Visible light photoreduction of CO_2 using CdSe/Pt/TiO_2 heterostructured catalysts

Supporting Information

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1. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) was used to determine the surface composition of the CdSe/Pt/TiO_2 powders. The powders were analyzed using a PHI 5600ci instrument, by placing them in a small well machined into the surface of the sample holder. Monochromatic Al Kα X-rays (1486.6 eV) were used and the pass energy of the analyzer was set at 58.7 eV. The insulating powders required charge neutralization with a low-energy electron gun. Binding energies were referenced to adventitious carbon at 284.6 eV. Elemental surface concentrations were calculated from peak areas based on manufacturer-provided sensitivity factors.

The Pt 4f spectrum was curve fitted using CasaXPS software after subtracting a Shirley background (Figure S1). The peak parameters used for the curve-fitting analysis were a combination of average values for peak positions taken from the literature and lineshapes resulting from optimizing the curve-fitting results for a series of CdSe/TiO_2 powders not described herein.

2. Preparation of CdSe/Pt/TiO_2 heterostructured catalysts

Preparation of Pt/TiO_2

Hexachloroplatinic acid (0.133 g, Alfa) was dissolved in 3-4 ml deionized water, and then added in a drop wise fashion to titanium dioxide (2.5 g, Degussa P25) to form a wet paste. This paste was dried on a hotplate at 120 °C, calcined in air for 1 h at 400 °C, and then reduced under hydrogen for 2 h at 400 °C. The final product was a dark grey powder which is ~2% Pt by weight.

Preparation of thermally annealed CdSe/Pt/TiO_2 catalysts (t-CdSe/Pt/TiO_2)

Commercial CdSe QDs in toluene were cleaned twice by precipitation with methanol. The cleaned CdSe QDs were dissolved in CH_2Cl_2 and added dropwise to Pt/TiO_2. The concentration of CdSe QDs can be adjusted and in most cases, the final mixture contains about 1% CdSe. After complete evaporation of the CH_2Cl_2, the mixture was annealed at 600 °C under N_2 to desorb the organic capping molecules.

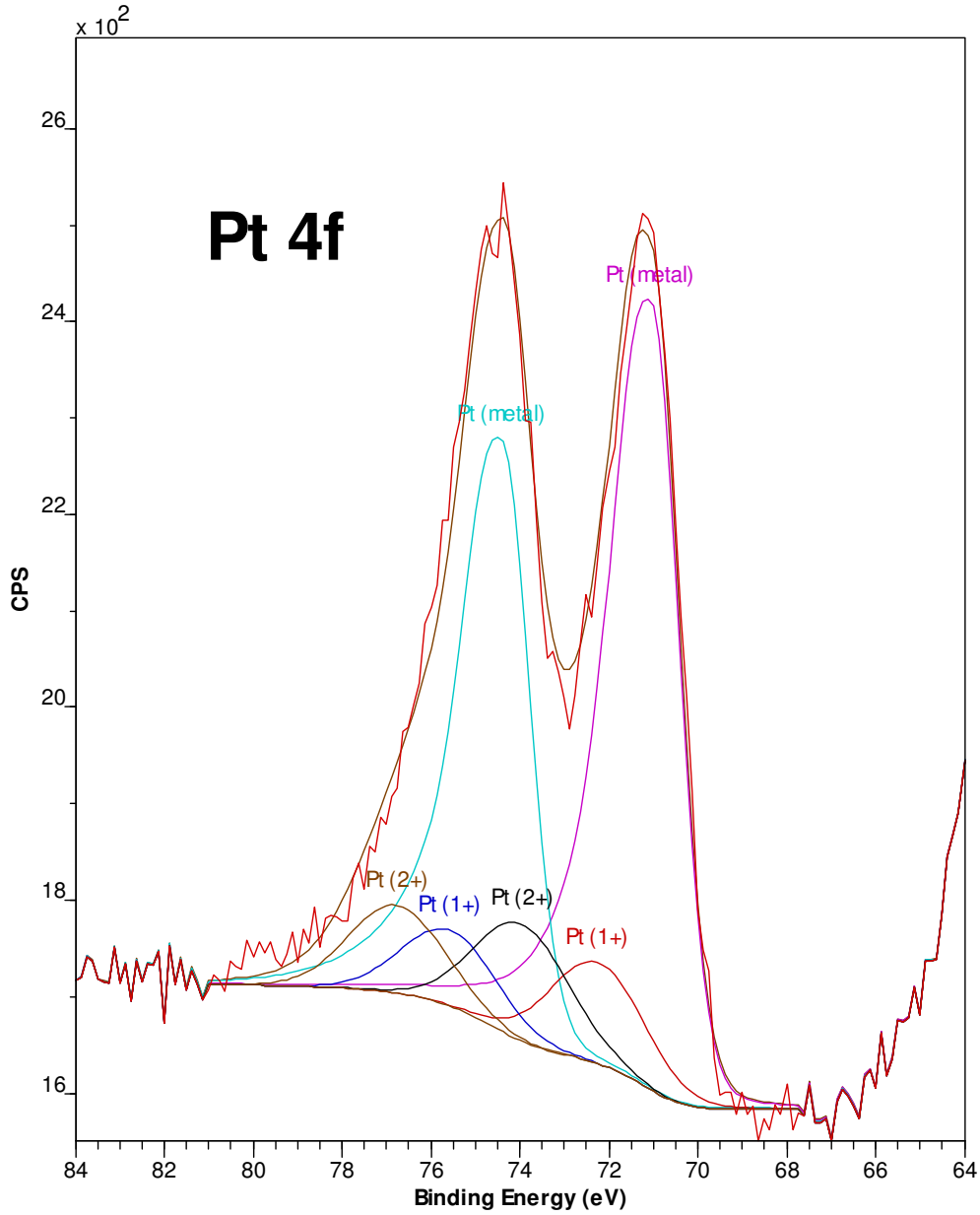

Figure S1. XPS spectra of a CdSe/Pt/TiO_2 sample showing the existence of multiple oxidation states of Pt.

Preparation of chemically treated CdSe/Pt/TiO_2 catalysts(c-CdSe/Pt/TiO_2)
Commerical CdSe QDs in toluene were cleaned twice by precipitation with methanol. The QDs were then treated with 1 M hydrazine in ethanol in the glove box for ~ 8 hrs. After treatment, the QDs were cleaned thoroughly by repeated sonication and centrifugation in large amounts of methanol. The chemically treated QDs were then dispersed in hexane by sonication and mixed with Pt/TiO_2. The powder was dried and kept under vacuum over night to remove residual solvent.

The removal of the capping molecules was confirmed by the disappearance of the CH stretch bands in the IR spectra of a 6 nm QD film after the hydrazine treatment (Figure S2A). The absorption property of the treated QDs was not affected by this process as evidenced by minimal changes in the UV/vis absorption spectra even after 5 hours of exposure to air for a thin film of hydrazine treated 6 nm CdSe QDs (Figure S2B). The 2.5 nm CdSe QDs also survive the treatment (data not shown).

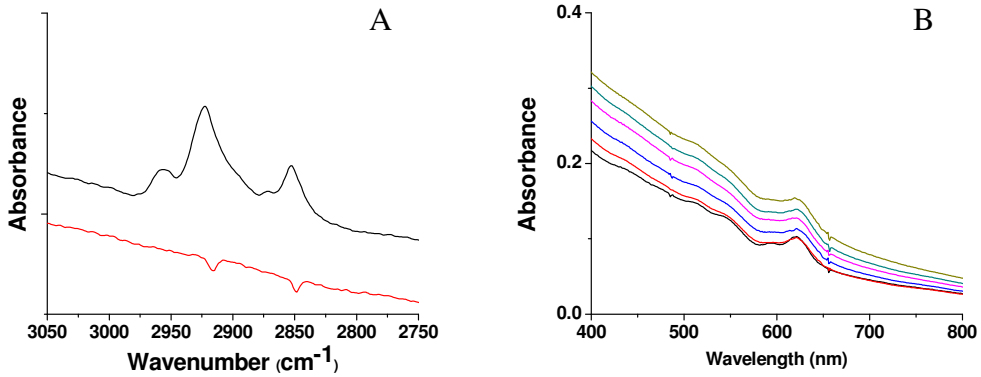

Figure S2. (A) CH stretch band of a thin film of 6 nm CdSe QDs before (black) and after (red) 1 M hydrazine in ethanol treatment. (B) UV/vis spectrum of the same film before (black) and immediately after (red) 1 M hydrazine treatment. The other four spectra of the treated film exposed to air were taken (from bottom to top) 1, 2, 3 and 5 hours after the treatment. These four spectra were offset for clarity. The red tail in the UV/vis spectra is due to light scattering in the QD film.

3. Optical properties of c-CdSe/Pt/TiO_2 heterostructured catalysts

The optical properties of CdSe/Pt/TiO_2 heterostructured catalysts are characterized using a Perkin Elmer Lambda 1050 UV/vis/NIR spectrometer equipped with a Labsphere 150 mm integrating sphere. Figure S3 shows the diffuse reflectance spectra of P25 TiO_2 nanoparticles, Pt/TiO_2, and c-CdSe/Pt/TiO_2 (Pt/TiO_2 sensitized by a hydrazine treated mixture of 2.5 and 6 nm CdSe QDs). The absorption features in the visible from CdSe QDs are clear in the diffuse reflectance spectrum of c-CdSe/Pt/TiO_2 sample. We note that the absorption feature from the 2.5 nm CdSe QDs are difficult to see because the absorption features of the 2.5 nm QDs overlap with the absorption of 6 nm CdSe QDs. When only 2.5 nm CdSe QDs are used and treated in the same fashion, absorption features consistent with this size of CdSe QDs are clearly distinguishable (data not shown).

4. Photoreduction experiments

Monitoring the photoreduction of CO_2 with FTIR spectroscopy

The progress of the photoreduction of CO_2 was monitored using FTIR Spectroscopy (Nicolet Nexus 670). The photocatalyst was placed in a crucible inside a stainless steel cube (MDC Vacuum Products) fitted with two KBr windows on opposite sides of the cube and one UV quartz viewport on top. The sample crucible was located beneath the path of the FTIR beam, permitting the analysis of gas phase analytes within the photocatalysis cell. The atmosphere of the cube could be evacuated using a turbo pump

(Varian V70) and dosed with CO_2 using a precision leak valve. Water was delivered from a sealed vessel by creating a negative pressure differential between the vessel and the reaction cell. Pressure within the FTIR cell was monitored using thermocouple and ion gauge detectors (Varian senTorr).

Once the FTIR cell had been loaded with a photocatalyst sample and dosed with H_2O and CO_2, it was subsequently irradiated through the quartz viewport using light from a 300 W Xe arc lamp (Newport), fitted with a manual shutter and an optical filter holder. Various long pass filters are used to control the light wavelengths employed in this study. A background spectrum taken at the beginning of each reaction cycle, while the system was under vacuum, served as the background for subsequent sample spectra.

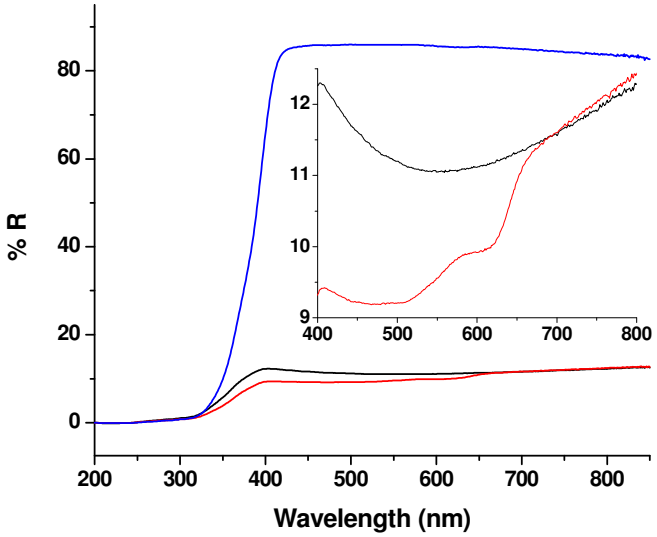

Figure S3. Diffuse reflectance spectra of P25 TiO_2 (blue), Pt/TiO_2 (black) and c-$CdSe/Pt/TiO_2$ (red). Inset is a zoom-in of the Pt/TiO_2 (black) and c-$CdSe/PtTiO_2$ (red) spectra in the 400 to 800 nm region.

Monitoring the photoreduction of CO_2 using GC analysis

A gas-tight photocatalysis cell was constructed using a stainless steel cube (MDC Vacuum Products) fitted with two inlet/outlet valves, one GC sampling port (HP 5890) connected via Swagelok fittings, and one UV quartz viewport; the other two sides were sealed with blank conflat covers. The total volume of the cell was ~ 300 ml. A small glass beaker was placed at the bottom of the photocatalysis cell as a stand for a watch glass, on which catalyst samples could be weighed and loaded for photoreaction. After a new septum was placed in the sampling port and a catalyst sample was loaded, the photocatalysis cell could be purged with CO_2 (UHP grade, Matheson) bubbled through deionized water.

The photocatalysis cell was subsequently irradiated through the quartz viewport using light from a 300 W Xe arc lamp (Newport), fitted with a manual shutter and an optical filter holder. Various long pass filters were used to control the light wavelengths employed in this study.

GC analysis of photoreduction products was performed on an HP 5890 Gas Chromatograph using a heated inlet and a thermal conductivity detector. The carrier gas was He and the column used is a 60/80 Carboxen 1000 15' x 1/8" SS (2.1 mm I.D.). Samples were injected manually using a 10 ml gas-tight syringe.

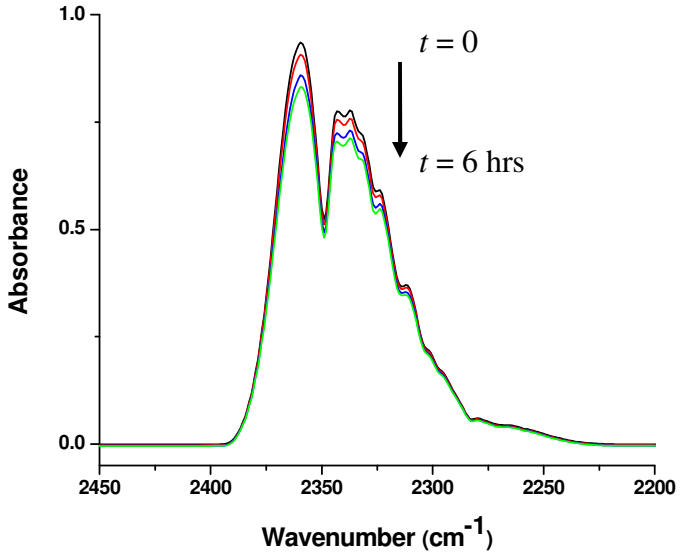

Figure S4. IR spectra of the CO_2 asymmetric stretch bands as a function of photolysis time under $\lambda > 420$ nm excitation using t-CdSe/Pt/TiO_2 photocatalyst. For clarity, only the spectra taken at $t = 0$ (before irradiation), 1, 3, and 6 hrs after light illumination (from top to bottom) are shown here.

5. Control experiments

Various control experiments were performed to verify the origin of the photoconversion of CO_2 under visible light irradiation. Figure S4 shows the CO_2 consumption as measured by the changes in the CO_2 absorption band in the IR as a function of time for a series of experiments. These experiments demonstrate that activity is only observed when t-CdSe/Pt/TiO_2 is illuminated by visible light. Under other conditions, such as no light or when Pt/TiO_2 is used, no activity is detected.

6. Calculation of photoconversion yield

The measured yield of the main product CH_4 in GC analysis is 86 ppm using 0.3 g of c-CdSe/Pt/TiO2 catalyst after 6 hours of $\lambda > 420$ nm irradiation (the catalyst becomes inactive after ~ 6 hours of continuous irradiation). This gives the total yield of CH_4 ~1.1 μmol over 6 hours and the production rate of 0.18 μmol h^{-1} or 48 ppm g^{-1} h^{-1}. In IR experiments, the CO_2 IR absorption band is reduced by 10% with the initial CO_2 pressure of 0.3 torr. This corresponds to a total conversion of CO_2 ~0.82 μmol over 6 hours, consistent with the GC anaylsis experiments. The slight difference is likely due to different reaction conditions and different photocatalysts used (c-CdSe/Pt/TiO_2 in GC analysis experiments vs t-CdSe/Pt/TiO_2 in IR experiments).

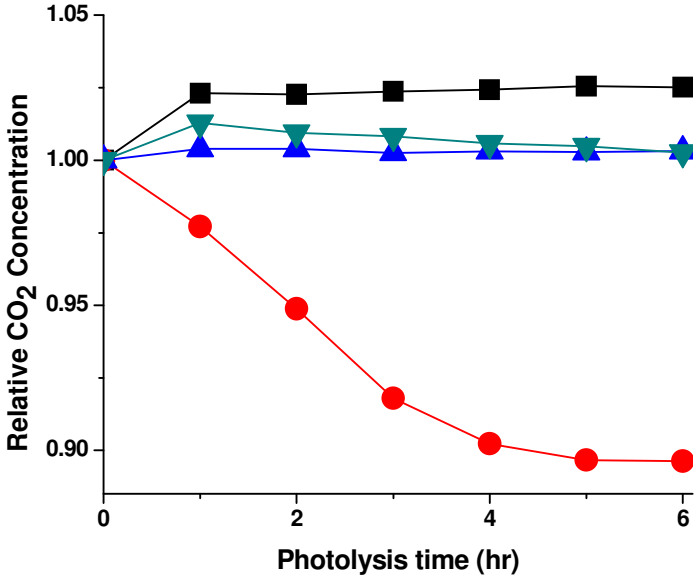

Figure S5. Photocatalytic reduction of CO_2 measured by IR spectroscopy using t-CdSe/Pt/TiO_2 photocatalysts under visible light $\lambda > 420$ nm irradiation (red), as well as a series of control experiments including Pt/TiO_2 under $\lambda > 420$ nm irradiation (blue), t-CdSe/Pt/TiO_2 photocatalysts in the dark (green), and t-CdSe under white light irradiation (black).