

*Electronic Supporting Information*

# High Surface Area, Amorphous Titania with Reactive $\text{Ti}^{3+}$ through Photo-assisted Synthesis Method for Photocatalytic $\text{H}_2$ Generation

*Dennis Zywitzki<sup>1</sup>, Hangkun Jing<sup>2</sup>, Harun Tüysüz<sup>1\*</sup>, Candace K. Chan<sup>2\*\*</sup>*

1. Department of Heterogeneous Catalysis, Max-Planck-Institut für Kohlenforschung, Mülheim an der Ruhr, Germany; [\\*tueysuez@kofo.mpg.de](mailto:*tueysuez@kofo.mpg.de)

2. Materials Science and Engineering, School for Engineering of Matter, Transport and Energy; Arizona State University, Tempe, AZ, U.S.A.; [\\*\\*candace.chan@asu.edu](mailto:**candace.chan@asu.edu)

## Experimental Methods

### 1. Synthesis and Evaluation of Photocatalysts

#### 1.1 Direct Injection

In a typical experiment, the photoreactor vessel was filled with 200 mL reaction solution (10 v/v% methanol in deionized water). The cryostat was set to 20 °C and the Ar flow was set to 114 sccm. Next, 2.5 mmol of precursor (Table S1) were added to the solution and the reactor volume was purged for 45 min. The mass flow controller (MFC) was then adjusted to 50 sccm. After the reaction solution was de-aerated (approximately 45 - 60 min), the UV-lamp was turned on and the H<sub>2</sub> evolution measurement was started.

**Table S1. Precursors and their respective injection volume.**

Label	Precursor	Injected Volume
DI-OEt	Ti(OEt) <sub>4</sub>	525 μL
DI-OBu	Ti(OBu) <sub>4</sub>	852 μL
DI-OiPr	Ti(O <sup>i</sup> Pr) <sub>4</sub>	741 μL

After the photoreaction, the reaction suspension was transferred into a beaker and settled overnight. The supernatant solution was decanted off and the remaining slurry was centrifuged for 40 min at 9000 rpm. The wet powder was dried at 60 °C overnight prior to characterization with BET, Raman, XRD, etc. These samples were labeled as “DI-OEt”, “DI-OBu” and “DI-OiPr”, where “DI” stands for direct injection and “OEt” for the ligand of the precursor species.

#### 1.2 Ex-situ Catalyst Preparation

In order to study the properties of the materials obtained after hydrolysis of the titanium alkoxide precursors but prior to UV-light irradiation, an ex-situ catalyst preparation method was used. Here, 2.5 mmol precursor was hydrolyzed in a beaker under heavy stirring in 200 mL reaction solution (10 v/v% methanol in deionized water). The mixture was stirred for 1 h. After settling, the supernatant was decanted off and the remaining slurry centrifuged. The wet sample was dried at 60°C overnight prior to characterization with BET, Raman, XRD, etc.

#### 1.3 H<sub>2</sub> Evolution Measurements of ES-Samples and P25 Reference

The as-prepared ES samples or 200 mg P25 were dispersed in 20 mL of the reaction solution (10 vol% MeOH in de-ionized water). The suspension was transferred into the UV-reactor and the beaker was flushed two times with 20 mL of the reaction solution. The remaining 140 mL

reaction solution were added and then purged with Ar at 114 sccm for 45 min. Afterwards, the flowrate was adjusted to 50 sccm and the UV-lamp was turned on. The H<sub>2</sub> evolution was measured for 2 h. For comparing H<sub>2</sub> evolution rates between different samples, it was assumed that the same amount of photocatalyst (200 mg) was in the 200 mL reaction solution.

#### ***1.4 In-Situ Photodeposition of Platinum Co-catalysts***

***DI-OEt/Pt:*** 4.26 mg of potassium tetrachloridoplatinate (contains 2 mg Pt, results in 1 wt% loading) were dissolved in 5 mL reaction solution (10 vol% MeOH in de-ionized water). The photoreactor vessel was filled with 195 mL of reaction solution. The cryostat was set to 20 °C and the Ar MFC was set to 114 sccm. Then, 2.5 mmol (525 µL) of titanium ethoxide were added to the solution. After 30 min, the K<sub>2</sub>PtCl<sub>4</sub> solution was added. The reaction volume was purged with Ar at 114 sccm for 30 min. Afterwards, the flow rate was adjusted to 50 sccm and the UV-lamp was turned on for the Pt photodeposition and simultaneous H<sub>2</sub> evolution measurement.

***DI-OEt-UV/Pt:*** The titanium ethoxide precursor was added to the photoreactor as described above for DI-OEt/Pt. Then, the UV-lamp was turned on and the photocatalyst was irradiated for 30 min and became blue in color. Next, the UV-lamp was turned off and the reactor was purged under Ar for 15 min. During this time period, the photocatalyst still remained blue. Then, the above K<sub>2</sub>PtCl<sub>4</sub> solution was added to the photoreactor under the protection of Ar. After the addition of K<sub>2</sub>PtCl<sub>4</sub>, the photocatalyst turned from blue to white within less than 10 seconds (see Supporting Video 1). The UV-lamp was then turned on for the H<sub>2</sub> evolution measurement.

## **2. Materials Characterization**

### ***2.1 UV-Vis Spectroscopy***

UV-Vis spectroscopy was performed with a Lambda-365 UV-Vis spectrometer by Perkin-Elmer. The diffuse reflectance of the solid samples was determined by inserting the powder into a powder-cuvette. This cuvette was placed on the top port of the integrating sphere. The spectral bandwidth was set to 5 and the scanning rate to 200 nm/min. The spectrum was recorded for the wavelengths in the range of 800 nm to 200 nm.

The extinction (absorption plus scattering) of the catalyst in suspension was measured by inserting the sample into a liquid-cuvette, which was placed in front of the integrating sphere in order to reduce the effect of scattering. The spectral bandwidth, scanning rate and range of wavelengths was the same as for the powdered samples.

### ***2.2 Nitrogen Physisorption***

BET surface area measurements were obtained from nitrogen physisorption measurements (Quantachrome NOVA 3200e). 100 – 200 mg sample were degassed under vacuum at 100 °C

overnight. The partial pressure area between 0.05 and 0.25 was used for calculating the surface-area via the BET-isotherm. The adsorbed volume at  $P/P_0 = 0.97$  was used to determine the total pore volume.

### ***2.3 Raman Spectroscopy***

Raman spectra were recorded on the powdered samples using an Ocean Optics QE Pro-Raman spectrometer using an excitation wavelength of 785 nm. The laser intensity was set to 1.506 and the integration time to 10 sec for  $\text{TiO}_2$  samples and to 120 sec for  $\text{TiO}_2/\text{Pt}$  samples, due to their overall higher absorption and the resulting low scattering intensity. Hombikat N10 was used to obtain the reference spectrum for anatase, and TR UOC008950 was used to obtain the reference spectrum for rutile. Both reference samples were obtained from Huntsman Pigments (Finland).

### ***2.4 Fourier-Transform Infrared Spectroscopy (FTIR)***

FTIR spectra were measured using a Nicolet Magna 560 spectrometer in ATR configuration. The rotameter, which controls the nitrogen-flowrate for purging the spectrometer, was set to 40 %, 1 h before the measurements were conducted. 20 min before measuring, the coolant tank for the detector was filled with liquid nitrogen. The samples were applied to the industrial diamond surface of the ATR-device and pressed on with a stamp. The final spectrum obtained was an average of 64 spectra.

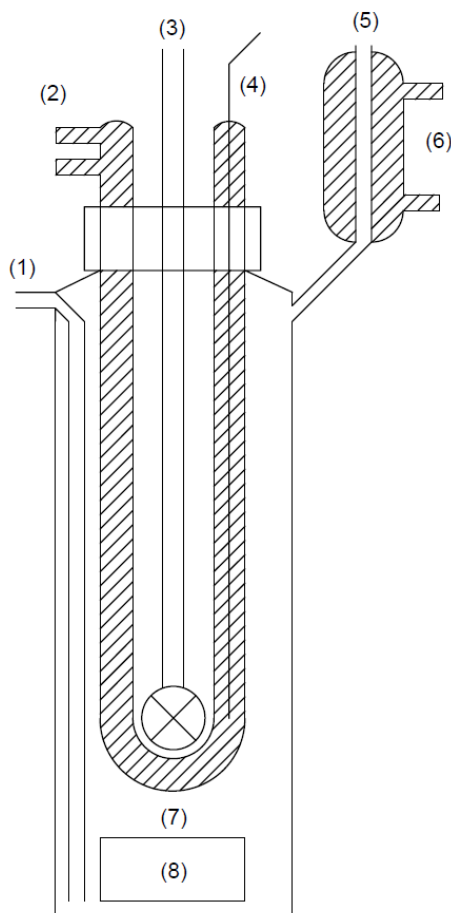
### ***2.5 X-ray Diffraction (XRD)***

Wide angle XRD patterns collected at room temperature were recorded on a Stoe theta/theta diffractometer in Bragg-Brentano geometry ( $\text{Cu K}\alpha_{1/2}$  radiation).

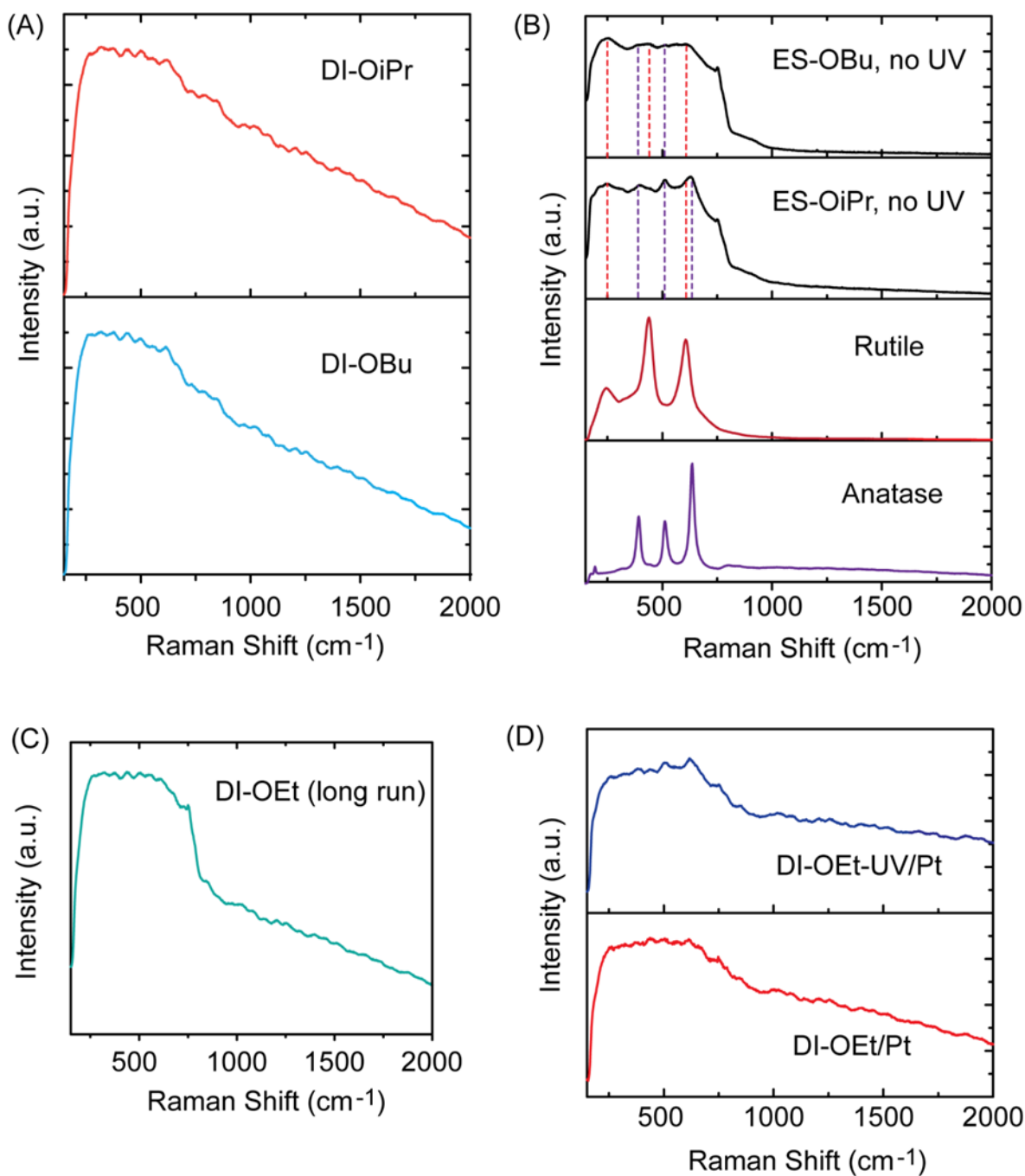
### ***2.5 X-ray Photoelectron Spectroscopy (XPS)***

XPS was performed on a VG ESCALAB 220i-XL with  $\text{Al K}\alpha$  anode (1486.6 eV) operated at 63 W and 15 kV. The X-ray takeoff angle was  $45^\circ$  and the data were acquired from the region within  $\sim 500 \mu\text{m}$  of the outer surface of the sample. Charge compensation was used because  $\text{TiO}_2$  is a wide bandgap semiconductor. A pass energy of 20 eV was used to obtain the high-resolution spectra (energy resolution 0.7 eV). The scans are 20 cycles for Ti  $2p$  and 30 cycles for Pt  $4f$ . The Ti  $2p$  spectra were calibrated with the  $\text{Ti}^{4+} 2p_{3/2}$  peak centered at 458.8 eV. For the Pt  $4f$  spectra, calibration was performed with the main C  $1s$  peak centered at 284.5 eV. Peak fitting was performed using CasaXPS processing software.

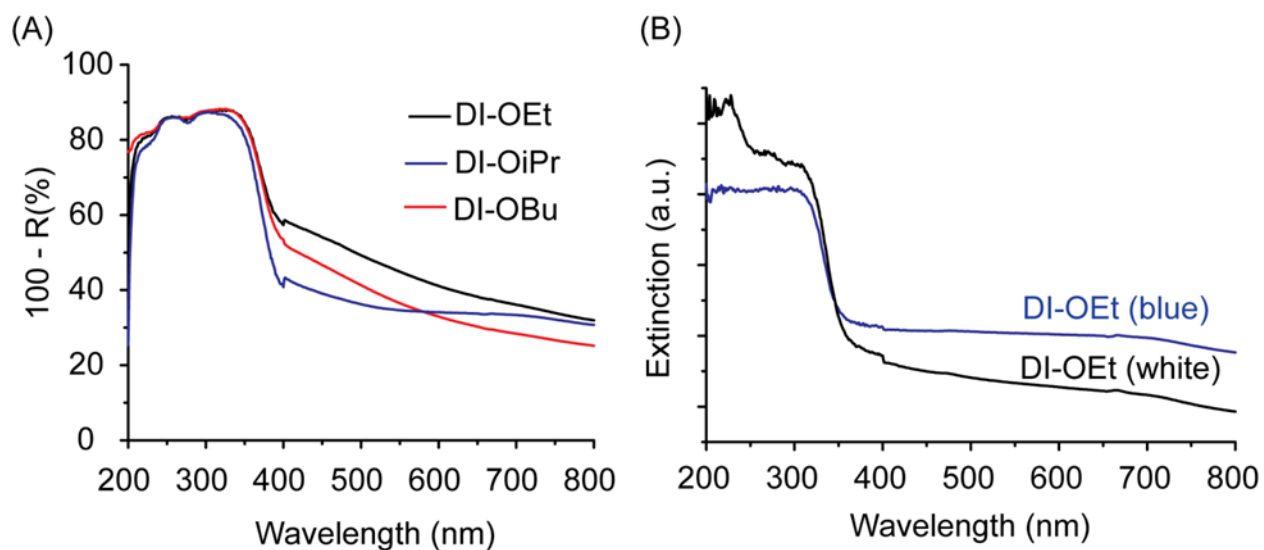
## Supporting Figures



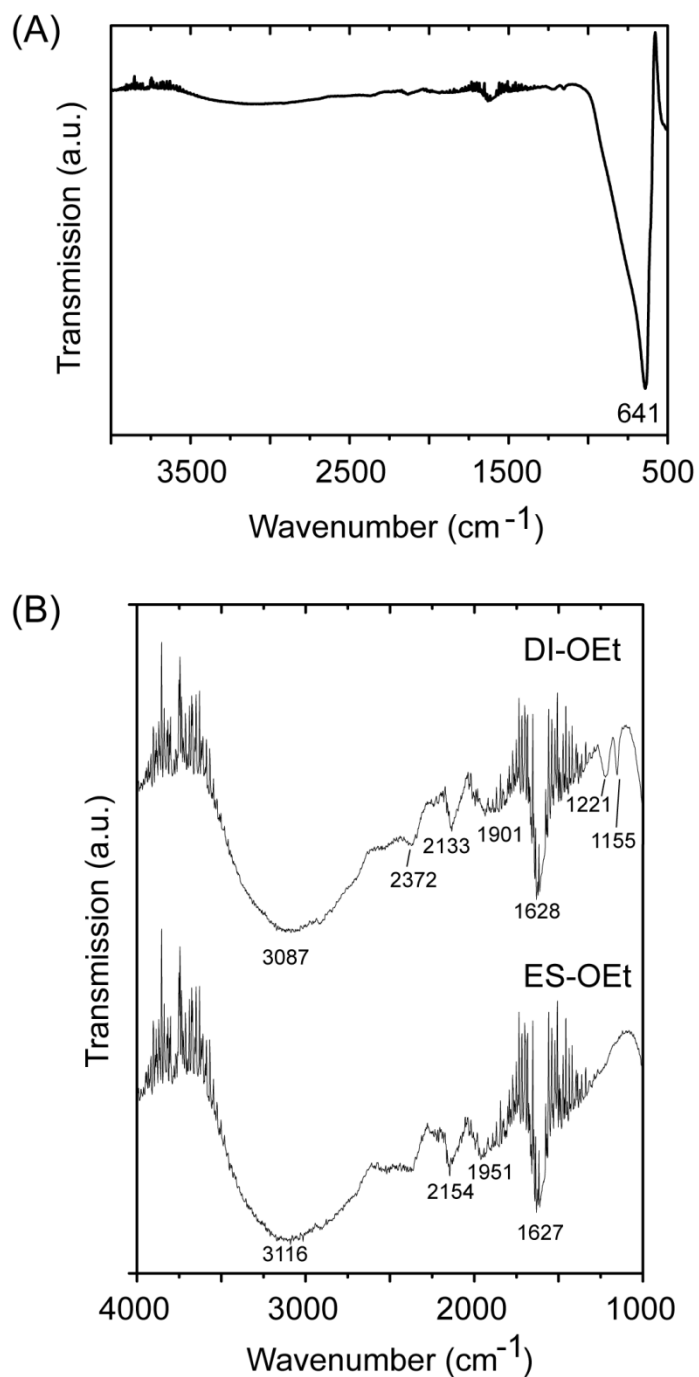
**Figure S1. UV-photoreactor setup.** In this setup, the Ar gas-flow is introduced through the reactor inlet (1) and controlled with a mass flow controller (MFC) into the reactor (7). The effluent gas flows through a small reflux-condenser (6) to the reactor outlet (5) into an Emerson XStream XEGP gas analyzing unit. UV-irradiation is supplied by a Peschl Ultraviolet TQ150 150 W middle pressure Hg-Lamp (3), which is constantly cooled by a cooling jacket (2) made of quartz glass in order to allow the UV-light to pass through. The reflux condenser and cooling jacket are supplied with cooling water that was controlled to approximately 20 °C in temperature using a cryostat. The cooling jacket is also equipped with a thermocouple (4), which is used to constantly check the coolant temperature. A magnetic stirrer (8) at the bottom of the reactor is used to continuously stir the suspension. The MFC is controlled by a LABVIEW interface, which also records the data supplied by the gas analyzer.



**Figure S2. Raman spectroscopy results** (A) DI-OBu and DI-OiPr samples after 2 h UV-irradiation; (B) ES-OBu and ES-OiPr samples without UV-irradiation, compared to anatase and rutile; (C) DI-OEt after irradiation for 8 h in two iterations of 2 and 6 h; (D) Platinized DI-OEt samples after irradiation for 2 h.

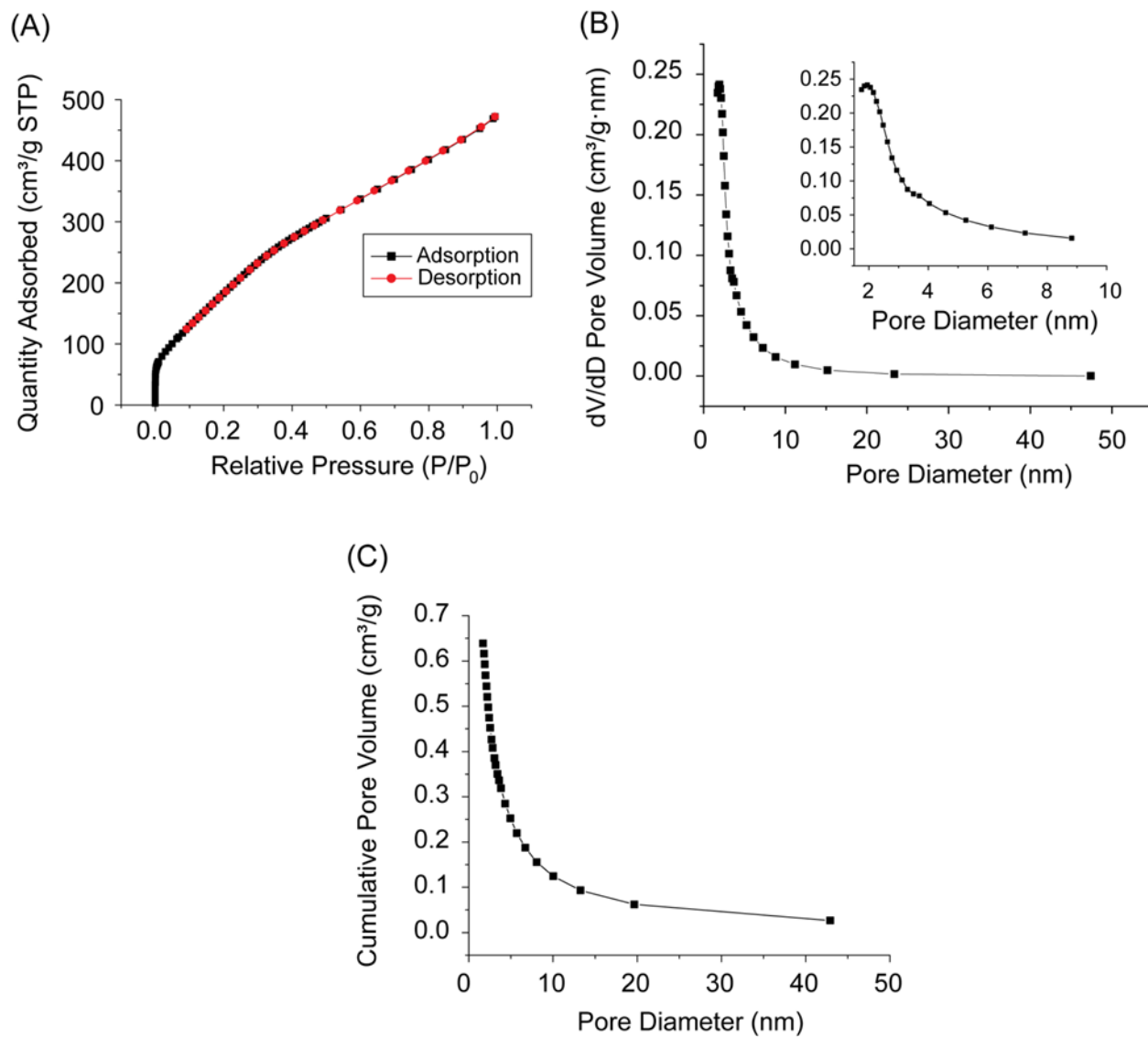


**Figure S3. UV-vis spectroscopy results** (A) Diffuse reflectance of direction injection powdered samples; (B) Extinction (absorption plus scattering) spectrum obtained on DI-OEt suspension in the blue colored state (after UV-irradiation) and in white colored state (after UV-irradiation, followed by exposure to air).

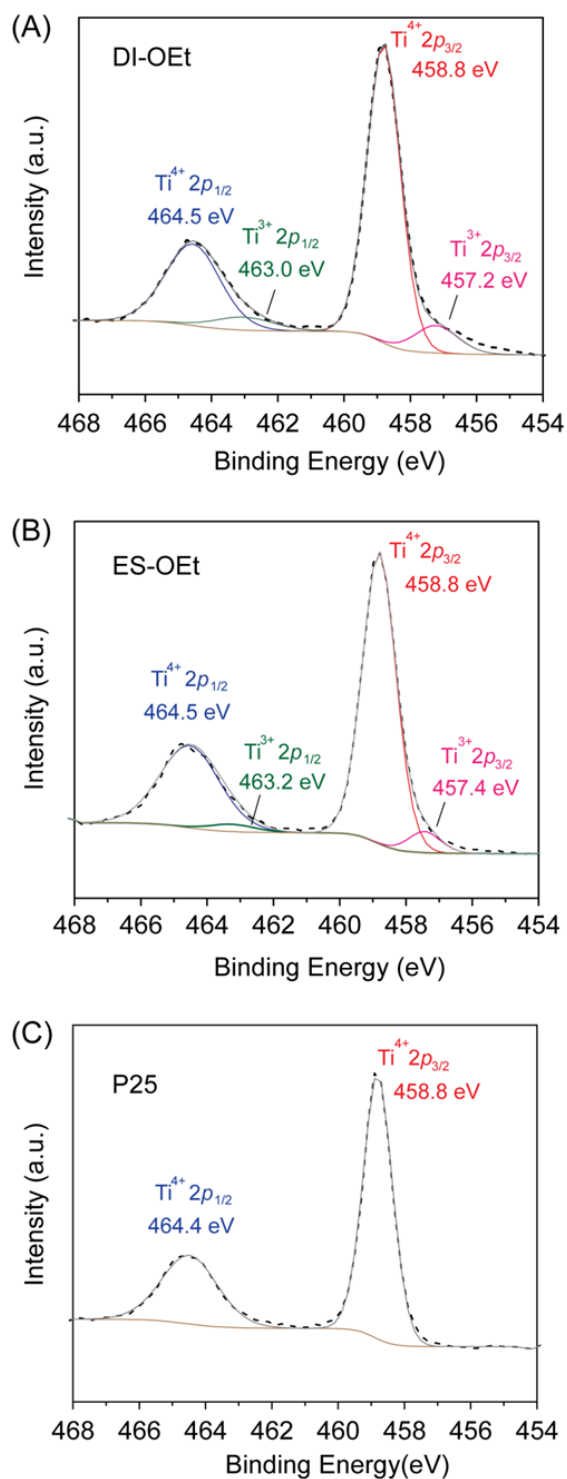


**Figure S4. FTIR spectroscopy results.** (A) DI-OEt from 500 – 4000 cm<sup>-1</sup>; (B) FTIR spectrum of DI-OEt and as-prepared ES-OEt (before irradiation) between 1000 – 4000 cm<sup>-1</sup>.

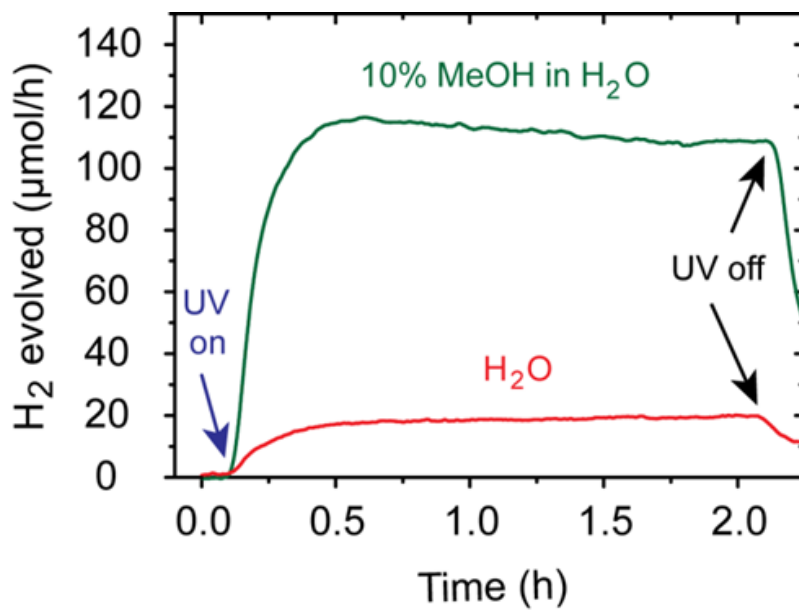




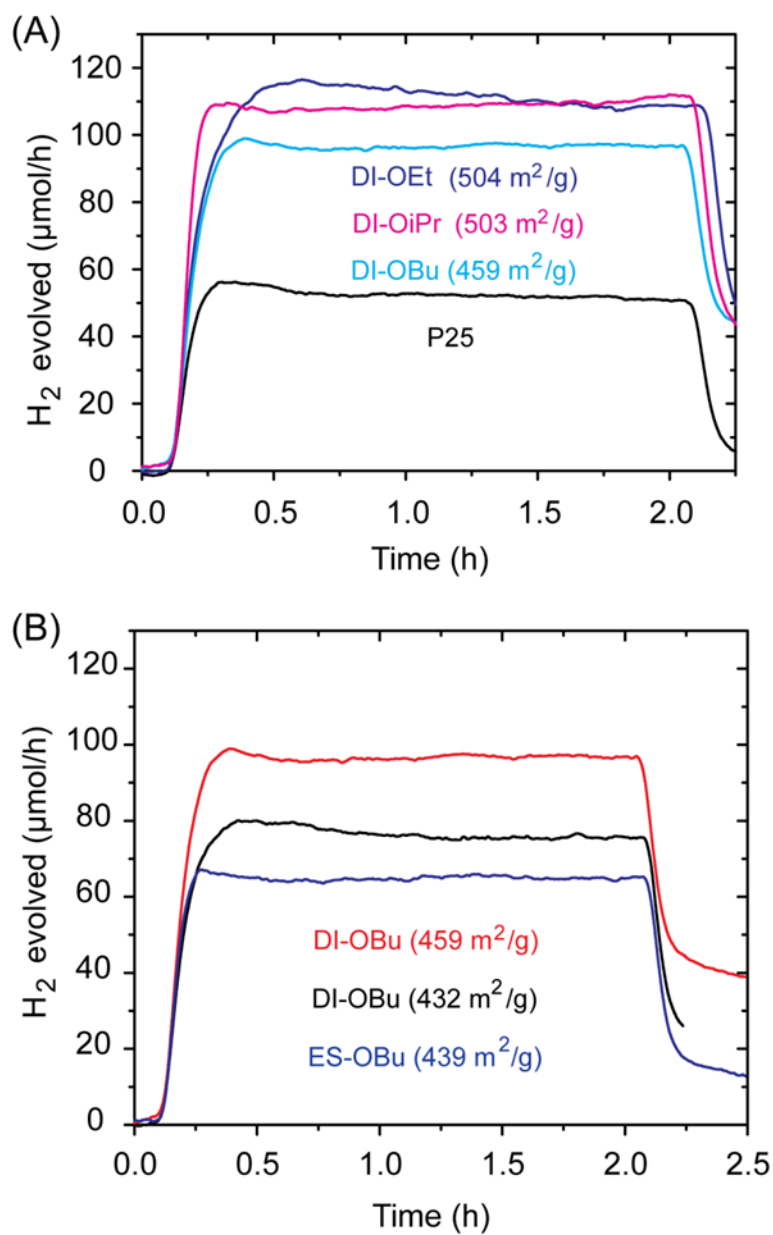
**Figure S5.** Nitrogen physisorption data for DI-TiOEt (A) N<sub>2</sub> adsorption-desorption isotherm, (B) pore size distribution, with zoom-in of pores < 10 nm in inset; (C) cumulative pore volume. (B) and (C) were calculated from the BJH desorption branch.



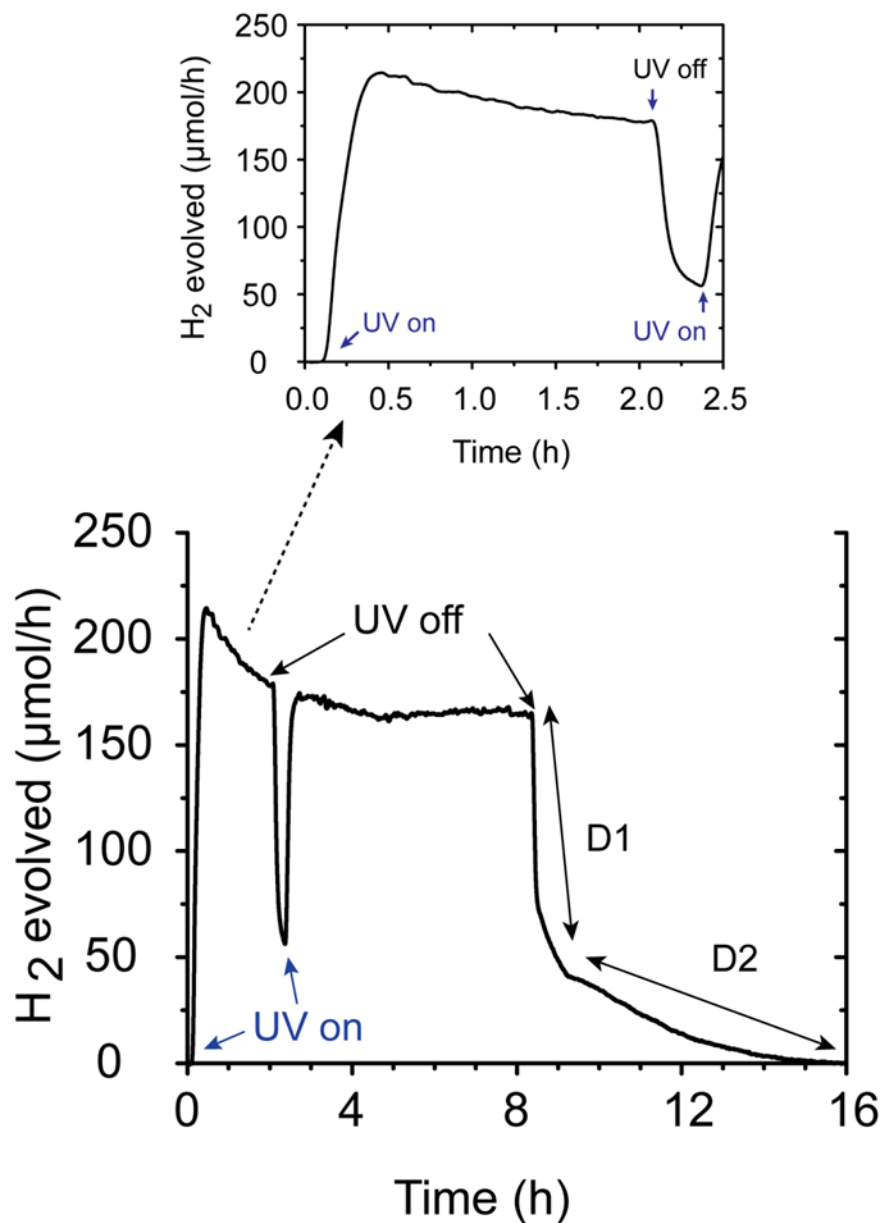
**Figure S6.** High resolution XPS scan of Ti 2p for (A) DI-OEt and (B) ES-OEt after photocatalytic reaction, with (C) pristine P25 shown for comparison. The experimental data are plotted with the dashed lines and deconvoluted to fit the peaks for  $\text{Ti}^{4+}$  and  $\text{Ti}^{3+}$ .



**Figure S7.** Photocatalytic H<sub>2</sub> production rates of DI-OEt samples tested in water with and without methanol as sacrificial agent. The BET surface area of the sample tested in H<sub>2</sub>O was 503 m<sup>2</sup>/g while the one tested in MeOH/H<sub>2</sub>O was 504 m<sup>2</sup>/g.



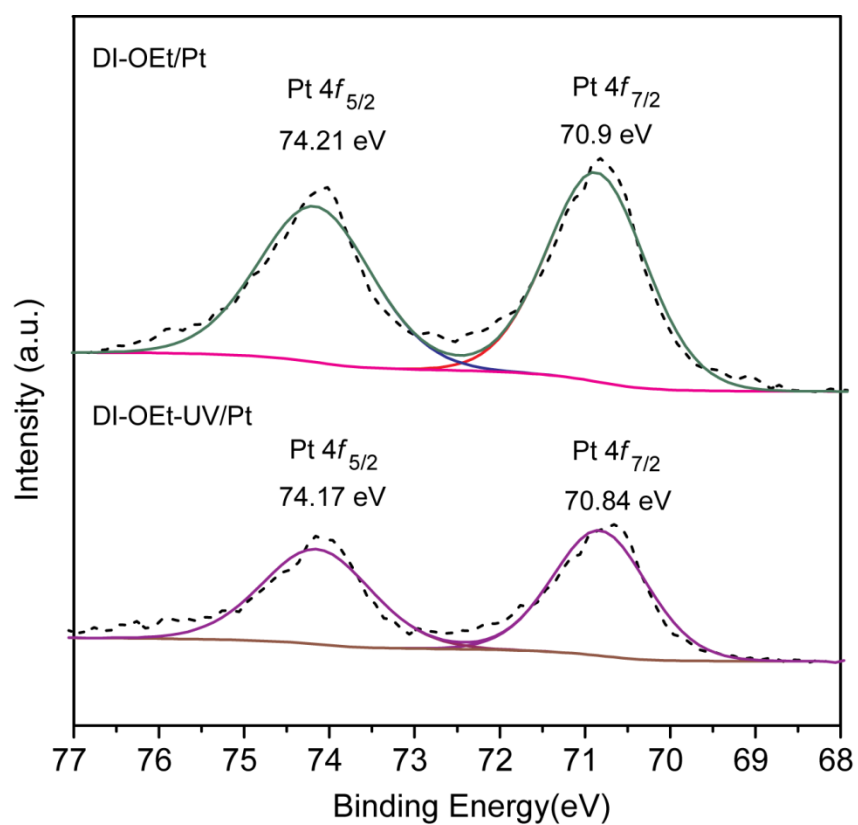
**Figure S8.** (A) Hydrogen evolution rate of DI samples prepared with different titanium alkoxide precursors (including BET surface area) compared to P25 over an irradiation time of 2 h. (B) Hydrogen evolution rate for DI-OBu compared to ES-OBu samples.



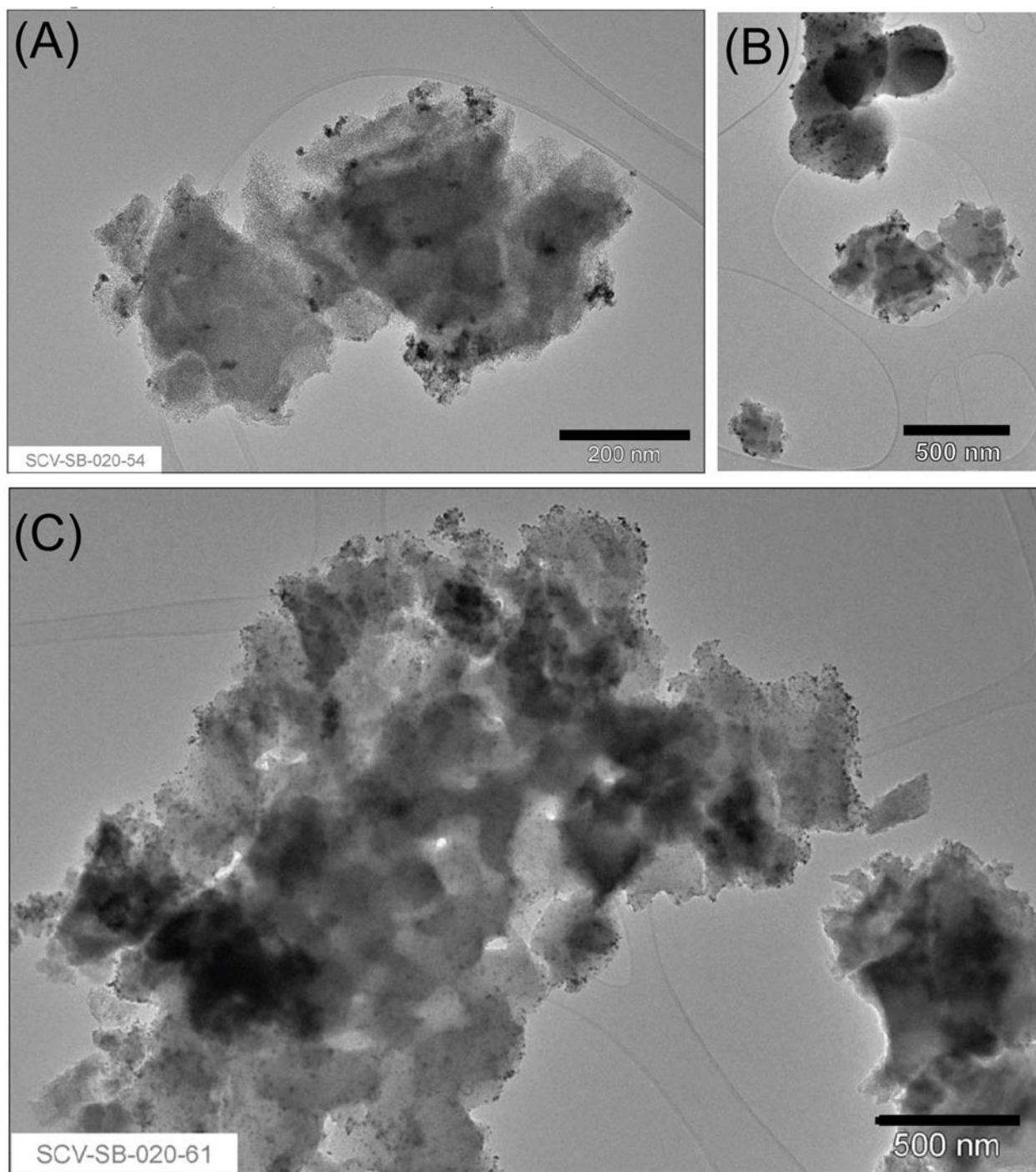
**Figure S9.** Long-term stability test of DI-OEt over 8 h of UV-irradiation, obtained over 2 h and 6 h periods of irradiation. The inset shows a zoomed-in plot of the first 2 h of UV-irradiation. After the 6 h period of UV-irradiation, the H<sub>2</sub> evolution rate was monitored in the dark. Two dark processes were observed: D1 is attributed to the purging of H<sub>2</sub> from the reactor that originated from the reaction of photogenerated electrons with electrolyte protons, while D2 is attributed to the formation of H<sub>2</sub> from the reaction of residual Ti<sup>3+</sup> species that were generated during the light irradiation with adsorbed protons.



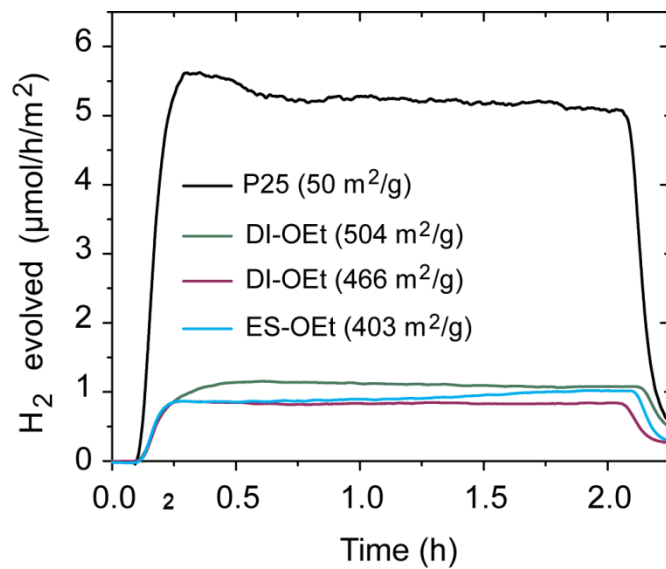
**Figure S10.** Photographs from left to right of DI-OEt/Pt, DI-OEt-UV/Pt, and DI-OEt powders.



**Figure S11.** High resolution Pt 4f XPS scan for (A) DI-OEt/Pt and (B) DI-OEt-UV/Pt. The experimental data are plotted with the dashed line.



**Figure S12.** Low magnification TEM images of (A)-(B) DI-OEt/Pt; (C) DI-OEt-UV/Pt.



**Figure S13.** Comparison of H<sub>2</sub> evolution rate by normalizing to the surface area for each photocatalyst, using the BET surface area and assuming 200 mg of photocatalyst was used in the catalytic reaction.