Ultra-stable CdS Incorporated Ti-MCM-48 Mesoporous Materials for Efficient Photocatalytic Decomposition of Water under Visible Light Illumination

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Supporting Information

Content

Section 1 Detailed synthesis of MCM-48 mesoporous photocatalysts

Chemicals for synthesis: Tetraethyl orthosilicate (TEOS, 98%) was obtained from Acros. Cetyltrimethylammonium bromide (CTAB, 98%) was purchased from Alfa Aesar. Ammonium hydroxide, methanol (HPLC grade), cadmium acetate dihydrate, and thiourea were obtained from Fisher Scientific. Ruthenium (III) chloride hydrate was purchased from Aldrich. 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

The host Si-MCM-48 and Ti-MCM-48 mesoporous materials were prepared by rapid and facile synthetic approaches at room temperature reported by us previously.[1, 2] CdS-MCM-48 and CdS-Ti-MCM-48 mesoporous materials were assembled by introducing CdS species into pre-formed Si-MCM-48 and Ti-MCM-48 *via* post-impregnation synthetic approaches. RuO_2-CdS-Ti-MCM-48 photocatalysts were synthesized by loading RuO_2 into pre-formed Ti-MCM-48 prior to the embedding of CdS species through the identical preparation method that was employed in obtaining CdS-Ti-MCM-48.

Synthesis of Si-MCM-48: 1.2 g (3.3 mmol) of Cetyltrimethylammonium bromide (CTAB) was added in 50 mL deionized water under vigorous stirring. After it was completely dissolved, 25 mL ethanol was poured into the clear solution. 6 mL of aqueous NH_3 (0.09 mol) was added to the surfactant solution and then 1.8 mL (8 mmol) of the tetraethyl orthosilicate (TEOS) was added immediately. After stirring at 300 rpm for 4 h, the gel was recovered by filtration, washed with distilled water, and dried in oven at 80 - 90 ^oC overnight. The dried powder was then ground finely and calcined at 550 ^oC for 6 hours at a heating rate of 3 ^oC min^{-1} to remove the template.

Synthesis of Ti-MCM-48: 1.2 g (3.3 mmol) of Cetyltrimethylammonium bromide (CTAB) was added in 50 mL deionized water under vigorous stirring. After it was completely dissolved, 25 mL ethanol was poured into the clear solution. 6 mL of aqueous NH_3 (0.09 mol) was added to the surfactant solution and then 1.8 mL (8 mmol) of the tetraethyl orthosilicate (TEOS) was added immediately. Finally, titanium precursor from titanium (IV) isopropoxide and ethanol stock solution was added. After stirring at 300 rpm for 4 h, the gel was recovered by filtration, washed with distilled water, and dried in oven at 80 - 90 ^oC overnight. The dried powder was then ground finely and calcined at 550 ^oC for 6 hours at a heating rate of 3 ^oC min^{-1} to remove the template. The samples with Si/Ti ratio of 50 in the gel were named Ti-MCM-48. The Si/Ti ratio in the final product is reported to be 47.[2]

Synthesis of CdS-MCM-48: CdS-MCM-48 was synthesized by post-impregnation method as noted below. Cadmium acetate dihydrate and thiourea were adopted as the Cd and S source, respectively. 0.5 g of calcined Si-MCM-48 was added to 25 mL of methanol and stirred vigorously in a round bottom flask. Then the required amount of $Cd(OAc)_2{\bullet}2H_2O$ was added slowly. The dispersion was stirred at room temperature for 48 h. Afterwards, thiourea dissolved in 25 mL methanol was added to the previous dispersion. The slurry was refluxed at 70 ^oC while being stirred for 5 h. The suspension was filtered and washed thoroughly with de-ionized water and methanol. Finally, the wet paste obtained was dried in an oven overnight and the sample was labeled as CdS-MCM-48. In this work, we synthesized the sample with Si/CdS ratio of 25 in the synthesis gel and the samples was denoted as CdS-MCM-48 (the calculated Si/CdS ratio from AAS studies was 45).[3]

Synthesis of CdS-Ti-MCM-48: 0.15 g pre-formed Ti-MCM-48 was added, along with an appropriate amount of cadmium acetate ($Cd(OAc)_2$), in 50 mL HPLC methanol under vigorous stirring in a round bottom flask at room temperature for 48 h. Afterwards, thiourea, adopted as the sulfur source in this work, dissolved in 25 mL HPLC grade methanol was added to the previously made solution. The slurry was then refluxed at 70 ^{o}C while being stirred for 5 h. The suspension was filtered and washed thoroughly with de-ionized water and heated methanol. Finally, the wet paste was dried in the oven overnight and the sample was labeled as CdS-Ti-MCM-48. In this work, the ratio of Si/Ti and Si/CdS was estimated to be 47 and 40 respectively.

Synthesis of RuO_2-CdS-Ti-MCM-48: 0.1 g pre-formed Ti-MCM-48 was added, along with an appropriate amount of ruthenium (III) chloride hydrate, in 20 mL HPLC methanol under vigorous stirring in a round bottom flask at room temperature for 4 h. Afterwards, the mixed slurry was dried in oven at 80 - 90 ^{o}C overnight. The dried powder was then calcined at 500 ^{o}C for 5 hours at a heating rate of 3 ^{o}C min^{-1} to yield 1wt.% RuO_2 loaded Ti-MCM-48. After that, the 1 wt.% RuO_2-Ti-MCM-48 was added with an appropriate amount of cadmium acetate ($Cd(OAc)_2$), in 50 mL HPLC methanol under vigorous stirring in a round bottom flask at room temperature for 48 h. Subsequently, thiourea, adopted as the sulfur source in this work, dissolved in 25 mL HPLC grade methanol was added to the previously made solution. The slurry was then refluxed at 70 ^{o}C while being stirred for 5 hours. The suspension was filtered and washed thoroughly with de-ionized water and heated methanol. Finally, the wet paste was dried in the oven overnight and the sample was labeled as RuO_2-CdS-Ti-MCM-48.

Structure characterizations: Powder X-ray diffraction patterns (XRD) of the synthesized photocatalysts were recorded on a Rigaku Ultima IV X-ray diffractometer using Cu Kα radiation of λ = 1.540806 Å. The diffractometer was operated at 40 kV and 40 mA and with a step width of 0.02° and the scan rate used was 0.24°/min. The low angle scans were conducted between 2θ = 2 - 6^o whereas the long angle scans were conducted between 2θ = 20 - 70^o. N_2 adsorption-desorption isotherms of the photocatalysts were performed on a Quantachrome Nova 2200*e* gas adsorption analyzer at 77K. Samples were dried in an air oven overnight and degassed at 100 ^{o}C extensively, prior to the adsorption measurements. 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. Diffuse reflectance (DR) spectra were obtained using a Cary 100 Bio UV-Visible spectrophotometer equipped with a Harrick DR accessory. Prior to the measurements, the samples were dried in an air oven for overnight and the DR spectra was recorded in the range from 200 – 600 nm using a mesoporous siliceous sample as background immediately after taking the sample from the oven. Transmission electron spectroscopy (TEM) image of a representative CdS-Ti-MCM-48 sample was obtained using a JEOL JEM-2100 LaB_6 transmission electron microscope (TEM) instrument equipped with the high-resolution (HRP) style objective-lens pole piece at an acceleration voltage of 200 kV. TEM images were recorded 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 (EDX) spectrometer is provided for compositional analysis and mapping at high count rates. UV-Vis diffuse reflectance spectra were acquired using a Cary 100 Bio UV-Visible spectrophotometer with praying mantis accessory (Harrick Scientific). A custom-designed Kratos Axis Ultra X-ray photoelectron spectroscopy (XPS) system was used to investigate surface components of the CdS-Ti-MCM-48 materials. Briefly, samples were pressed into indium foil and mounted onto a copper stub. These samples were then transfer to analysis chamber to proceed 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. The composition of the surface was determined by dividing the individual peak area after background subtraction by their respective atomic sensitivity factors. X–band continuous wave Electron paramagnetic resonance (EPR) experiments were conducted on a Bruker Elexsys E580 spectrometer equipped with Oxford CF935 helium flow cryostat with ITC–5025 temperature controller. Samples dispersed in 1 M Glycerol/H_2O were purged with argon and illuminated at 77 K, and EPR spectra were recorded at 5 K immediately after illumination. A 300–W Xe UV lamp (ILC) equipped with IR and 400 nm cut off filters was used as the light source. The g factors were calibrated for homogeneity and accuracy by comparison to a coal standard, $g = 2.00285 \pm 0.00005$.

Photocatalytic water splitting: The photocatalytic activities of the samples were examined in a gas-closed system. A catalyst sample of 40 mg was dispersed in 10 mL of deionized water and 10 mL ethanol or 20 mL of pure deionized water in a 30 mL glass reactor. Prior to light irradiation, the photoreaction system was purged with high-purity argon for 30 min to remove air. The light source was a 300-W Xe lamp equipped with an optical cutoff filter ($\lambda > 400$ nm). The reaction proceeded under vigorous stirring using a magnetic stirring rod coated with polytetrafluoroethylene (PTFE). The evolved H_2 and O_2 gas was analyzed using gas chromatography SRI 8610C (molecular sieve column, TCD detector, argon as carrier gas) and previously used calibration graphs.

References

1. B. Boote, H. Subramanian and K. T. Ranjit, *Chemical Communications*, 2007, 4543-4545.
2. D. Zhao, S. Budhi, A. Rodriguez and R. T. Koodali, *International Journal of Hydrogen Energy*, 2010, **35**, 5276-5283.
3. R. Peng, D. Zhao, J. Baltrusaitis, C.-M. Wu and R. T. Koodali, *RSC Advances*, 2012, **2**, 5754-5767.

Section 2 High angle XRD patterns of all samples

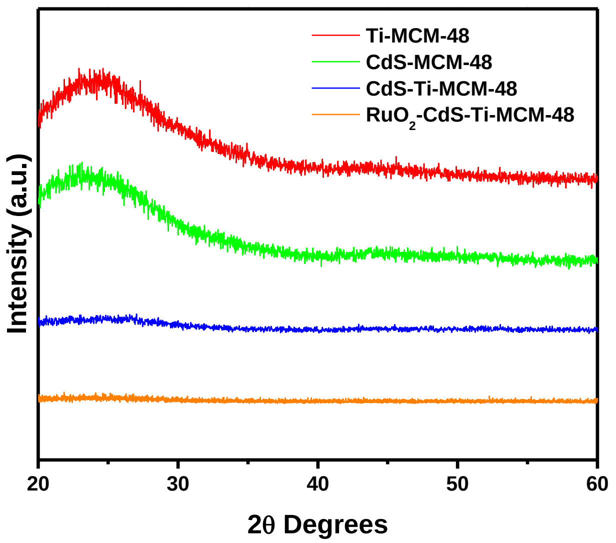


Figure S1. High angle XRD patterns of all studied samples.

Section 3 N_2 physisorption studies of all samples

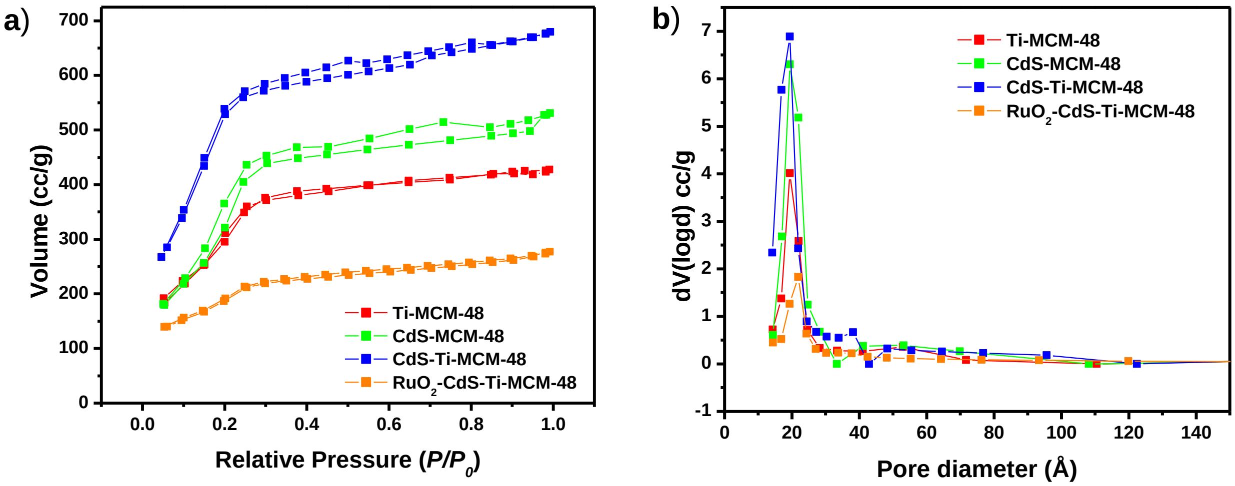


Figure S2. a) N_2 physisorption isotherms of the studied samples. b) Pore size distribution of the studied samples.

Section 4 XPS spectra of fresh CdS-Ti-MCM-48 sample

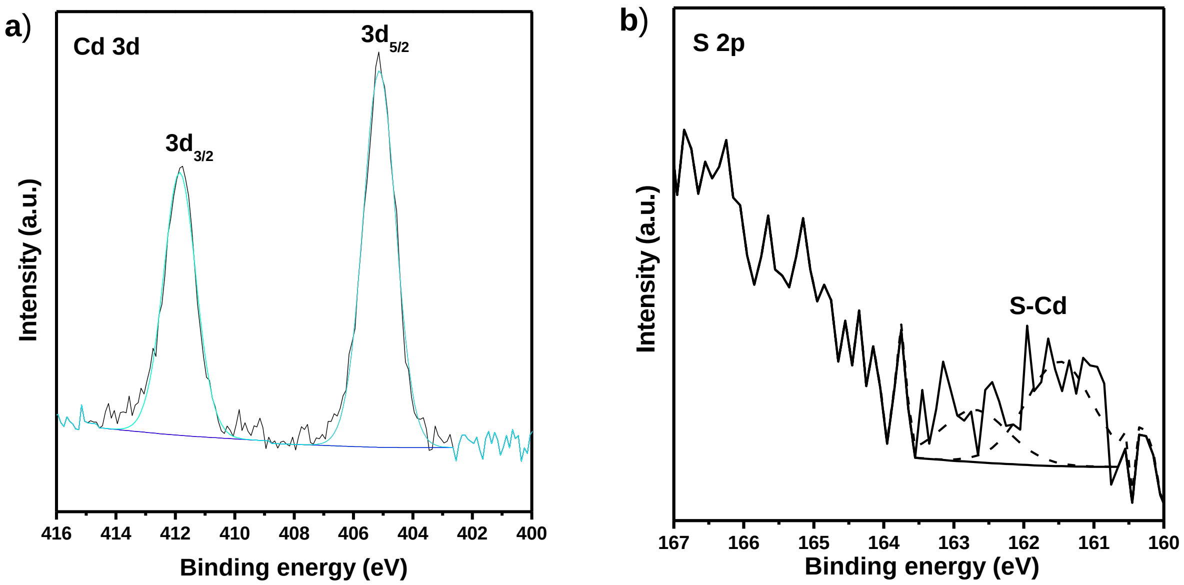


Figure S3. a) XPS of Cd peaks from CdS-Ti-MCM-48 sample. b) XPS of S peaks from CdS-Ti-MCM-48 sample.

Section 5 TEM analysis of CdS-Ti-MCM-48 sample

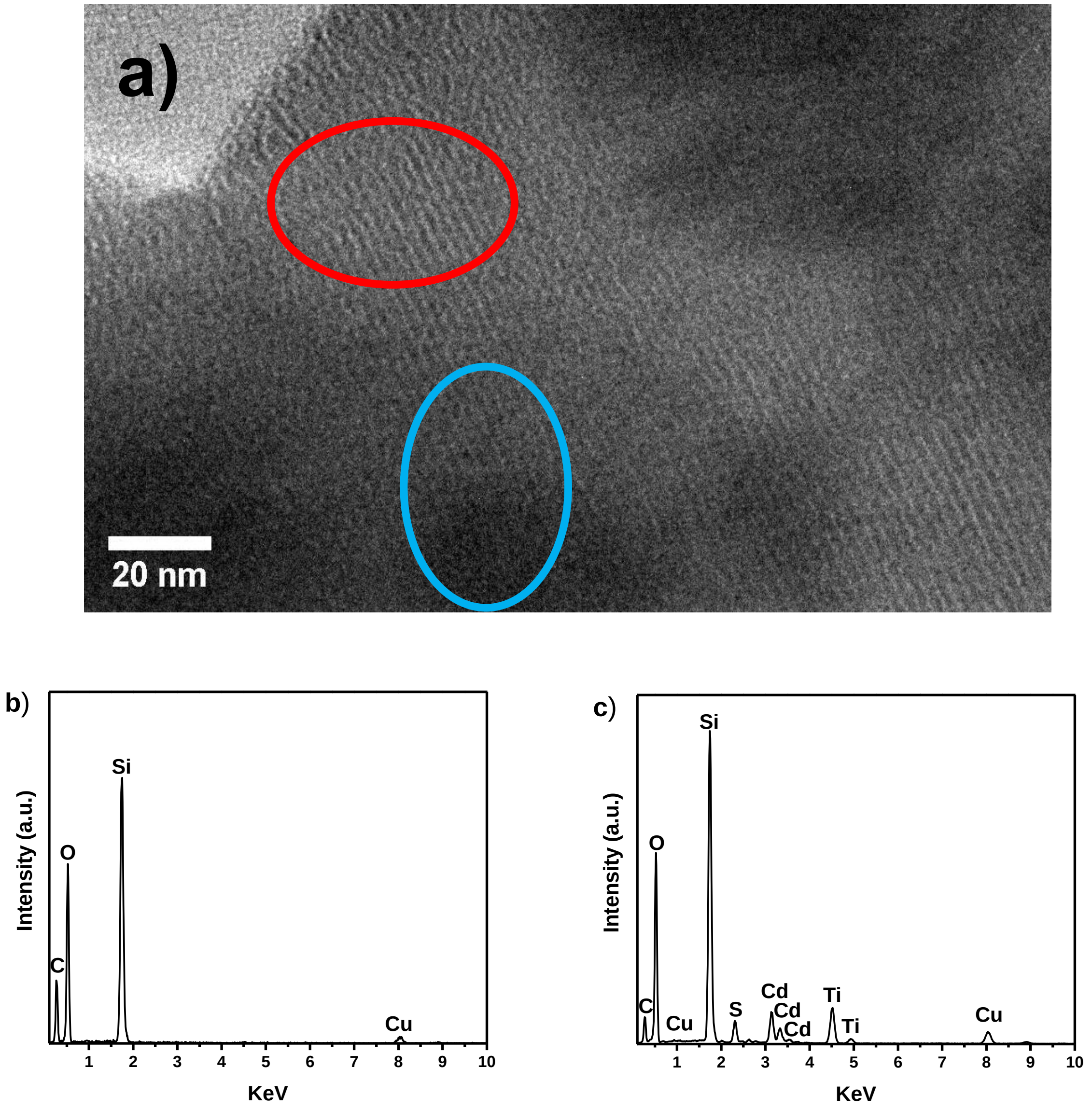
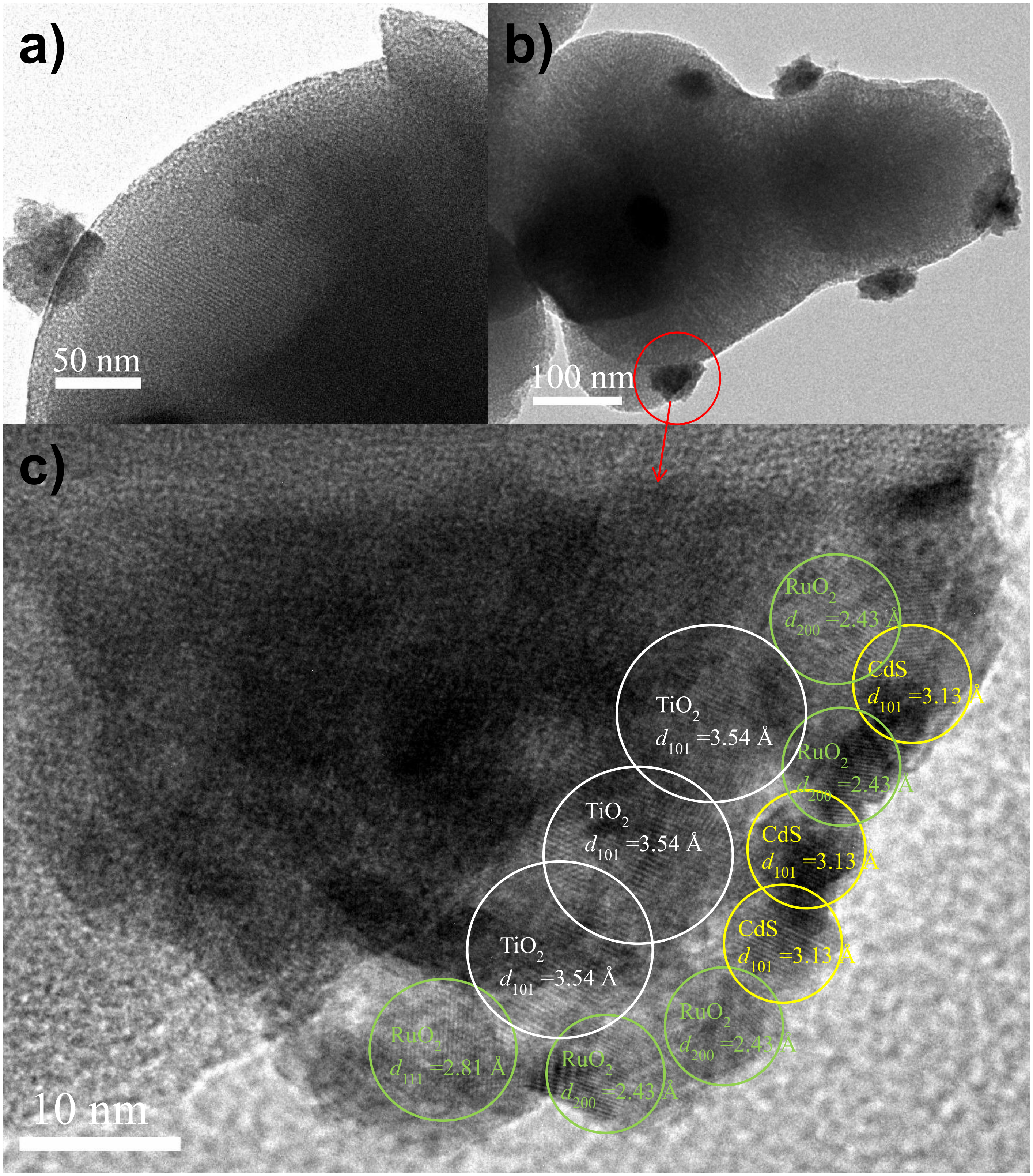


Figure S4. a) TEM image of CdS-Ti-MCM-48. b) EDS plot of blue open circle area. c) EDS plot of red open circle area.

Section 6 TEM analysis of RuO_2-CdS-Ti-MCM-48 sample



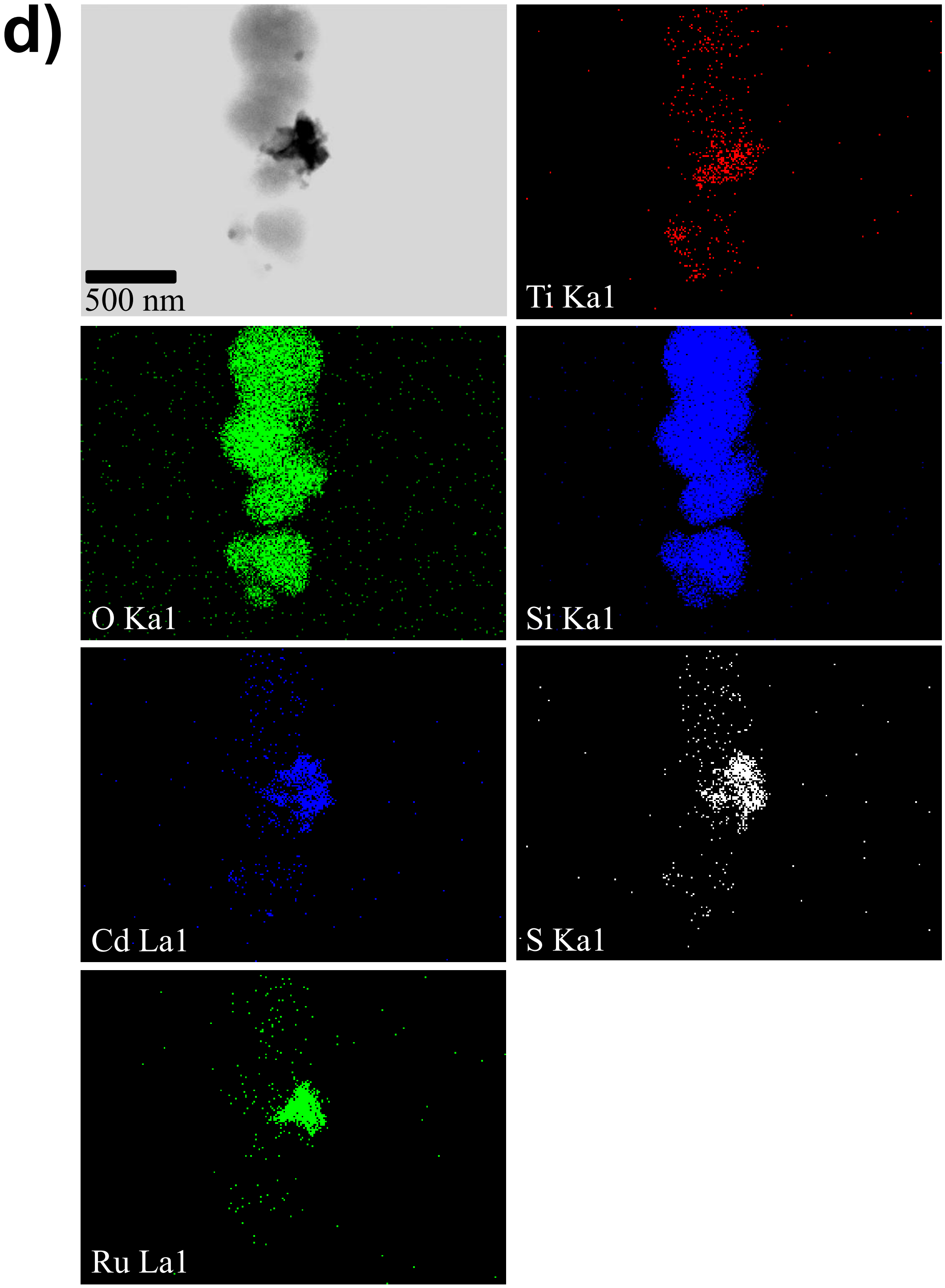


Figure S5. a) TEM image of RuO_2-CdS-Ti-MCM-48. b) TEM image of RuO_2-CdS-Ti-MCM-48. c) HRTEM image of RuO_2-CdS-Ti-MCM-48. d) EDS mapping of RuO_2-CdS-Ti-MCM-48.

Section 7 Photocatalytic splitting of pure water over RuO_2-CdS-Ti-MCM-48 sample

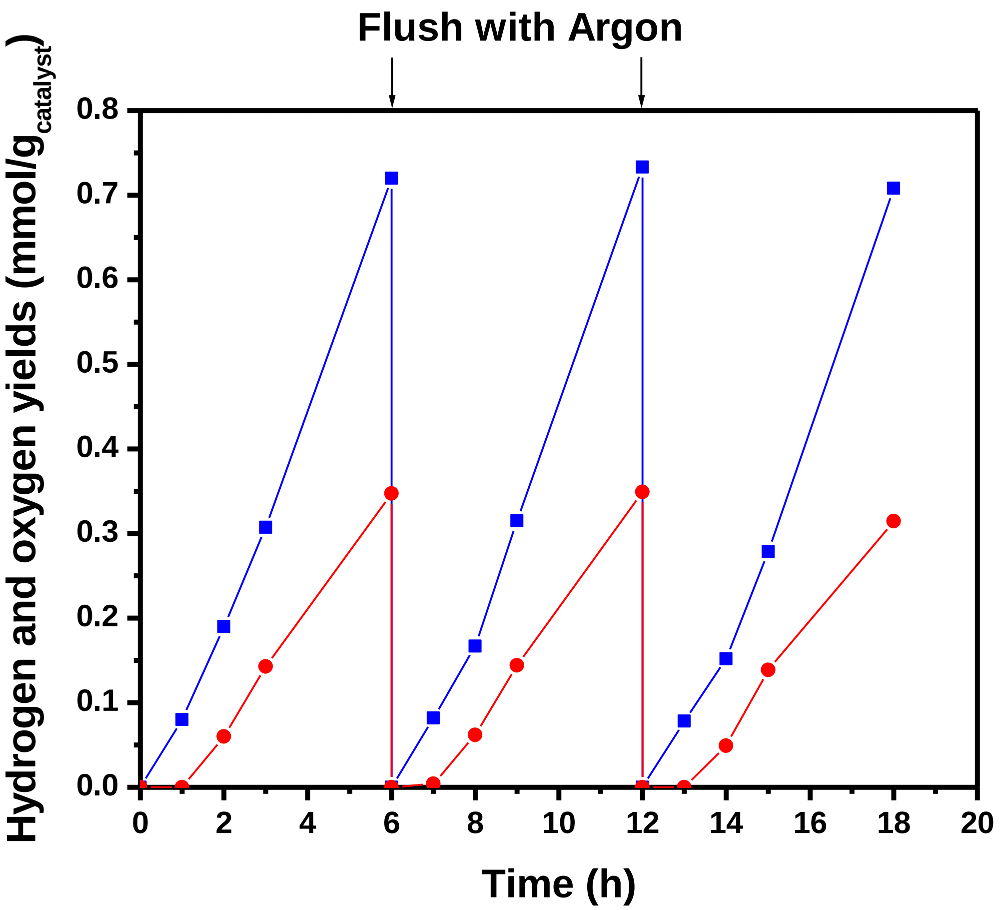


Figure S6. Photocatalytic splitting of pure water over RuO_2-CdS-Ti-MCM-48. Closed squares (blue) and circles (red) denote H_2 and O_2 yields, respectively.

Section 8 EPR analysis of CdS-Ti-MCM-48 and RuO_2-CdS-Ti-MCM-48 samples

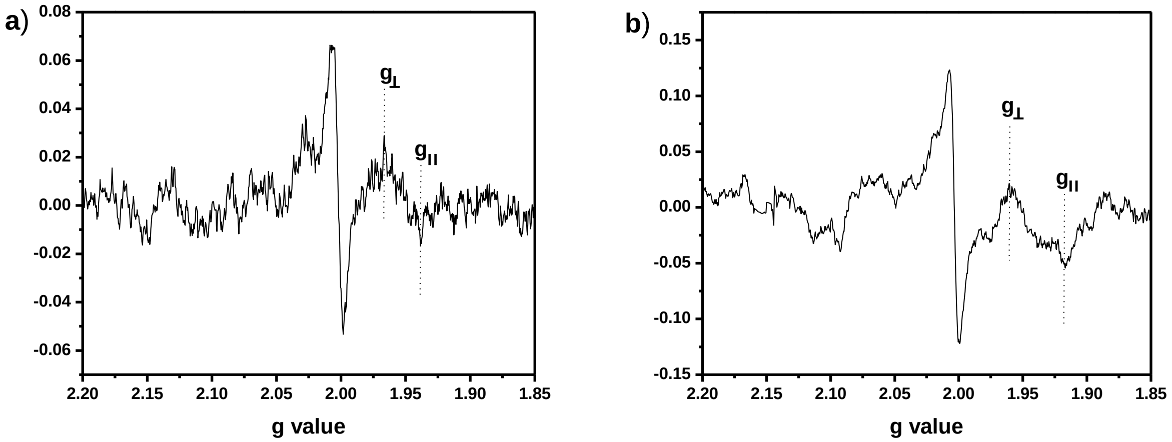


Figure S7. a) EPR spectra of CdS-Ti-MCM-48 and b) RuO_2-CdS-Ti-MCM-48 samples. A strong signal near *g* = 2.004 is due to organic radicals formed by the reaction of photogenerated holes with glycerol.

Section 9 XPS spectra of spent CdS-Ti-MCM-48 sample

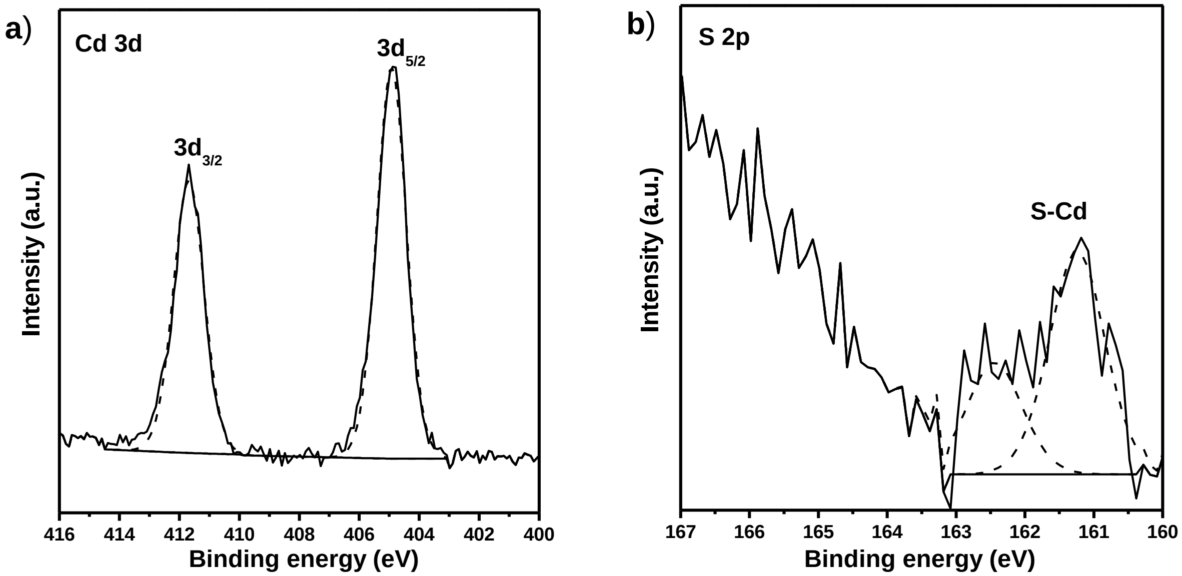


Figure S8. a) XPS of Cd peaks from CdS-Ti-MCM-48-spent sample. b) XPS of S peaks from CdS-Ti-MCM-48-spent sample.

Section 10 Table S1

Table 1. Textural properties of all samples.

Material	**Si/Ti[a] (mol)**	**Si/CdS[a] (mol)**	**Surface Area (m^2g^{-1})**	**Pore Volume (cm^3g^{-1})**	**Pore Size (Å)**
Ti-MCM-48	47	NA	1312	0.76	19.4
CdS-MCM-48	NA	45	1546	0.82	19.4
CdS-Ti-MCM-48	47	40	1139	0.66	19.3
RuO_2-CdS-Ti-MCM-48	47	42	797	0.58	19.9

[a] Molar ratio in the final product determined by AAS; NA denotes Not applicable.