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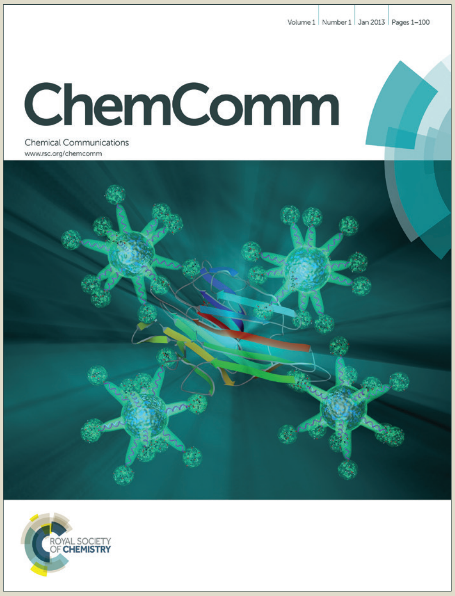

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ARTICLE TYPE

The first depleted heterojunction TiO_2/MOF-based solar cell

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A single-step hydrothermal synthesis of a TiO_2/Mil-125 composite was applied for the first time to produce a depleted perovskite/TiO_2−MOF heterojunction solar cell with 6.4% power conversion efficiency (PCE), characterized by durable stability in air.

Metal-organic frameworks (MOFs) are an attractive class of porous solids with potential applications in gas storage, separation, energy conversion and catalysis.[1-5] The use of photoactive MOFs in photocatalytic processes[6-9] and photoelectric solar energy converters[10-12] has recently been reported. It has also been shown[12] that coating the surface of titania particles with a nanoscale-thick layer of ZIF-8 resulted in a substantial increase in open-circuit voltage (V_{oc}) due to inhibited interfacial charge recombination (TiO_2/dye and TiO_2/electrolyte) while producing dye-sensitised solar cells. However, under these conditions the environment and photocell operation time greatly affected the stability parameters. From this point of view, the application of TiO_2−MOF composites as photoactive filling material (Fig. 1a) with impregnation of methylammonium triiodoplumbate(II) $(NH_3Me)PbI_3$ crystals, corresponding to three-dimensional perovskite structures, led to formation of a depleted quasi-bulk heterojunction TiO_2/MOF-based solar cell (Fig. 1b).

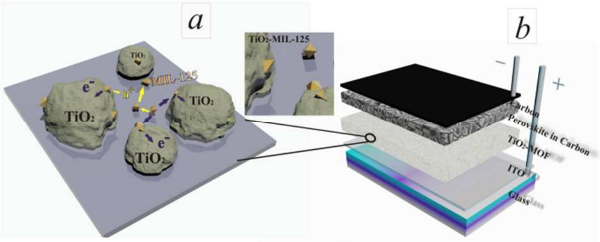

Fig. 1 Visualisation of the structure of photoactive MOF@TiO_2 composite(a) and structure of depleted quasi-bulk heterojunction TiO_2/MOF-based solar cell (b).

Three-dimensional perovskite structures in contact with highly porous TiO_2−MOF coatings possess a number of major advantages such as large absorption coefficient, high carrier mobility and high stability.[13] In this work we have used highly photoactive MIL-125 ($Ti_8O_8(OH)_4$-(O_2C-C_6H_4-$CO_2)_6$, quasi-cubic tetragonal structure) as an attractive materia based on the synthetic procedure described previously.[16] Moreover, the single-step synthesis of a TiO_2−MOF composite proposed in this work substantially simplifies the procedure of obtaining the corresponding materials. In the present case, the synthesis of MIL-125@TiO_2 was carried out by adding H_2O as a limiting reactant with respect to $Ti(OC_3H_7)_4$ (see Table S1, ESI) which resulted in step-by-step growth of a heterophase system. At the first step, as a result of hydrolysis and condensation of titanium isopropoxide, a titanium oxyhydroxide precipitate was formed. Through hydrothermal treatment, this was converted to the crystalline anatase phase. The formation of MIL-125 was apparently due to hydrothermal interaction of the hydrolysis products of titanium isopropoxide and yet unreacted terephthalic acid. The MOF content with respect to TiO_2 was changed via the initial concentrations of chemicals, but did not exceed 5%, see Table S1 (ESI). The as-synthesized solid was washed twice with methanol and dried at 200 °C to remove the solvent. The presence of a lightweight organic phase surrounding the anatase crystallites was indicated by EXAFS spectra (Fig. S1, ESI) appearing as an overlap of anatase and MIL-125 spectra. The peak at 1.2 Å is most probably due to anomalous adsorption caused by partial reduction to Ti^{III}. It was impossible to trace the formation of the MOF using large-angle X-ray scattering (Fig. S2, ESI) and Attenuated Total Reflectance (ATR) FT-IR spectroscopy (Fig. S3, ESI) due to the small amount and weak diffraction with respect to the highly crystalline anatase. Also, the presence of $-CO_2$ absorptions for the MIL-125/TiO_2 composite as compared to pure terephthalic acid and TiO_2 at 1692 and 1677 cm^{-1} (Fig. S2, ESI) confirms coordination [14].

These vibrations should not, however, be attributed only to the formed MOF, taking into account the probability of bonding to the anatase surface or the formation of hybrid phases as reported previously.[15] The evidence of the formation of the MOF-TiO_2 heterophase system is provided by TEM (Fig. 2a), HRTEM (Fig. 2b,c), and SAXS (Fig. 2d) images. As seen in the images, multicomponent composition of the material can be revealed only by detailed analysis. The high resolution images demonstrated long-range ordered structure only of anatase (Fig. 2c). For the MOF, no long-range structure was visible: instead, a pattern of wormhole porosity was observed (Fig. 2b). However, a peak in the SAXS images (Fig. 2d) at 6.7° confirms the presence of the 3D phase, in full agreement with previously performed X-ray powder diffraction analysis[16] and corresponds to MIL-125.

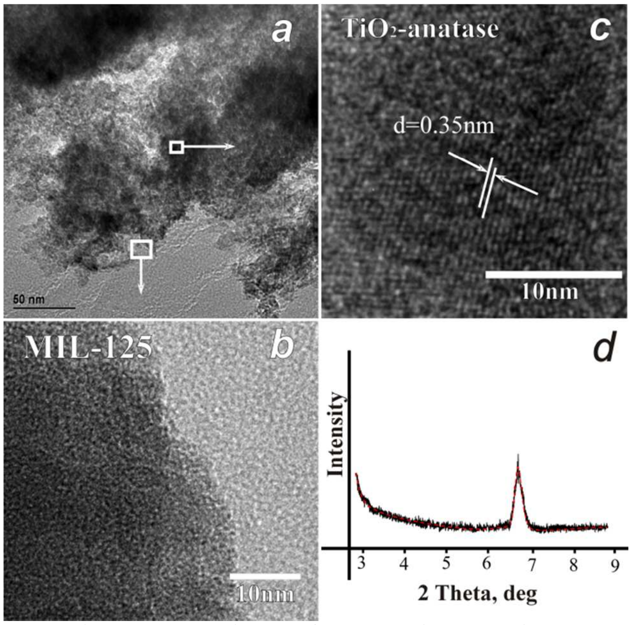

Figure 2. (a) TEM images of 3% MOF-TiO_2 composite, HRTEM images of different parts: MIL-125 (c) and anatase-TiO_2 (b), and (d) SAXS of as-synthesised composite.

Another confirmation of the presence of MIL-125, in contrast to other hybrid compounds,[15] can be obtained from the thermal analysis data (see Fig. S4, ESI) shown for the 3% MIL-125−TiO_2 sample. The figure reveals that the mass loss occurred in two stages: first, the release of guest molecules, methanol and H_2O, between 40 °C and 150 °C (6%), and second, degradation of the framework (between 360 and 400 °C, 3%). The absence of DMF in the analysed sample is confirmed organic elemental analysis (OAE) (table S2). The data obtained are in agreement with those of MIL-125[16] and rule out the possibility of formation of hybrids and titanium terephthalate whose thermal stability does not exceed 310 °C.

At the same time, as shown previously,[12] the MOF content with respect to TiO_2 should be within a specific range and not exceed 5%. This depends on two factors. On the one hand, a high content of a secondary phase provides a substantial decrease in current short circuit (I_{sc}),[12] but on the other hand, it causes an increase in V_{oc}. This is due to the fact that the higher conduction band edge of MOFs leads to transfer of photo-excited electrons into the conduction band of TiO_2 (decreasing I_{sc}) through the quantum tunneling effect, thus, the suppression effect on charge recombination may be strengthened by involving growth of a secondary MOF phase (resulting in higher V_{oc} values). Taking this into consideration, we have used in our synthesis the component ratios leading to a content of the MIL-125 with respect to TiO_2 which does not exceed 5%. It should be noted that in the present case the formation of the composite occurred during hydrothermal synthesis to produce MOFs on the surface of thick titania nanoproducts (Fig. 2a). Such an approach will certainly not allow for coating all the formed anatase particles with a thick porous MOF layer. However, even such a low MOF content of on the surface of anatase crystals promotes a substantial increase in specific surface area. Low-temperature adsorption-desorption data indicate the formation of a developed micro-mesopore system and a high BET specific surface area of the 3% MIL-125–TiO_2 sample (S_{BET} = 525 m²/g, $S_{Langmuir}$ = 1033 m²/g, Fig. S6, ESI). It is noteworthy that such a broad pore distribution is due to the microporous structure of MIL-125 and ink-bottle-like mesopores[17] in between titania particles, as confirmed by a characteristic hysteresis shape (I and IV types), as well as by reduced values of average sizes for micro- and mesopores separately (Fig. S6b,c, ESI). In addition, we have observed a fast photochromic effect upon UV-visible excitation (see Fig. S7a, ESI). Using the suspension of the synthesised 3% MIL-125–TiO_2 composite in methanol a high index of optical density was reached in 5 min, while imitating sunlight effects, thus proving the assumption of high photoactivity of the composite obtained. Determination of the optimal MOF concentration in the TiO_2/MIL-125 composite structure was performed by photopolarisation measurements (the evaluation procedure is outlined in the ESI). The photocurrent response measurement was carried out under visible light irradiation to investigate the photo-induced charge separation efficiency for MOF-doped TiO_2 samples containing different amount of MOFs. As shown in Fig. 3a, the photocurrent response attains its maximum at 3% MOF-TiO_2 (39 µA/cm²). An increase in concentration to 5% does not result in an increase in photocurrent; on the contrary, we have observed a decrease (35 µA/cm²). Typically, the increase of V_{oc} is ascribed to the prohibited charge recombination due to the energy barrier effect of MOFs in titania. The suppression effect on charge recombination may be strengthened by involving a quantity

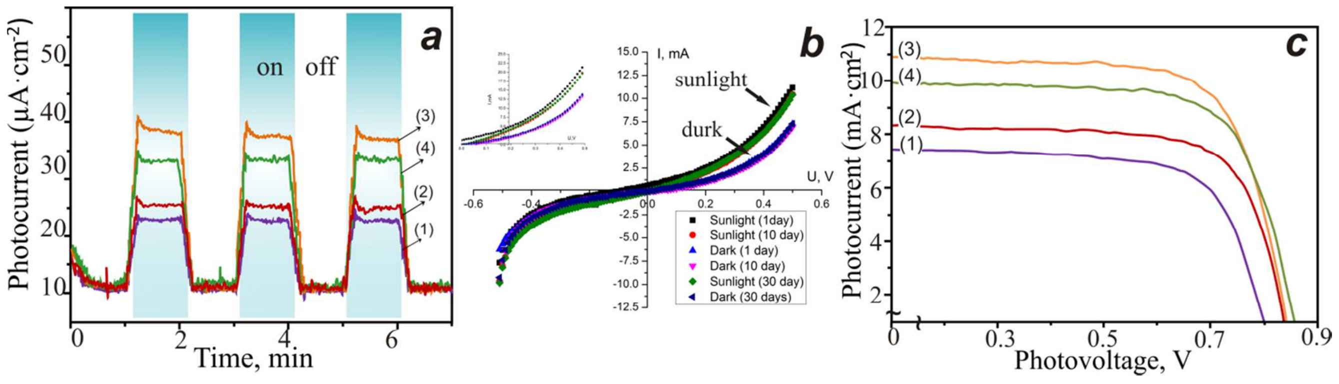

Figure 3. Photocurrent responses (a) and I_{sc}–V_{oc} characteristics (c) of the cells based on MOF/TiO_2 products containing different amounts of MIL-125(1-2%; 2-3%;3-4%;4-5%); b) Voltamperic characteristics of a cell based on 3% MIL-125/TiO_2 versus operation time.

Table 1. The main parameters of a perovskite/TiO_2−MOF-based heterojunction solar cell prepared with different amounts of MIL-125.

Sample	S_{BET}, m^2/g	$S_{Langmuir}$, m^2/g	I_{sc}, mA	V_{oc}, V	FF	PCE, %	I, µA (photocurrent response)
Pure TiO_2	47	-	5.25	0.82	0.61	2.5	16
2% MIL-125@TiO_2	470	880	7.4	0.8	0.72	4.3	24
3% MIL-125@TiO_2	525	1033	10.9	0.85	0.69	6.4	39
4% MIL-125@TiO_2	540	1050	9.9	0.86	0.6	5.1	35
5% MIL-125@TiO_2	570	1108	7.5	0.83	0.68	4.2	26
TiO2/ZIF-8(DSSC)[12]	-		10.28	0.75	0.69	5.34	-

MOFs, resulting in a higher $V_{oc.}$ However, quantity of MOFs should be strictly limited, because of decrease Jsc significantly, as manifested by Table1 and [12]. The data obtained suggest that using MOFs as surface modifiers for TiO_2 anodes[18,22] while producing quasi-bulk perovskite-based solar cells is a matter of interest due to increased adsorption capacity, hence heterojunction area. Three-dimensional structures have already been used as light harvesters for mesoscopic heterojunction solar cells.[19] To assess the activity of the material 3% MOF@TiO_2, we have constructed a depleted quasi-bulk heterojunction TiO_2/MOF-based solar cell for the first time, as described in the ESI, with a carbon counter-electrode. Previously, work on modifying TiO_2 with perovskite nanocrystals has been performed[13,18,20] to produce solid photocells with high stability and efficiency. We suggest increasing the area of the perovskite junction through the micro-mesoporous structure of the synthesised composite for inhibited interfacial charge recombination at the interface. Fig. 3b shows voltamperic characteristics of an operating photocell under dark and illuminated conditions versus time. The diode behaviour of the photocell with an increase of I–V characteristics with lighting is clearly observed. To assess a degree of efficiency of the constructed solar cell, we have plotted V_{oc} against I_{sc} (Fig. 3c). Under 100 mW/cm^{-2} solar light the 3% MOF@TiO_2-based monolithic device produced $V_{oc} = 0.85$ V and $I_{sc} = 10.9$ mA/cm^{-2}, corresponding to a PCE of 6.4%. These data demonstrate a substantial increase in PCE with respect to previous results[18,21] and may well be compared to full printable mesoscopic titania-based heterojunction solar cells with using non-modified carbon as a counter-electrode. Moreover, the constructed solar cell is characterised by durable stability in ambient atmosphere. A change in η did not exceed 0.3% in dry air at room temperature without encapsulation for 30 days. These impressive results indicate a superior stability to that of dye-sensitised solar cells.[12]

In conclusion, we have applied a single-step hydrothermal synthesis for the first time to produce a MIL-125@TiO_2 composite, a highly photoactive material with good prospects for constructing quasi-bulk depleted monolithic perovskite/MOF @TiO_2− heterojunction solar cells. SAXS, TG, EXAFS spectra and HRTEM data confirmed the presence of MIL-125 in the composite structure. Using TGA and EDS data, the MOF/anatase mass ratios were determined, which could be intentionally varied between 2 and 5%. The results of the photopolarisation measurements were employed to determine the optimal MOF concentration promoting the greatest photocurrent response. The greatest increase (39 $\mu A/cm^2$) was found for 3% MOF−TiO_2. A MIL-125@TiO_2-based heterojunction solar cell revealed high stability over time (up to 30 days), with a PCE of about 6.4%. Thus, we have shown the possibility of using MOF@TiO_2 composites for the successful production of solid solar cells with high stability.

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Notes and references

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For chemicals and characterisation see Supplementary Material.

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