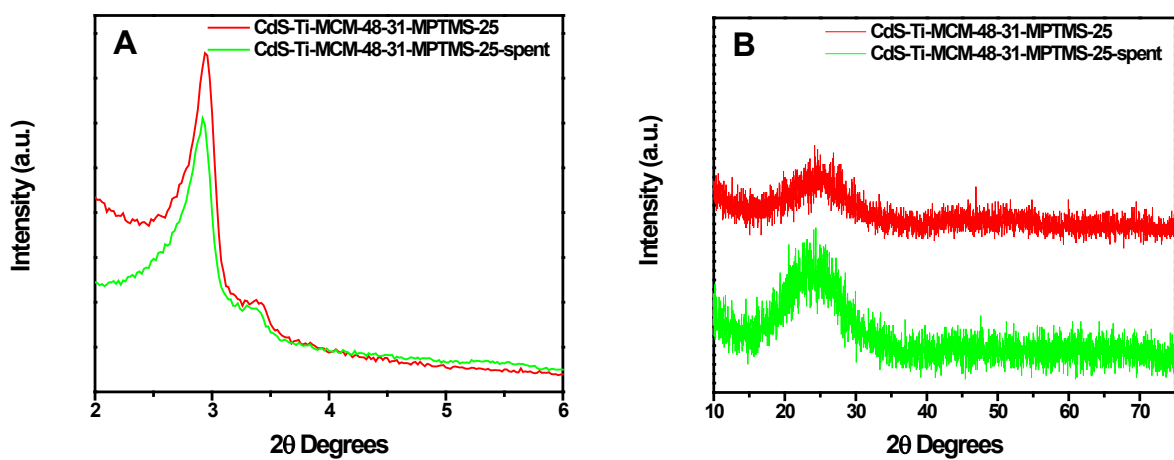


Figure S3. (A) Low angle XRD patterns of fresh and spent CdS-Ti-MCM-48-31-MPTMS-25 samples and (B) High angle XRD patterns of fresh and spent CdS-Ti-MCM-48-31-MPTMS-25 samples.

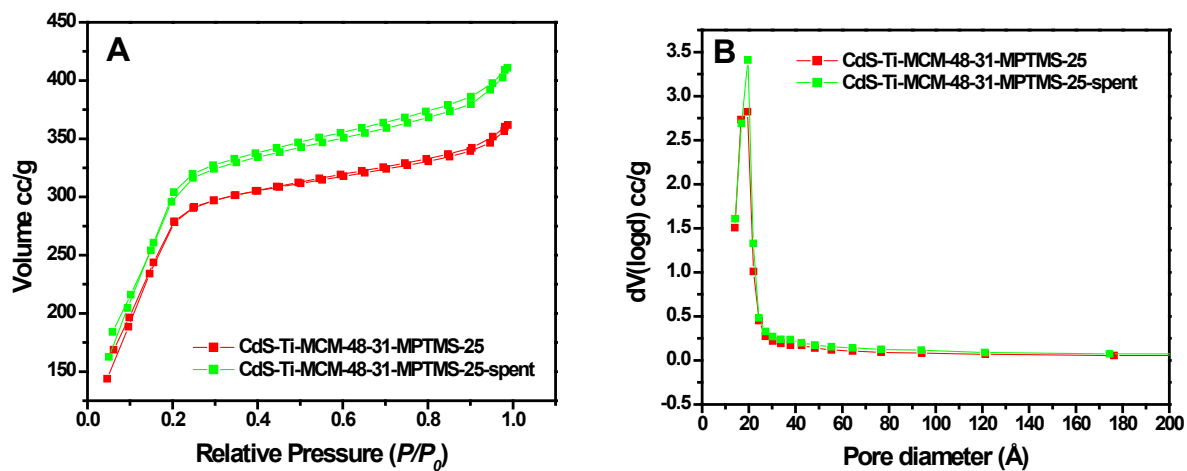


Figure S4. (A) Nitrogen physisorption isotherms of fresh and spent CdS-Ti-MCM-48-31-MPTMS-25 samples and (B) Pore size distribution plots of fresh and spent CdS-Ti-MCM-48-31-MPTMS-25 samples.