Electronic Supplementary Material (ESI) for ChemComm.
This journal is © The Royal Society of Chemistry 2014

The first depleted heterojunction TiO_2/MOF-based solar cell

Alexander V. Vinogradov*[ab], Haldor Zaake-Hertling,[c] Evamarie Hey-Hawkins[c], G.A. Seisenbaeva[d], V.G. Kessler[d] and Vladimir V. Vinogradov[ab]

[a]G.A. Krestov Institute of Solution Chemistry, Russian Academy of Sciences, Ivanovo 153045, Russian Federation.
[b] National Research University of Information Technologies, Mechanics and Optics, St. Petersburg, 197101, Russian Federation.
[c]Leipzig University, Faculty of Chemistry and Mineralogy, Institute of Inorganic Chemistry, D-04103 Leipzig, Germany
[d]Department of Chemistry, BioCenter, Swedish University of Agricultural Sciences, Box 7015, 75007 Uppsala, Sweden.
E-mail: vinogradoffs@gmail.com

Electronic Supplementary Information

Conditions of synthesising the MIL-125/TiO_2 composite:

Synthesis of the MIL-125/TiO_2 composite was performed in a single step by hydrothermal treatment. The stoichiometric MIL-125 to TiO_2 ratios were determined by the initial concentrations of reactants, see Table S1. In general, the synthesis of the MIL-125/TiO_2 composite was carried out by mixing terephthalic acid (TFA) (Aldrich, 98%) with titanium isoproproxide $Ti(OiPr)_4$ (Aldrich, 98%) and adding dimethylformamide (DMF) (AcrosOrganics, extra-dry), dry methanol (MeOH) (Aldrich, 99.9%), and bidistilled water. The mixture was stirred gently for 5 minutes at room temperature, placed in a 40 mL Teflon liner and then put into a metallic digestion bomb at 160 °C for 18 hours. Back to room temperature, the white solid formed was isolated by filtration, washed twice with methanol and dried in air at room temperature.

Table S1. The initial amounts of components.

Amount of MIL-125 with respect to TiO_2, %	H_2O, mL	DMF, mL	MeOH, mL	TFA, mmol	$Ti(OiPr)_4$, mmol
2	0.15	12	0.14	0.1	3
3	0.17	12	0.16	0.1	3
4	0.19	12	0.18	0.1	3
5	0.21	12	0.2	0.1	3

1. EXAFS spectra

The Ti-K-edge X-ray absorption spectra of the MIL-125/TiO_2 composite were recorded at the wiggler beam line I811 at the MAX-Lab, Lund University, Lund, Sweden. The facility operated at 1.5 GeV and a maximum current of 250 mA. The EXAFS station was equipped with a Si[111] double crystal monochromator. The data collection was performed in luminescence mode. Higher order harmonics were reduced by detuning the second monochromator to 30% of maximum intensity at the end of the scans. The energy scale of the X-ray absorption spectra was calibrated by assigning the first inflection point of the K edge of a titanium foil to 4966 eV. The IFEFFIT program package (for more detail http://cars9.uchicago.edu/ifeffit/) was used for data treatment.

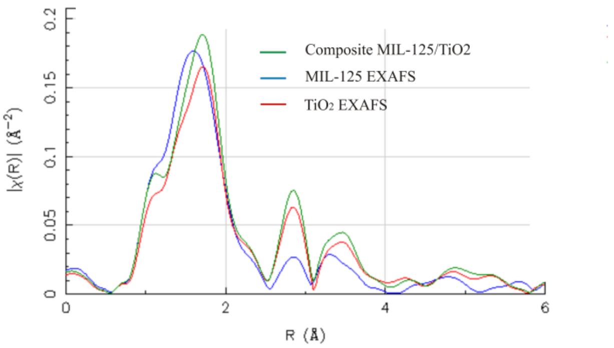

Figure S1. EXAFS spectra of the synthesised MIL-125/TiO_2 composite in comparison with pure MIL-125 and titania.

2. XRD

X-ray powder patterns were obtained using a Bruker SMART Apex-II diffractometer operating with MoKα radiation (λ = 0.71073 Å). Bruker Apex-II and EVA software were used for integration and data treatment.

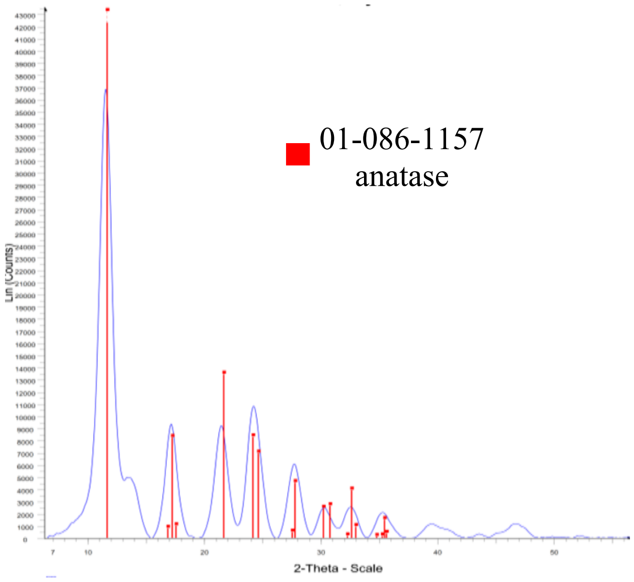

Figure S2. X-ray powder pattern of as-synthesied 3% MIL-125/TiO_2 composite with highlighted characteristic diffraction peak of anatase.

3. Attenuated Total Reflectance (ATR) FT-IR spectroscopy

The IR measurements were performed using a Bruker Vertex 80v FTIR spectrometer at a resolution of 0.01 cm^{-1}. The ATR cell equipped ZnSe crystal (45° angle of incidence) was used as the internal reflection element.

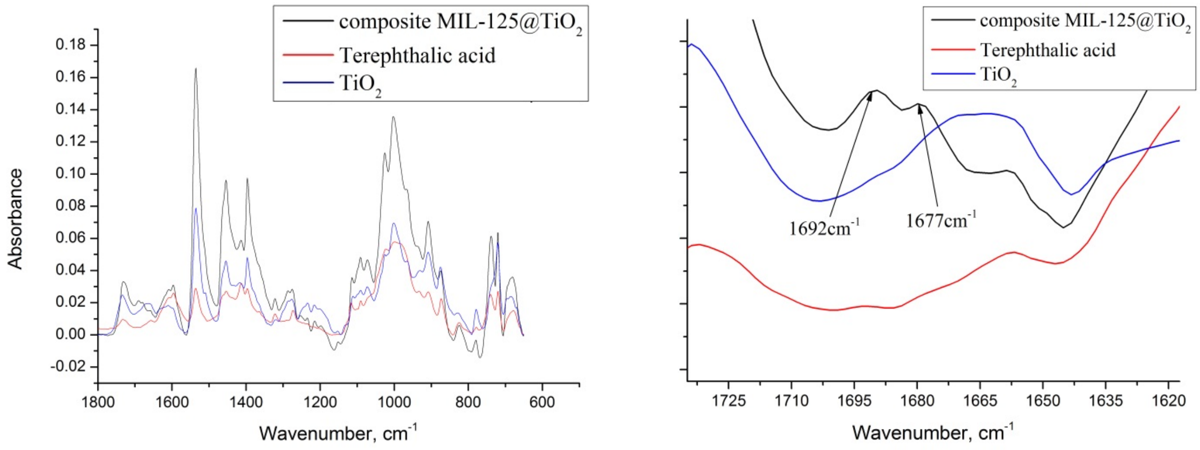

Figure 3S. FTIR spectra of as-synthesised 3% MIL-125/TiO$_2$ composite.

4. Thermal analysis

Thermogravimetry analysis (TG-DTA) was carried out using an STA 449 F1 Jupiter system (Netzsch) in air (heating rate 1K per minute). The mass of the sample was 10 mg.

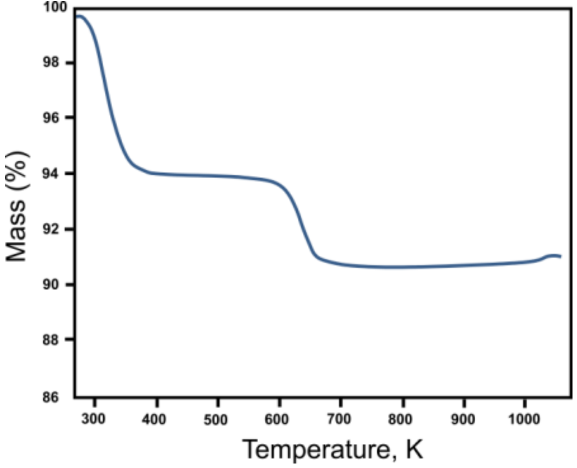

Figure S4. TG analysis of as-synthesised 3% MIL-125/TiO$_2$ composite.

5. SEM and EDS analysis

To study the samples using scanning electron microscopy (SEM), a silicon wafer was coated with the 3% MIL-125/TiO$_2$ composite and, after complete drying in a vacuum desiccator, was investigated without additional sputtering using an ultra-high resolution electron microscope Magellan 400L (Field Emission Inc.).

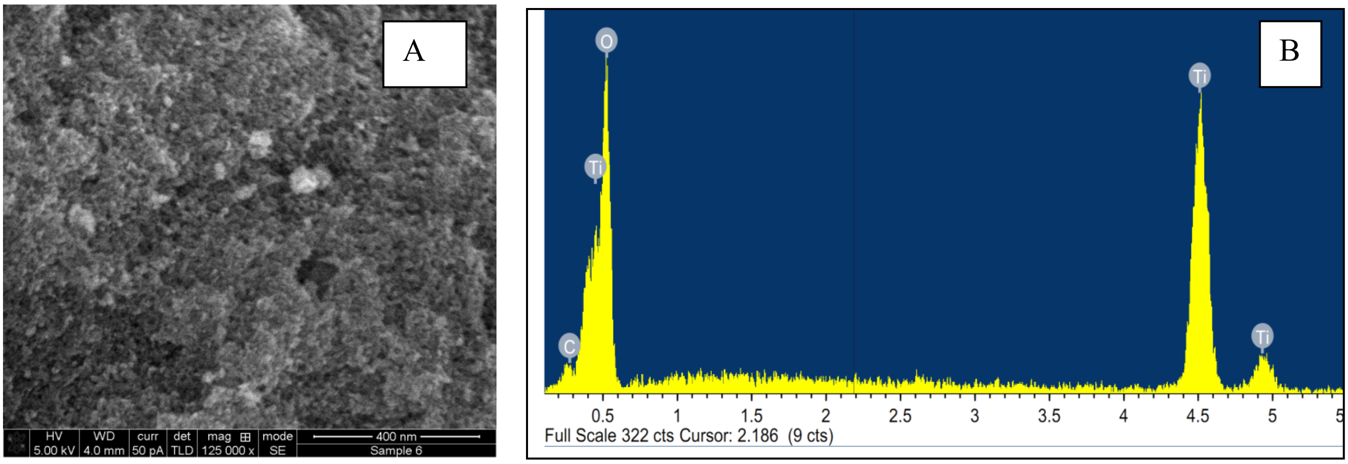

Fig. S5. SEM image (A) and EDS analysis (B) of as-synthesised 3% MIL-125/TiO_2 composite.

Element	Weight, %	Atomic, %
C	03.07	3.90
O	52.82	74.77
Ti	44.11	21.33

6. Surface Area (Quantachrome Nova 1200).

20 mg of as-synthesised 3% MIL-125/TiO_2 composite activated under vacuum (10^{-3} Torr) for 15 hours at 120 °C. Specific surface area measurements and pore size distribution have been performed using low-temperature nitrogen adsorption-desorption. The data obtained correspond to a micro-mesoporous state, as confirmed by characteristic isotherm shape (I and IV types).

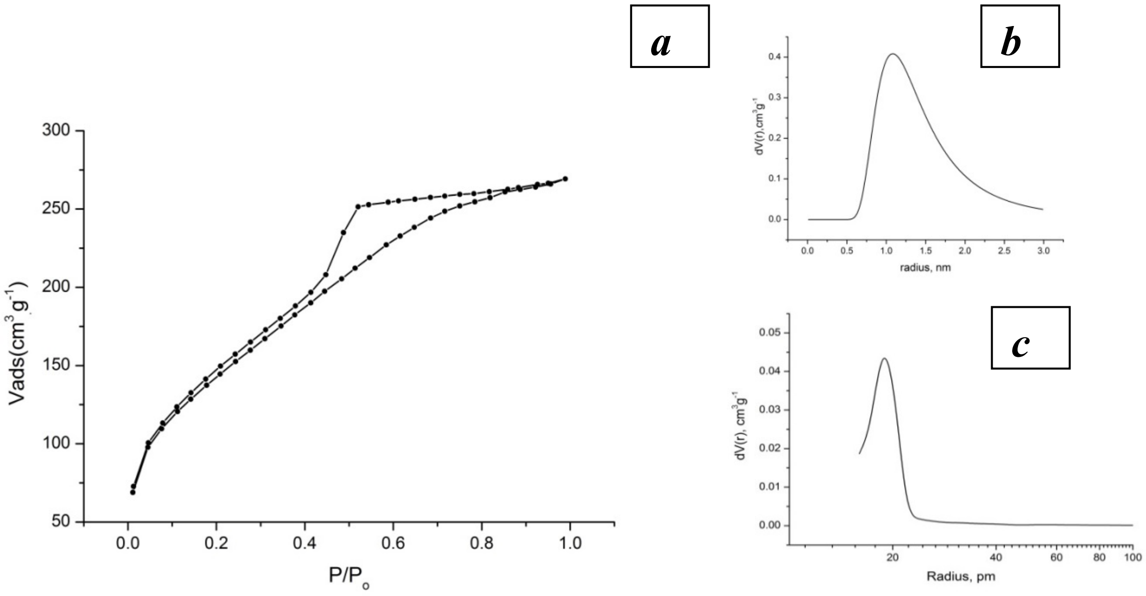

Figure S6. Nitrogen sorption isotherm (a) of 3% MIL-125/TiO_2, BJH mesopore size distribution (b) and micropore size distribution calculated using the Dubinin–Astakhov (DA) method[1].

For calculating the specific surface area for mesopores and their size distribution, we have employed the BET and BJH methods, respectively, Fig. S6a,c. The assessment of microporosity was performed using the Langmuir method for $S_{m2/g}$ and the Dubinin–Astakhov method for pore size distribution. Although N_2 at 77 K is considered standard adsorbate when surface area and pore size are analysed, it is nevertheless universally recognised that nitrogen adsorption is unable to give satisfactory results for quantitative assessment of porosity, especially in the ultramicropore region with a width of less than 0.7 nm. Therefore, the analysis of low-temperature nitrogen adsorption isotherms does not allow obtaining quantitative characteristics for microporosity conditioned by molecular sizes of the MIL-125 cavities. However, the analysis of low-temperature nitrogen adsorption on as-synthesised 3% MIL-125/TiO_2 composite reveals that the adsorption isotherm is described well enough by the equation for microporous sorbents with non-Gauss micropore volume distribution over their width: $W = W_0\exp[-(\varepsilon/\beta E_0)^n]$, where W is the adsorption value; W_0 is the maximum adsorption; $\varepsilon = RT\ln(p_0/p)$ is the adsorption potential; E_0 is the characteristic adsorption energy for a standard adsorbate; β is the affinity coefficient; n is a non-integer number (usually between 1 and 3); R is the universal gas constant; T is the absolute temperature. In the present case, the equation parameters were as follows (correlation coefficient 0.998): $W_0 = 0.419$ cm^3/g, $E_0 = 1.750$ kJ/mol, $\beta = 0.3918$, $n = 1.0$.

$S_{BET} = 525$ m^2/g; $S_{Langmuir} = 1033$ m^2/g

Pore Volume BJH = 0.234 cm^3/g; Pore Radius BJH = 1.8 nm

Pore Volume DA = 0.419 cm^3/g; Pore Radius DA = 1.01 nm

7. Fast photochromic effect

The assessment of photochromic activity of a suspension of 3%MIL-125/TiO_2 in methanol was performed using a glass capillary tube (Ø = 2 mm) under solar light irradiation (100 mW/cm^2) (Fig. S7a). The total irradiation time amounted to 5 min. Investigation of the kinetics (λ = 550 nm, UV-Vis spectrophotometer Agilent 8453, blank – suspension 3%MIL-125/TiO_2 in methanol without illumination) of photochromic darkening of the 3%MIL-125/TiO_2 composite was carried out for 20 minutes in a suspension of methanol (Fig. S7b).

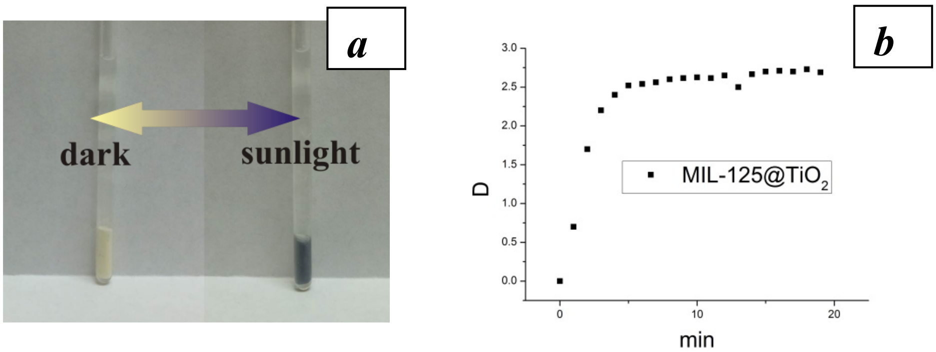

Figure S7: a) Pictures of the 3%MIL-125/TiO_2 composite after absorbance of methanol (a) and photochromic kinetics for 20-minute-long solar-light radiation (b) for the 3%MIL-125/TiO_2 composite.

8. Solar cell manufacturing

Solar cell manufacturing was accomplished by analogy with Ref. [2], where a layer of nanoporous TiO_2 was replaced by that of the synthesised MIL-125/TiO_2 composite. As a counter electrode graphite was used. The current–voltage characteristics of the cells were measured using a Keithley 2400 Source meter (Keithley Co. Ltd). The chopped (≈ 0.25 Hz) light from a Xe lamp was used as the light source -($\lambda > 400$ nm, 100 mW/cm^2).

9. Photocurrent analysis.

To prepare the operating electrodes, 250 mg of the MIL-125/TiO_2 powder was first dispersed in 2.0 mL acetone and sonicated for 30 min to form a slurry, then the resulting slurry was coated on conductive glass using a screen-printing technique. The photocurrents were measured using a standard three-electrode photoelectrochemical cell in an electrochemical workstation (CV-27, BAS). The as-prepared composite, platinum-gauze and Ag/AgCl were used as operating counter and reference electrode, respectively. A sodium sulfate solution (1 M) was used as an electrolyte. The chopped (≈ 0.25 Hz) light for the photocurrent operation was the filtered light ($\lambda > 400$ nm, 150 mW/cm^2) from a Xe lamp.

10. Elemental analysis

Organic elemental analysis (OEA) was carried out by Thermo Scientific™ FLASH 2000 Series OEA. There was detection quantification of carbon, hydrogen, nitrogen, oxygen and other solid part. The mass of the sample was 0,2 g

Table S2. Elemental analysis of the samples.

Amount of MIL-125 with respect to TiO_2, %	C, at %	N, at %	H, at %	O, at %	Other part
2	2.2	0	1.2	39.2	57.4
3	3.1	0	1.4	40.1	55.4
4	4.6	0	2.1	41.2	52.1
5	5.2	0.1	2.9	41.8	50

Additional characterisation

A SAXS study was performed using a SmartLab X-Ray diffractometer (Rigaku, Japan) in the range of 2θ = 3 to 9° with CuKα radiation (λ = 1.5418 Å). The samples for transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) were prepared by dispersing small amounts of samples in ethanol to form a homogeneous suspension. A drop of the suspension was deposited on a carbon-coated copper grid for HRTEM observation (FEI TECNAI G2 F20, operated at 200 kV). While studying stability, the analysis of I–V characteristics for operating solar cells was carried out using LucasLabs S-302-4, Keithley 4200 (for a detailed description see http://nanoscience.huji.ac.il/unf/Probe%20Station_main.html).

References:

1. M.M. Dubinin, in *Progress in Surface and Membrane Science*, edited by D.A. Cadenhead, J.E Danielli, and M.D. Rosenberg (Academic Press, New York, 1975), **9**.
2. Z. Ku, Y. Rong, M. Xu, T. Liu, H. Han, *Scientific reports*, 2013, **3**, 3132.