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Supplementary Material

Step-by-Step Growth of HKUST-1 on Functionalized TiO_2 Surface: An Efficient Material for CO_2 Capture and Solar Photoreduction

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1.1 Structural and Adsorption Analysis

Table S1. Structural parameters and porosity of TiO_2 RE NPs.

Sample	$L_{(101)}$ (nm)	$L_{(101)\ TEM}$ (nm)	Pore volume (DCPV, $cm^3\ g^{-1}$)	SSA_{BET} ($m^2\ g^{-1}$)
RE TiO_2	16.5	45-60	0.21	170.5
HKUST-1*	/	/	0.33	692.2

Average crystallite sizes (L_{XRD}), calculated by the Scherrer equation, the crystal width estimated from the TEM images ($L_{(101)\ TEM}$), the specific surface areas (SSA_{BET}) and BJH pore volumes (DCPV).
* In the case of HKUST-1 we have reported the data from the literature (Ref 31) since the production of HKUST-1 alone, under the synthesis conditions, does not give a fair comparison.

1.2 TEM Analysis

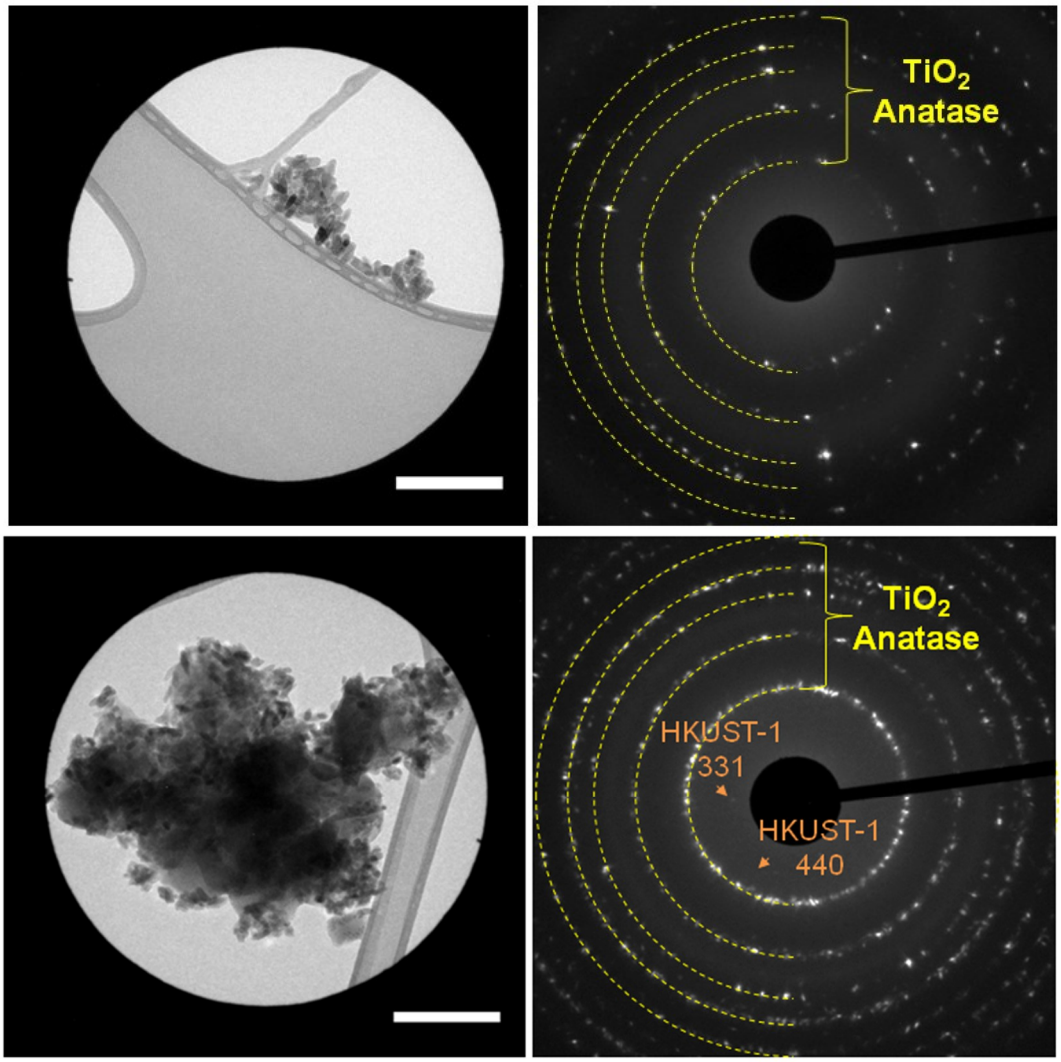
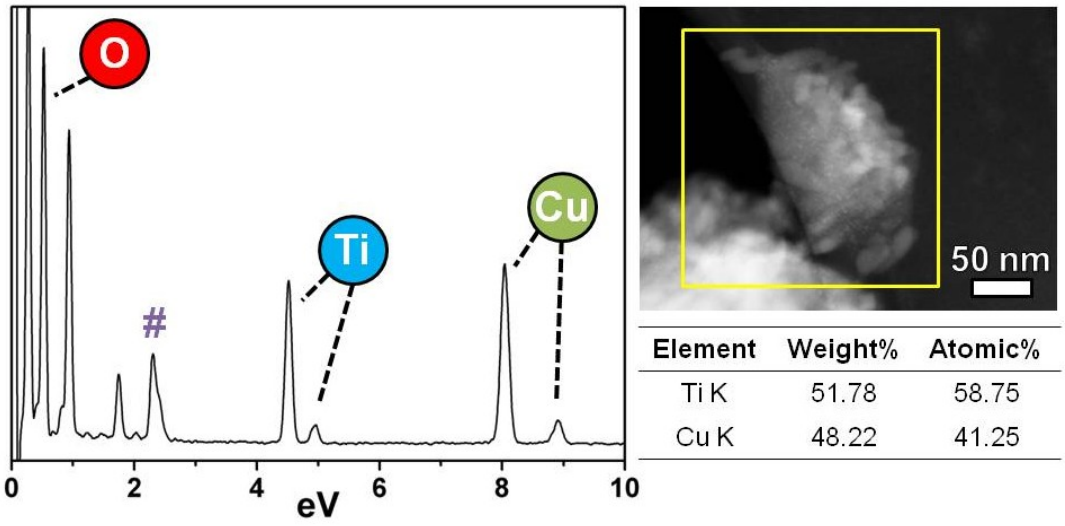


Figure S1. TEM micrographs and related SAED analysis of: above TiO_2 anatase crystals and below the TiO_2/HKUST-1 hybrid system. the latter shows some faint reflection at d-spacing > 3.5Å indexed as HKUST-1. All scale bars are 200 nm, TiO_2 anatase reflexes are indexed as 101, 103, 200, 105 and 213 planes (from the centre to outside).



Element	Weight%	Atomic%
Ti K	51.78	58.75
Cu K	48.22	41.25

Figure S2. STEM-EDS spectra (on the left side) of selected and representative grain (on the top-right side) and related quantitative analysis (on the bottom-right side) of TiO_2/HKUST-1. On the spectra, the peak # is related to the Mo signal, from supported holey carbon Molybdenum TEM grid.

1.3 DR-UV-Vis Spectra

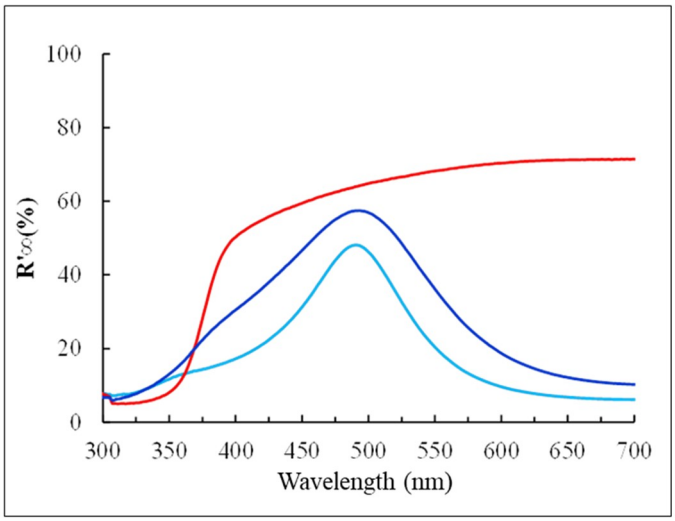


Figure S3. Kubelka-Munk function of TiO2-PHA (red line), pure HKUST-1 (sky blue line) and TiO2/HKUST-1 (blue line).

1.4 XPS Analysis

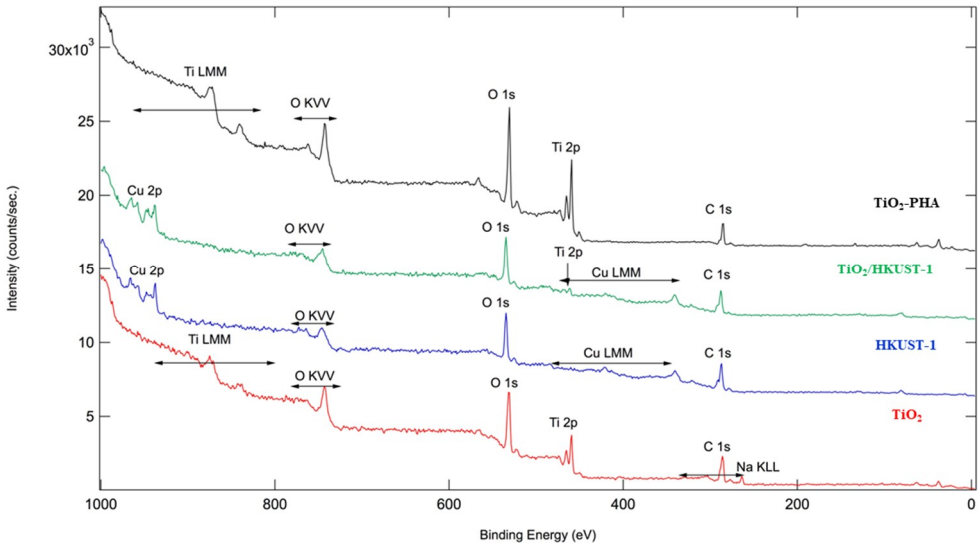


Figure S4. XPs survey spectra of TiO_2, TiO_2-PHA, HKUST-1 and TiO_2/HKUST-1.

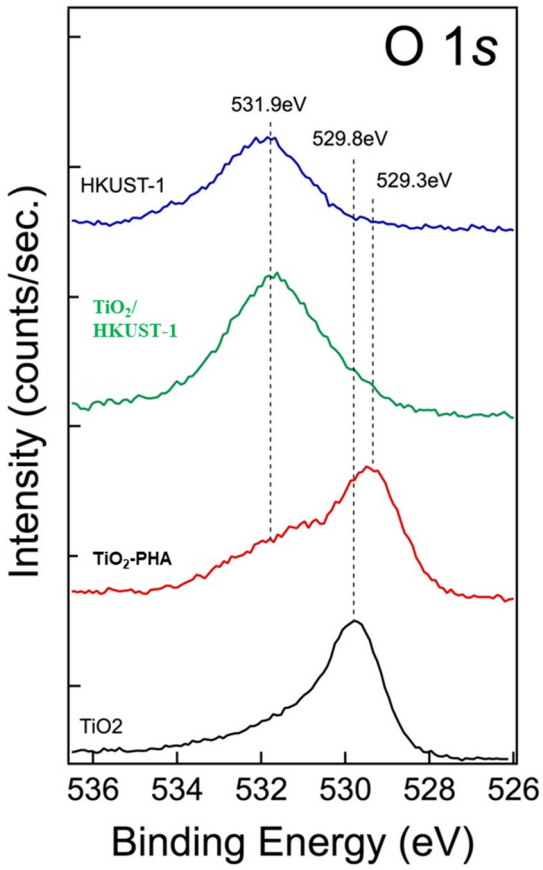


Figure S5. High resolution XPS spectra of O1s in HKUST-1, TiO_2, TiO_2-PHA and TiO_2/HKUST-1.

1.5 Photocatalytic Activity

Table S2. Results of the photocatalytic runs in the presence of the bare TiO_2-PHA sample.

TiO_2-PHA			
1st run			
Time (h)	**CH_4 (μM)**	**CH_3CHO (μM)**	**CO (μM)**
1	1.65	0.85	0.00
2	2.45	0.74	0.01
3	3.50	0.89	0.01
4	4.93	1.16	0.01
5	6.20	1.24	0.02
6	8.97	1.48	0.02
2nd run			
1	0.20	-	-
2	0.36	-	-
3	0.50	-	-
4	0.45	-	-
5	0.66	-	-
6	0.69	-	-

Table S3. Results of the photocatalytic runs in the presence of the bare HKUST-1 sample.

HKUST-1			
1st run			
Time (h)	**CH_4 (μM)**	**CH_3CHO (μM)**	**CH_3CH_2OH (μM)**
1	0.57	16.17	-
2	1.52	70.04	331.33
3	1.93	82.33	407.90
4	2.23	87.56	439.00
5	2.57	115.71	476.45
6	2.80	107.27	536.23
2nd run			
1	0.05	-	-
2	0.08	-	-
3	0.13	-	-
4	0.23	-	-
5	0.37	-	-
6	0.42	-	-

Table S4. Results of the photocatalytic runs in the presence of the sample TiO_2/HKUST-1.

TiO_2/HKUST-1		
1st run		
Time (h)	**CH_4 (μM)**	**CH_3CHO (μM)**
1nd run		
1	0.53	-
2	0.98	-
3	1.14	-
4	1.30	-
5	1.56	-
6	2.19	-
2nd run		
1	0.24	-
2	0.67	-
3	1.00	-
4	1.32	-
5	2.07	-
6	2.63	-

1.6 Hybrid Catalyst Characterization after Photocatalysis

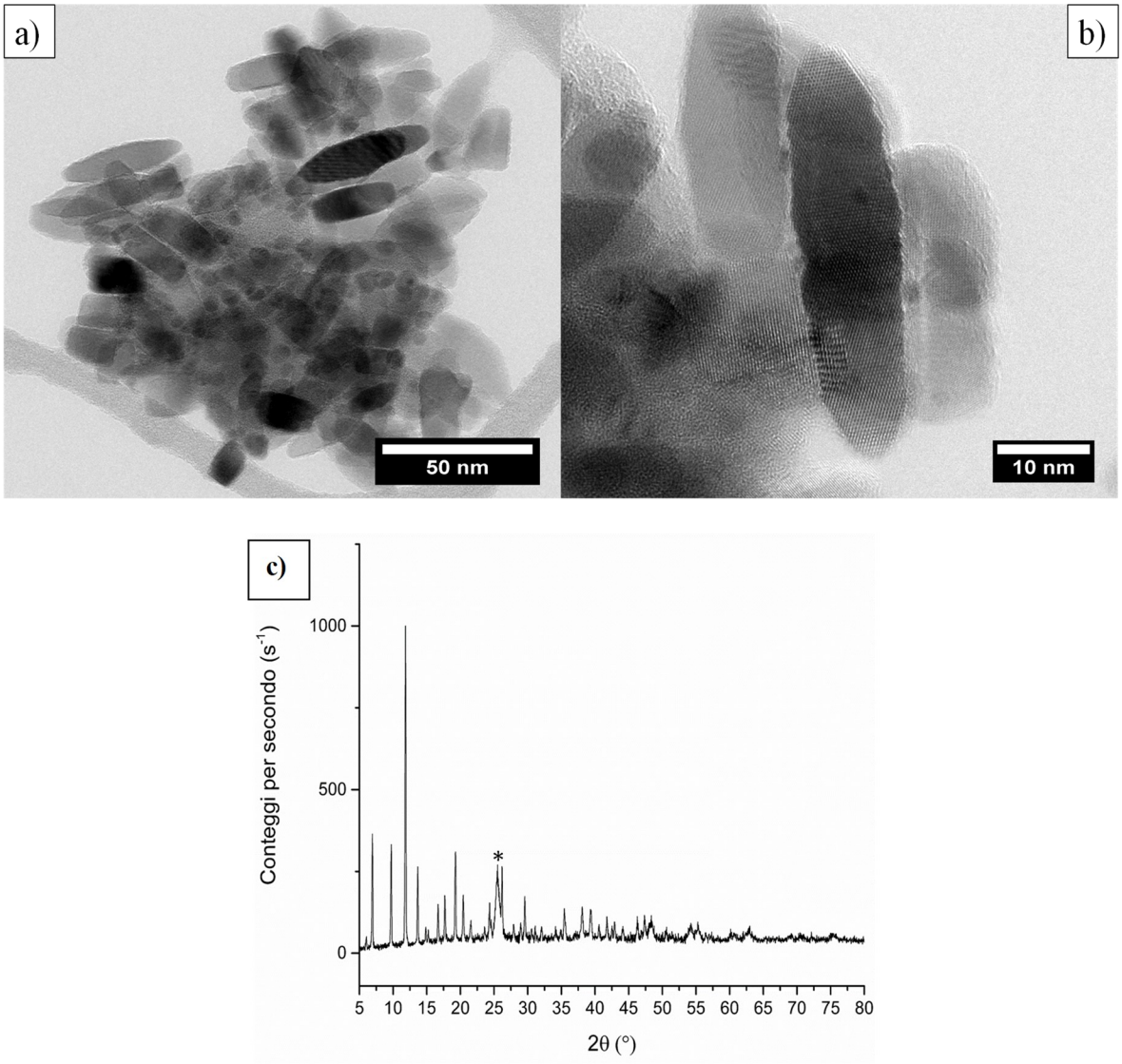


Figure S6. (a,b) TEM image and (c) XRPD pattern of TiO_2/HKUST (the asterisks refer to anatase) after the second photocatalytic run. There are no morphological, phase and composition changes after the reactions.