

Visible Light Induced Hydrogen Generation using a Hollow Photocatalyst with Two Cocatalysts Separated on Two Surface Sides

Minh-Hao Pham,^a Cao-Thang Dinh,^a Gia-Thanh Vuong,^a Ngoc-Don Ta,^b and Trong-On Do^{a,}*

^a Department of Chemical Engineering, Centre en catalyse et chimie verte (C₃V), Laval University, Quebec, G1V 0A6, Canada

^b School of Chemical Engineering, Hanoi University of Science and Technology, Hanoi, Vietnam

Corresponding Author: trong-on.do@gch.ulaval.ca

SUPPORTING INFORMATION

Chemicals

FeCl₃·6H₂O (Aldrich, 97 %), Fe(NO₃)₃·9H₂O (Aldrich, ≥ 98 %), 2-amino-1,4-benzenedicarboxylic acid (Aldrich, 99 %), Pluronic F127 (EO₉₇PO₆₉EO₉₇, average M_n = 12,600, Aldrich), CH₃COOH (Fisher, 99.7 %), titanium(IV) (triethanolaminate)isopropoxide (80 wt% in 2-propanol, Aldrich), titanium(IV) butoxide (Aldrich, 97 %), 2-propanol (Aldrich, 99.5 %), titanium(IV) tetraisopropoxide (Aldrich, 97 %), ethanol (95 %), H₂PtCl₆·6H₂O (Aldrich, ≥ 37.5 % Pt basis) and lactic acid (Aldrich, 85–90 % in water). All chemicals were used as received without further purification.

Synthesis of MIL-88B nanocrystals

MIL-88B nanocrystals were prepared by following our previously reported approach.¹³ Briefly, the aqueous dispersion (15 mL) of 2-aminoterephthalic acid (60 mg, 0.33 mmol), FeCl₃·6H₂O (180 mg, 0.66 mmol), Pluronic F127 (160 mg) and acetic acid (0.6 mL, 10.5 mmol) was heated at 110 °C for 24 h. The resulting solid was isolated and washed several times with ethanol by centrifugation to remove the surfactant and excess reactants.

Titanium precursor grafting on MIL-88B nanocrystals

The as-made MIL-88B (100 mg) was dried overnight at 150 °C under vacuum to remove terminal water molecules. To this dehydrated form, 2 M TEAI solution in 2-propanol (4 mL) was poured and stirred at room temperature for 2 h. The TEAI-grafted MIL-88B was then collected, washed with 2-propanol by centrifugation and dried overnight at 100 °C.

TiO₂ coating on MIL-88B nanocrystals

TEAI-grafted MIL-88B (100 mg) was dispersed in 80 mL of 6 mM TEAI solution in ethanol (5 vol. % H₂O) and then refluxed for 24 h under vigorous stirring. The MIL-88B@TiO₂ core-shell was collected and washed several times with ethanol by centrifugation.

Preparation of α-Fe₂O₃-TiO₂-PtO_x

0.57 mL of H₂PtCl₆ aqueous solution (10 mM) was added to the suspension of MIL-88B@TiO₂ (100 mg) in deionized water (12 mL) and stirred for 1 h at room temperature, followed by a rotary evaporation with a water bath at 50 °C to remove the water. The resulting product was calcined in air with heating rate at 5 °C min⁻¹ at 500 °C for 3 h to yield a dark red PtO_x-loaded composite.

Preparation of PtO_x-[Fe-doped TiO₂]

Fe-doped TiO₂ (Fe/Ti = 0.01) was prepared by sol-gel method.^{S1} 50 mL of ethanol solution containing 5 mL of titanium(IV) tetraisopropoxide was added dropwise into 50 mL of distilled water containing

45 mg of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (pH adjusted to 1.5 with nitric acid) under vigorous stirring. After stirred for 24 h, the resulted solution was evaporated at 45 °C using a rotary evaporator and dried at 70 °C overnight. The obtained powder was calcined at 400 °C for 1 h to obtain Fe-doped TiO_2 . The loading of PtO_x cocatalyst on the Fe-doped TiO_2 was the same as the procedure for $\alpha\text{-Fe}_2\text{O}_3\text{-TiO}_2\text{-PtO}_x$.

Preparation of $\text{PtO}_x\text{-[Fe}_2\text{TiO}_5]$

Fe_2TiO_5 (Fe/Ti = 1) was prepared by sol-gel method.^{S2} 50 ml of 2-propanol solution containing 3.5 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was added into 20 mL of 2-propanol solution containing 3.0 mL of titanium(IV) butoxide, followed by dropwise addition of 0.7 mL H_2O under stirring. After stirred for 4 h and further aged for 12 h, the mixture was evaporated at 70 °C and dried at 120 °C for 4 h. The obtained powder was calcined at 350 °C for 1 h and 700 °C for 5 h to obtain Fe_2TiO_5 . The loading of PtO_x on the Fe_2TiO_5 was the same as the procedure for $\text{PtO}_x\text{-[Fe-doped TiO}_2]$.

Photocatalytic H_2 evolution

Visible light-induced H_2 evolution was carried out in 300 mL septum-sealed glass reactor. In each run, 20 mg of the photocatalyst was well dispersed with magnetic stirring in a 50 mL of aqueous solution containing lactic acid (10 wt.%). The reactor was deoxygenated by bubbling nitrogen to remove oxygen and then placed in front of a 300 W Xe-lamp with a 420 nm cut-off filter (FSQ-GG420, Newport) under constant stirring. 0.5 mL of the gas in the headspace of the reactor was analyzed by GC to determine the amount of evolved H_2 .

Characterizations

Transmission electron microscopy (TEM) images were obtained on a JEOL JEM 1230 microscope operating at 120 kV. High resolution TEM images were performed on a Tecnai G² 20 instrument operated at 200 kV. Scanning electron microscopy (SEM) images were taken on a JEOL 6360 instrument at an accelerating voltage of 3 kV. Powder X-ray diffraction (XRD) patterns were collected on a Bruker SMART APEX II X-ray diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) at a scan rate of $1.0^\circ \text{ min}^{-1}$. All samples were dried at 100 °C overnight to remove guest solvent molecules within the pores before the XRD scan. XPS measurements were carried out in an ion-pumped chamber (evacuated to 10^{-9} Torr) of a photoelectron spectrometer (Kratos Axis-Ultra) equipped with a focused X-ray source ($\text{Al K}\alpha$, $h\nu = 1486.6 \text{ eV}$). The UV-vis spectra were recorded on a Cary 300 Bio UV-visible spectrophotometer. N_2 adsorption-desorption isotherms were carried out at the temperature of liquid nitrogen with a Quantachrome Autosorb-1 system. The BET surface areas were calculated in the range of 0.05–0.3 P/P_0 . Thermogravimetric analysis (TGA) was performed with a TGA/SDTA 851e

thermogravimetric analyzer from room temperature to 600 °C with a heating rate of 5 °C min⁻¹ under an air flow of 50 mL min⁻¹.

Operation conditions for GC analysis:

- + Carrier gas: nitrogen at 15 Psi
- + Column: Carboxen-1010 Plot Capillary 30 m x 0.53 mm.
- + Detector: TCD
- + Column temperature: 30 °C
- + Retention time of H₂: 0.9 min

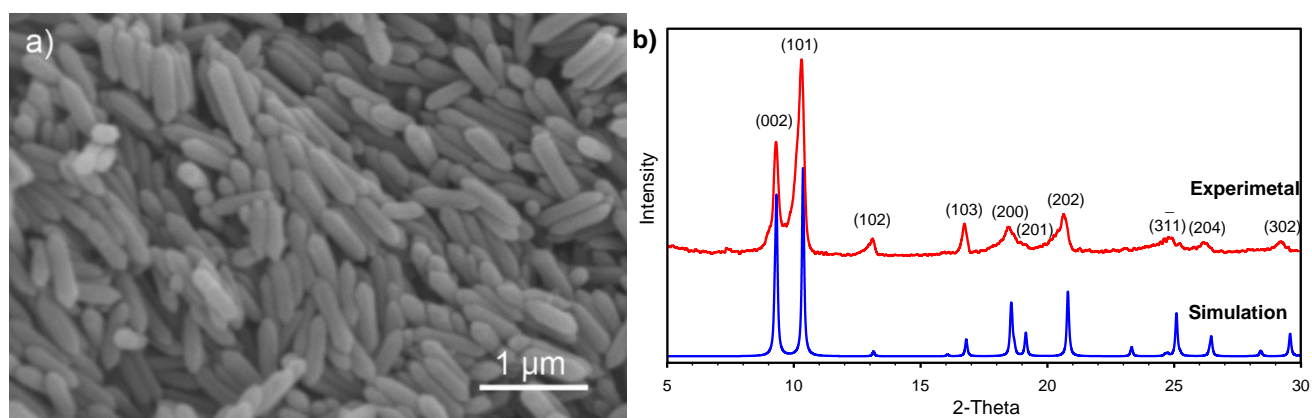


Fig. S1 SEM image (a) and XRD pattern (b) of the starting MIL-88B nanocrystals

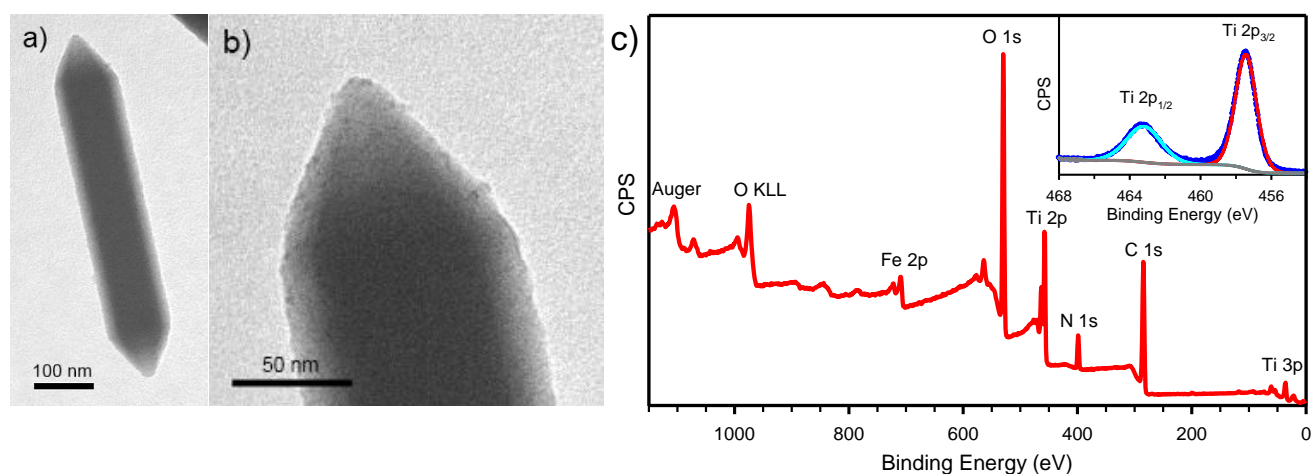


Fig. S2 TEM images (a, b), XPS survey and high-resolution Ti 2p (inset) spectra (c) of TEAI-grafted MIL-88B nanocrystals.

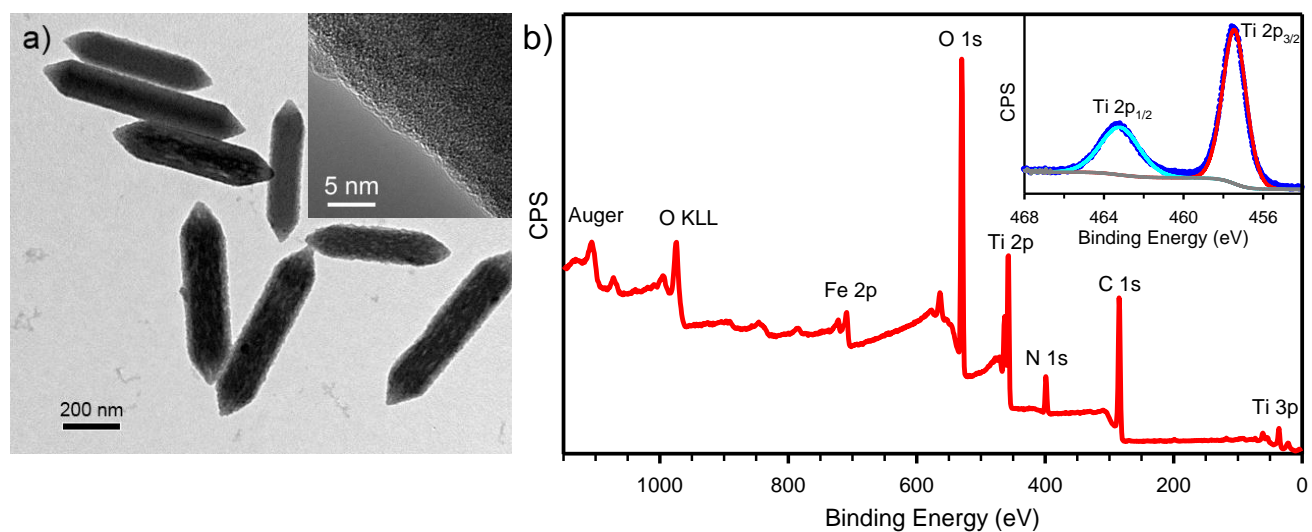


Fig. S3 TEM and HRTEM (inset) images (a), XPS survey and high-resolution Ti 2p (inset) spectra (b) of coated MIL-88B@TiO₂ nanoparticles prepared with the concentration of TEAI at 6 mM TEAI.

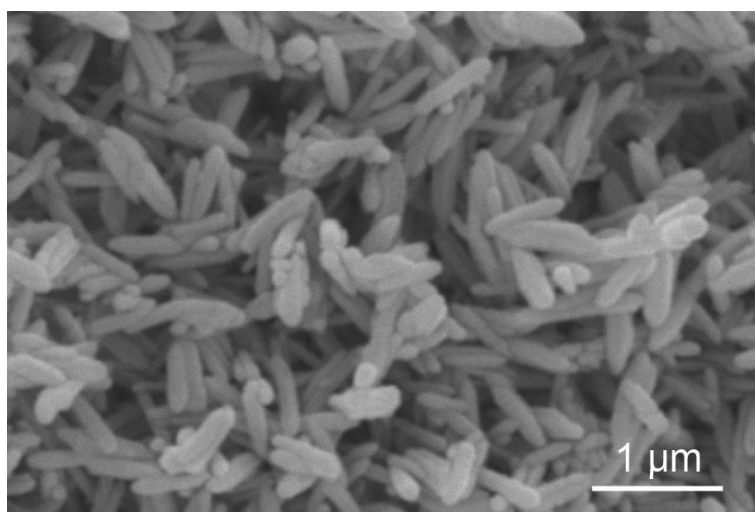


Fig. S4 SEM image of the α -Fe₂O₃-TiO₂-PtO_x sample after calcination.

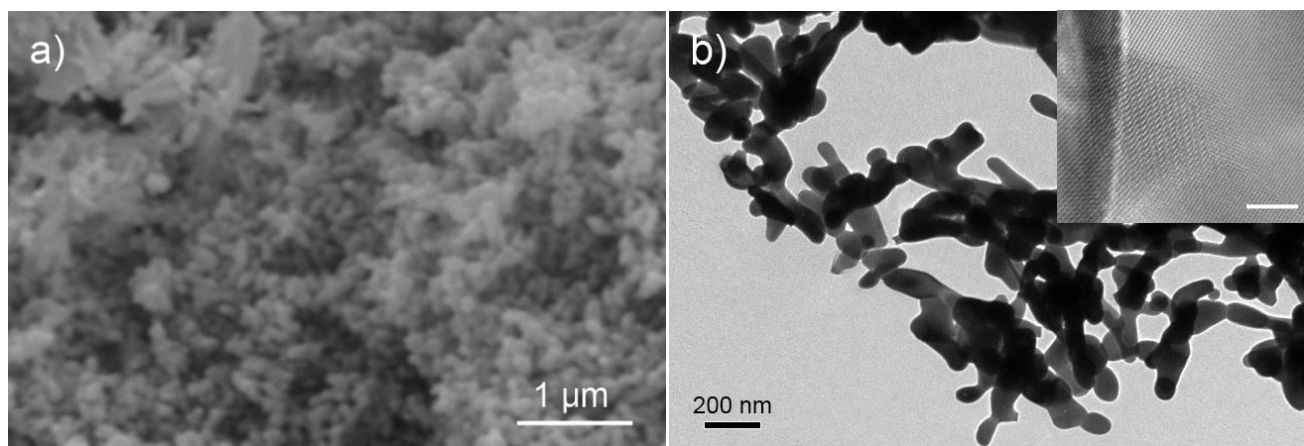


Fig. S5 SEM (a) and TEM (b) images of the iron oxide sample obtained after calcination of the pristine MIL-88B nanocrystals. HRTEM image (inset) indicates the fusion of iron oxide nanoparticles. (scale bar of 5 nm).

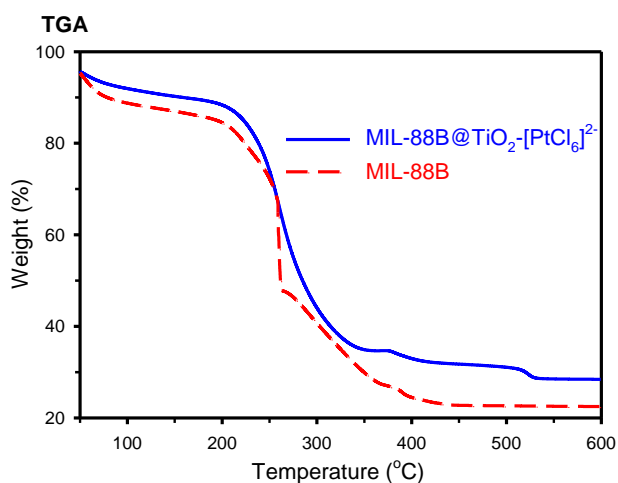


Fig. S6 Thermogravimetric analysis (TGA) of MIL-88B and MIL-88B@TiO₂-[PtCl₆]²⁻. The weight retention differential of 8.0 % at 500 °C attributed to the coated TiO₂ and loaded PtO_x.

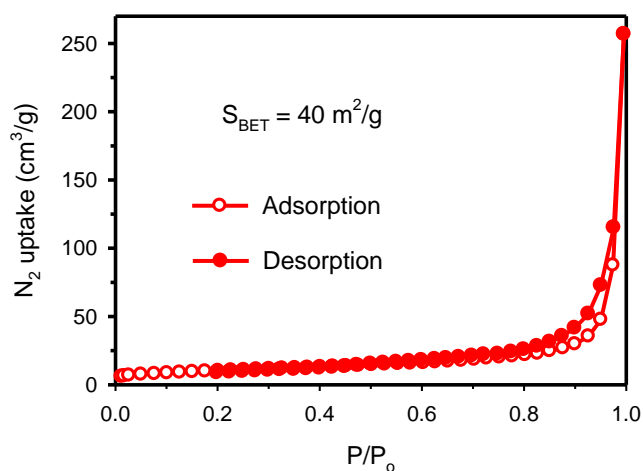


Fig. S7 N₂ adsorption-desorption isotherms at 77 K of the α -Fe₂O₃-TiO₂-PtO_x sample

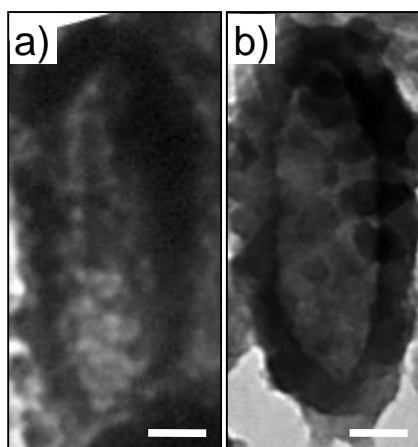


Fig. S8 The hollow nanoparticles with various thicknesses of Fe₂O₃-TiO₂ hybrid wall prepared with the concentration of TEAI at 25 mM (a) and 50 mM (b) while keeping the same other reaction parameters (scale bar of 50 nm).

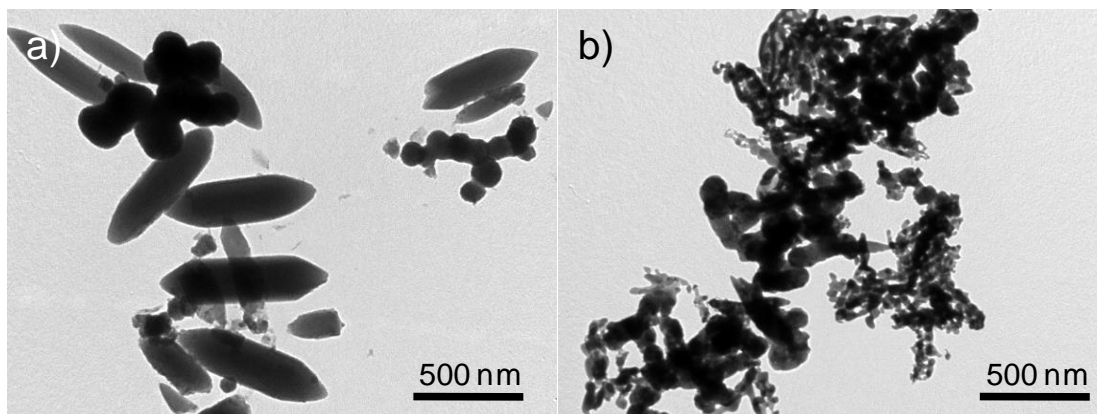


Fig. S9 TEM images of the sample prepared using titanium (IV) butoxide without amine group as grafting reagent instead of TEAI: A separated mixture of TiO₂ nanoparticles and MIL-88B nanocrystals before calcination (a), and TiO₂ particles and Fe₂O₃ particles after calcination (b).

Table S1 Photocatalytic activities of the hollow hybrid and the benchmarks for H₂ evolution

Photocatalyst	Precursor	Evolved H ₂ gas ($\mu\text{mol}\cdot\text{h}^{-1}$)
Fe ₂ O ₃ -TiO ₂ -PtO _x Hybrid	TEAI	22
Fe ₂ O ₃ -TiO ₂ -PtO _x Mixed Oxide	Ti(OBu) ₄	trace
PtO _x -Fe ₂ O ₃	Pristine MIL-88B	trace
PtO _x -TiO ₂	P25	trace
PtO _x -Fe ₂ TiO ₅	Fe/Ti = 1.0 ^(S2)	trace
PtO _x -[Fe-doped TiO ₂]	Fe/Ti = 0.01 ^(S1)	6
Without catalyst	–	0

References

- S1 J. Choi, H. Park, M. R. Hoffmann, *J. Phys. Chem. C* 2010, **114**, 783.
S2 A. Khaleel, *Colloids and Surfaces A: Physicochem. Eng. Aspects* 2009, **346**, 130.