

## Nanometer-sized Titania hosted inside MOF-5

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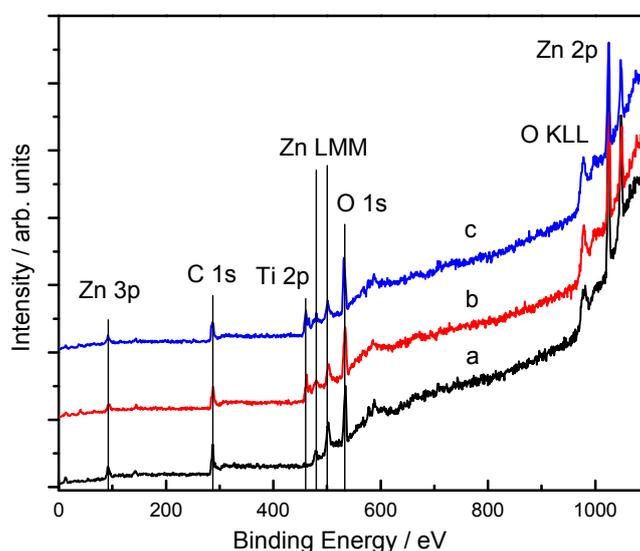
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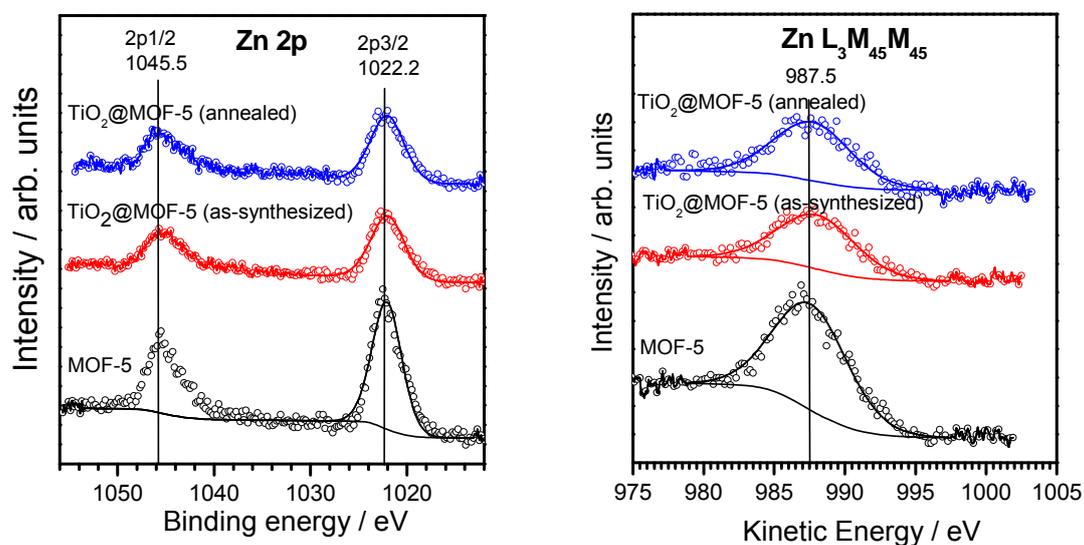
### Supporting Information

XPS measurements were carried out in an ultra-high vacuum (UHV) set-up equipped with a high resolution Gamdata-Scienta SES 2002 analyzer. Monochromatic Al K $\alpha$  X-ray source (1486.6 eV; anode operating at 14 kV and 55 mA) was used as incident radiation. The base pressure in the measurement chamber was around  $2 \times 10^{-10}$  mbar. XP spectra were recorded in the fixed transmission mode. The analyzer slit width was set to 0.4 mm and a pass energy of 200 eV was chosen, resulting in an overall energy resolution better than 0.7 eV. Charging effects were compensated by applying a flood gun. The binding energies were calibrated based on the hydrocarbon C1s peak at 285 eV. Prior to individual elemental scans a survey scan was taken for all the samples in order to detect all the elements present.

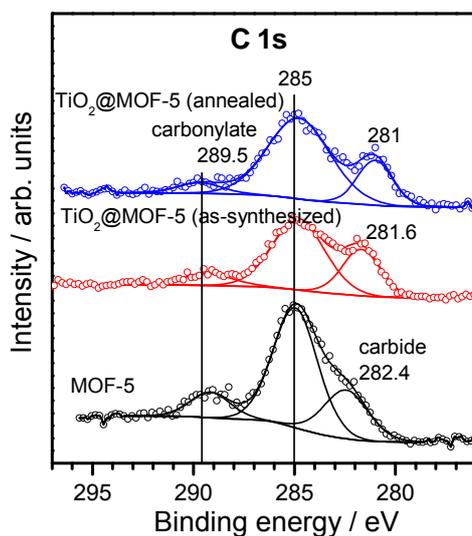
**Figure S1** XP survey spectra of the different MOF samples: (a) MOF-5; (b) TiO<sub>2</sub>@MOF-5 (as-synthesized) (c) TiO<sub>2</sub>@MOF-5 (annealed, 250°C 2d).



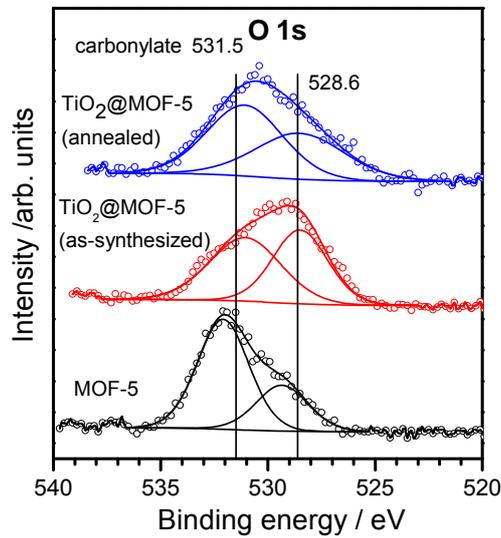
**Figure S2** High-resolution XP Zn 2p, Zn L<sub>3</sub>M<sub>45</sub>M<sub>45</sub>, C1s, O1s and Ti 2p spectra of MOF-5 and TiO<sub>2</sub>@MOF-5 samples (as-synthesized and annealed).



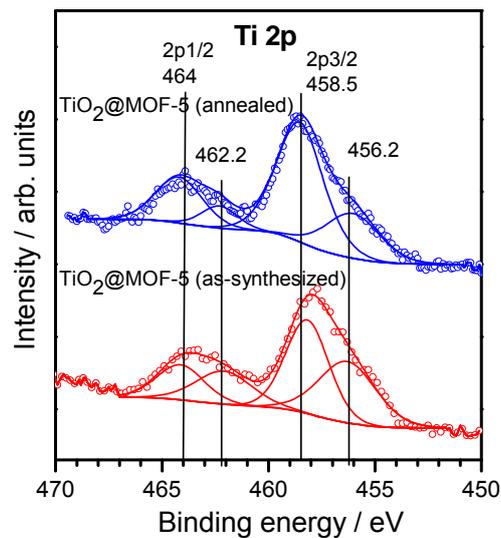
The Zn 2p spectrum shows two peaks at 1022.5 and 1045.5 eV which are assigned to the 2p<sub>3/2</sub> and 2p<sub>1/2</sub> components, respectively. The Zn 2p core levels are not sensitive to the oxidation state of zinc. The latter can be clearly identified by the Zn L<sub>3</sub>M<sub>45</sub>M<sub>45</sub> Auger spectra. The corresponding peak observed at 987.5 eV (kinetic energy, KE) demonstrates the presence of Zn<sup>2+</sup> species in MOF-5



The C1s spectra are dominated by the intense hydrocarbon peak at 285 eV. The weak peak at 289.5 eV is characteristic for the carbonylate species (-COO) in MOF-5. In addition, a carbidic C1s peak is observed at 282.4 eV and shifts to lower binding energies after the modification of MOF-5 with TiO<sub>2</sub>, indicating the formation of TiC species.

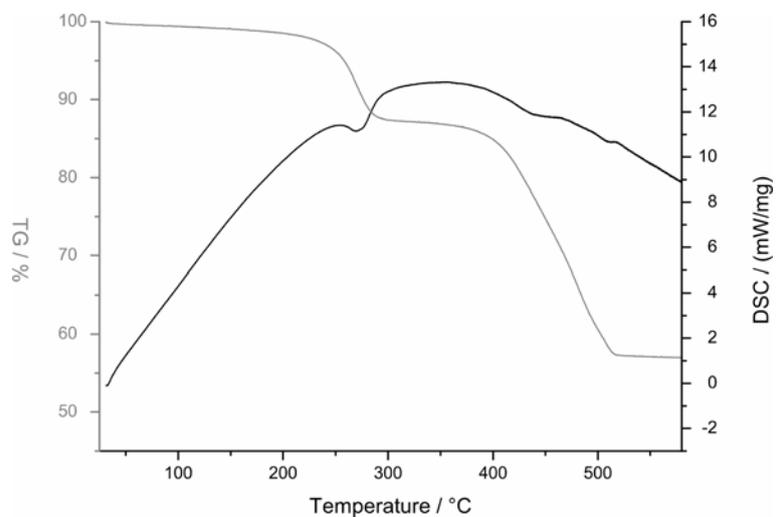


The existence of the carbonylate species is also confirmed by the O1s peak at about 531.5 eV. For MOF-5, an additional peak is detected at 529.3 eV which is related to the presence of Zn<sub>4</sub>O groups in the MOFs structure. After the inclusion of TiO<sub>2</sub>, the oxide-related O 1s peak increases in intensity and shifts slightly to lower binding energies, revealing the formation of TiO<sub>2</sub> species.



The formation of TiO<sub>2</sub> is further identified by the XPS data for Ti 2p core levels. At room temperature, the doublet peak observed at 458.5 and 464 eV is characteristic for TiO<sub>2</sub> species. Another doublet peak is seen at 456.2 and 462.2 eV which can originate from the TiO<sub>2</sub> precursors (TiO(Pr)<sub>4</sub>). After heating to higher temperatures (T=250 °C), the TiO<sub>2</sub> precursors further decompose to yield TiO<sub>2</sub> as supported by the increase of the TiO<sub>2</sub> relative concentration.

**Figure S3** TG/DTA of a TiO<sub>2</sub>@MOF-5 sample (as-synthesized).



**Figure S4** TG/DTA of TiO<sub>2</sub>@MOF-5 sample annealed at different temperatures in comparison to a typical MOF-5 sample.

