Electronic Supplementary Information (ESI)

Bimetal-organic framework derived multi-heterostructured $TiO_2/Cu_xO/C$ nanocomposites with superior photocatalytic H_2 generation performance

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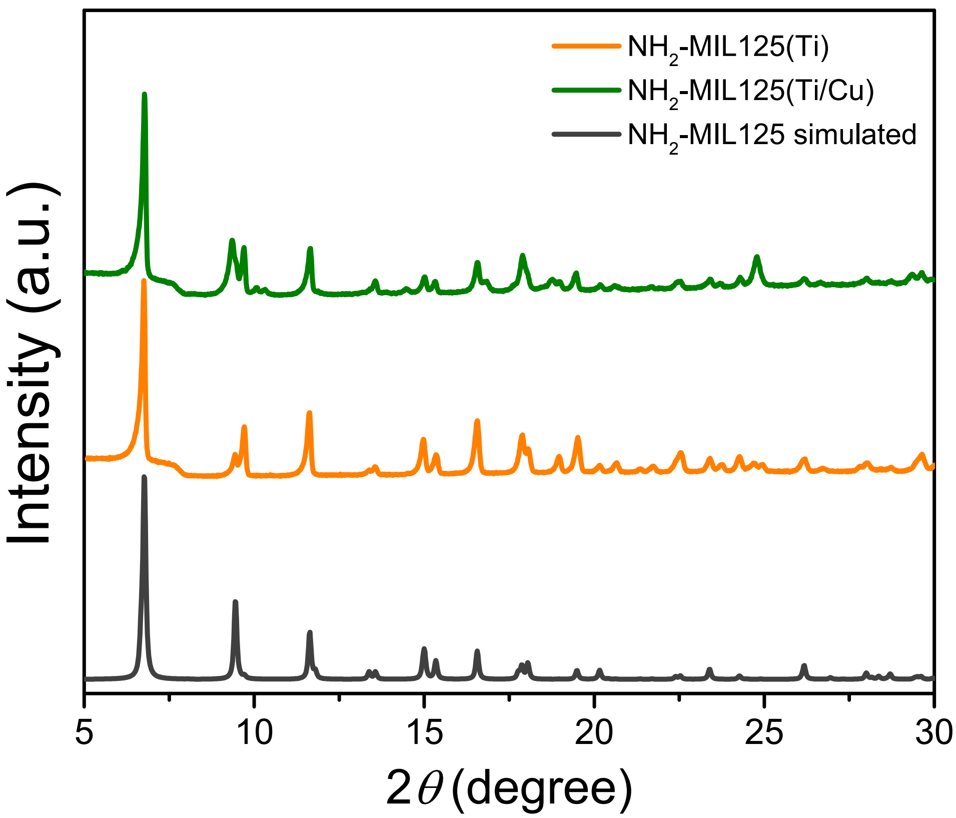

Fig. S1 PXRD patterns of as-synthesized NH_2-MIL-125(Ti) and NH_2-MIL-125(Ti/Cu).

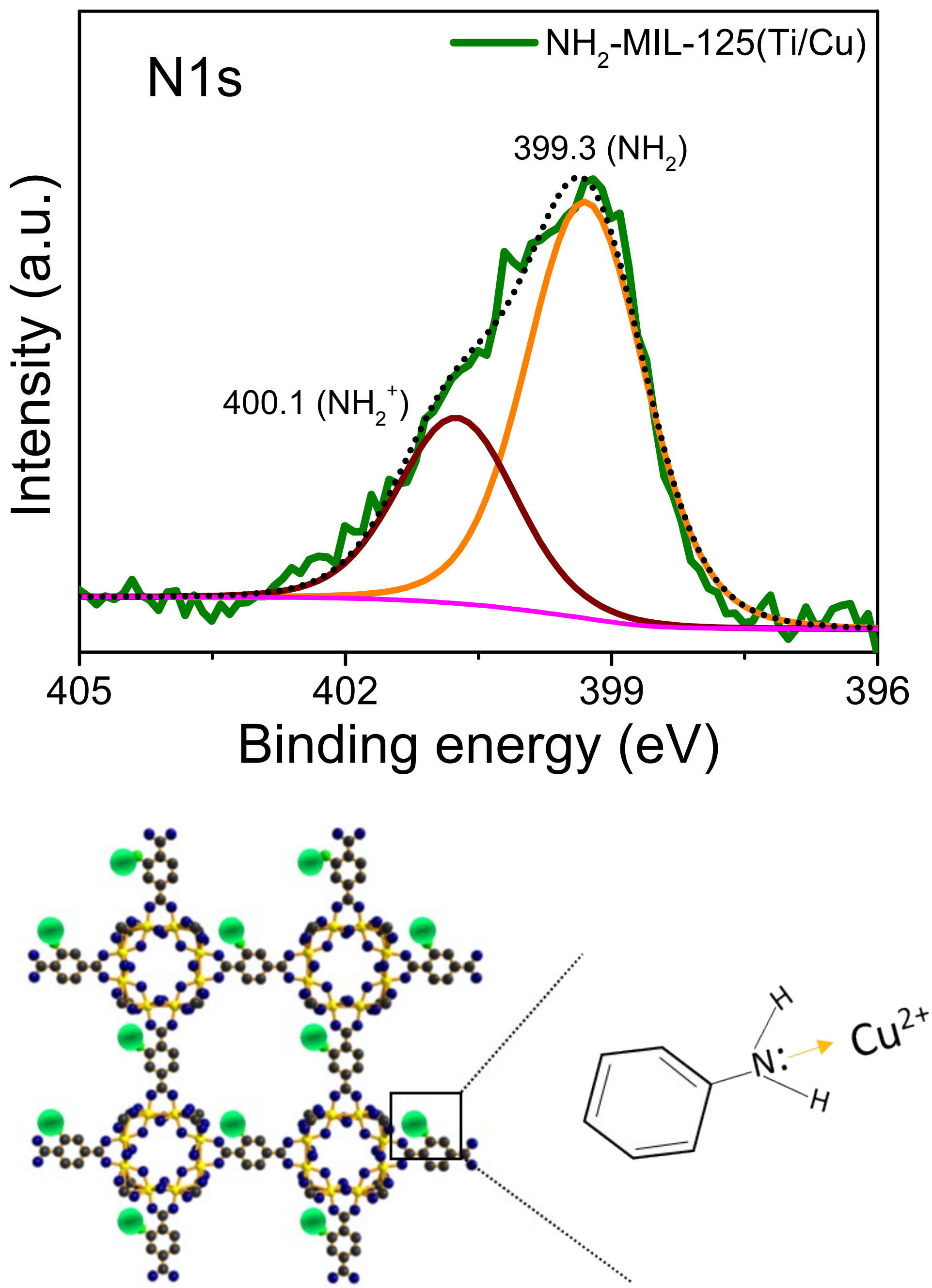

Fig. S2 Deconvoluted N 1s XPS spectra of as-prepared NH_2-MIL-125(Ti/Cu).

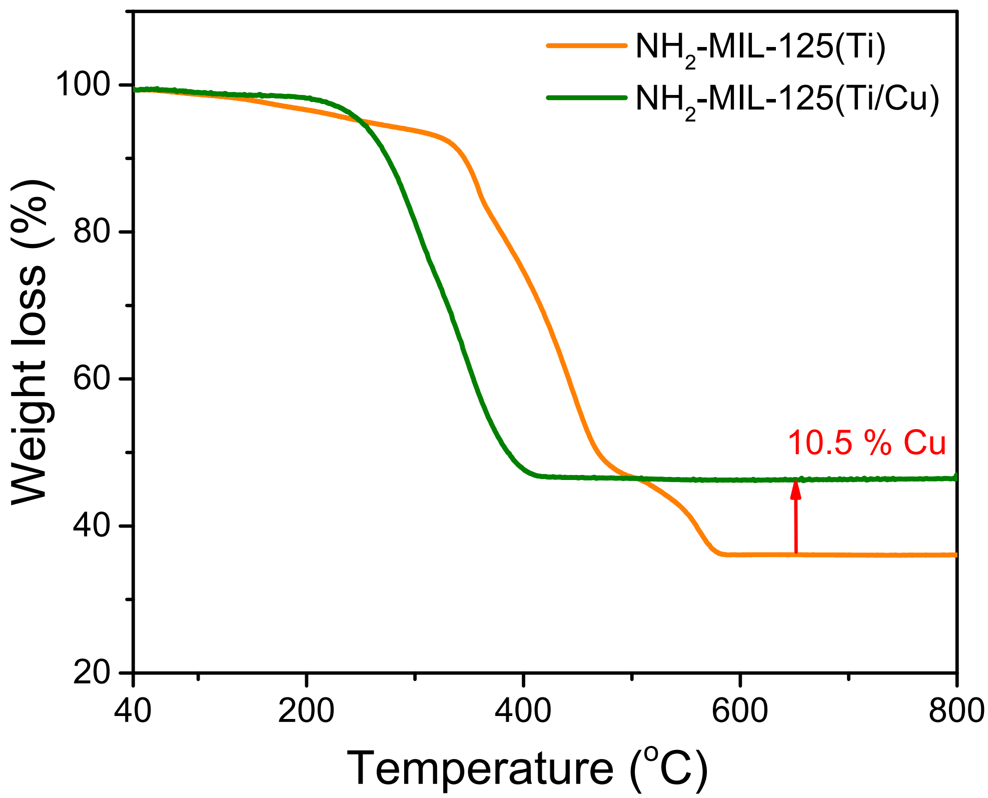

Fig. S3 TGA profiles of as-prepared NH_2-MIL-125(Ti) and NH_2-MIL-125(Ti/Cu) in air.

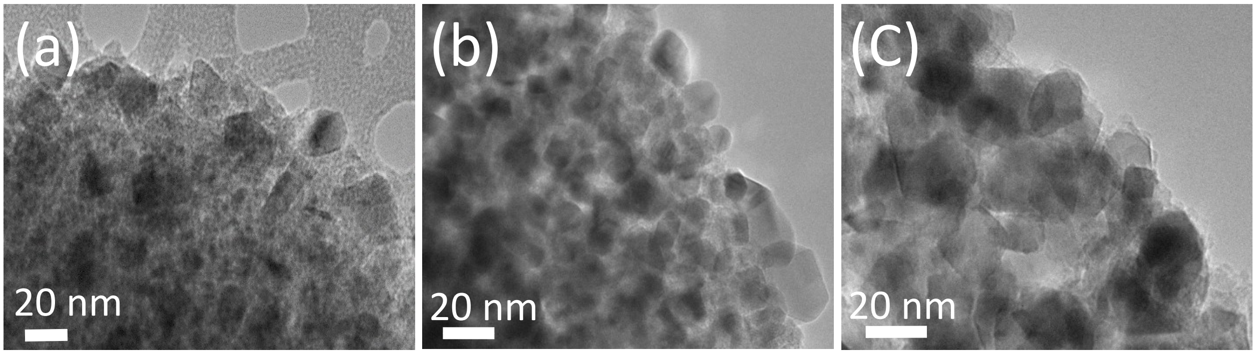

Fig. S4 TEM images of (a) TiCuC550, (b) TiCuC700 and (c) TiCuC800.

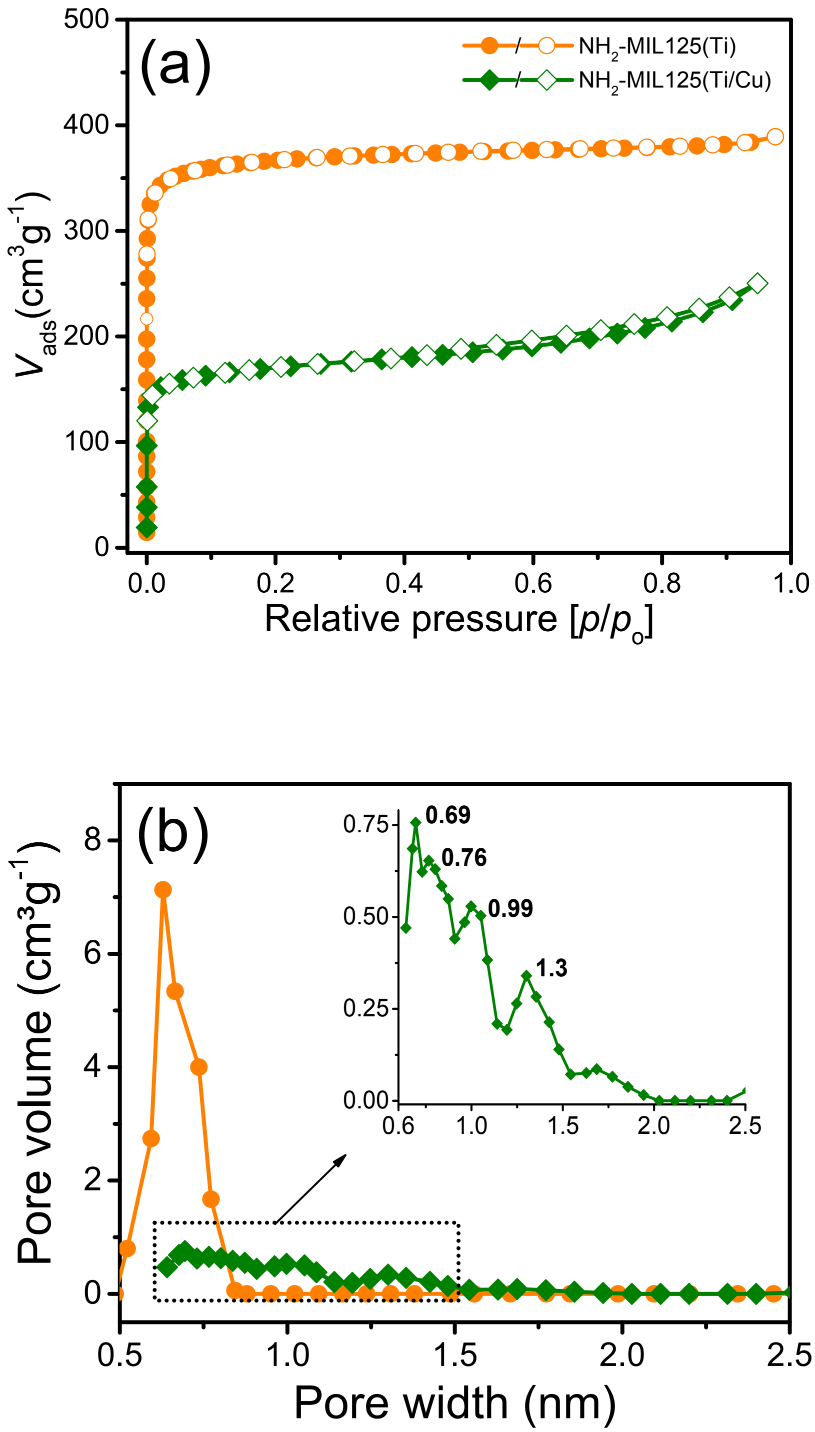

Fig. S5 (a) N_2 sorption isotherms and (b) Pore size distribution of NH_2-MIL-125(Ti) and NH_2-MIL-125(Ti/Cu).

Table S1 Textural properties of NH_2-MIL-125(Ti) and NH_2-MIL-125(Ti/Cu).

Sample	Specific surface area ($m^2 g^{-1}$)	Total pore volume ($cm^3 g^{-1}$)
NH_2-MIL-125(Ti)	1462	0.60
NH_2-MIL-125(Ti/Cu)	654	0.38

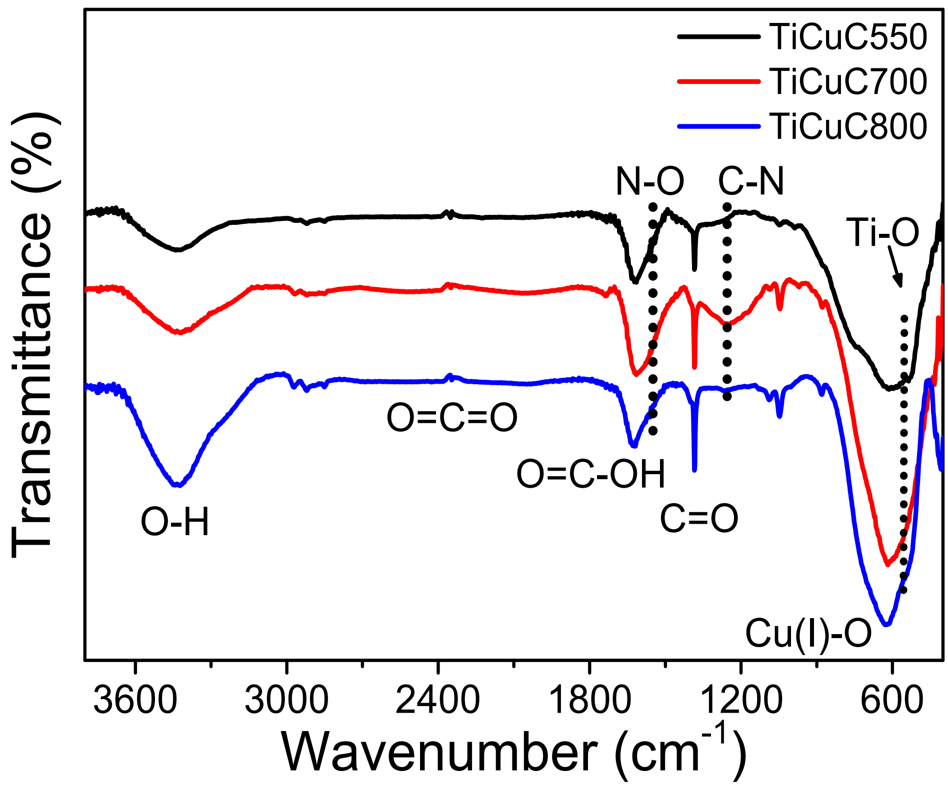

Fig. S6 FTIR spectra of TiCuC550 (black), TiCuC700 (red) and TiCuC800 (blue).

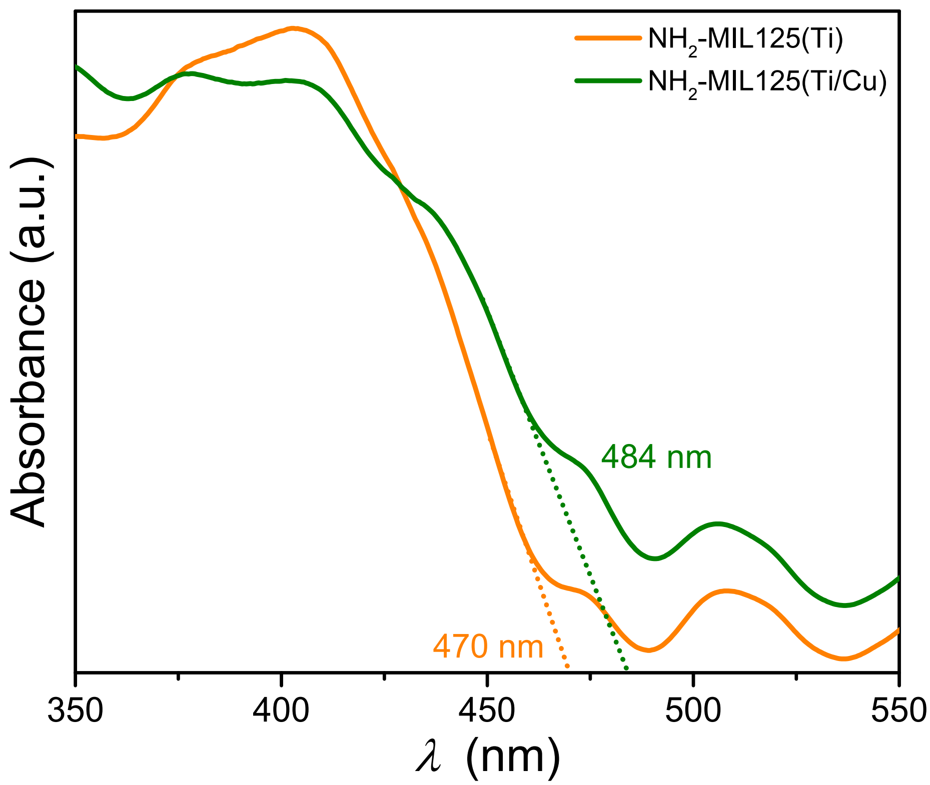

Fig. S7 UV-Vis absorption spectra of NH_2-MIL-125(Ti) and NH_2-MIL-125(Ti/Cu).

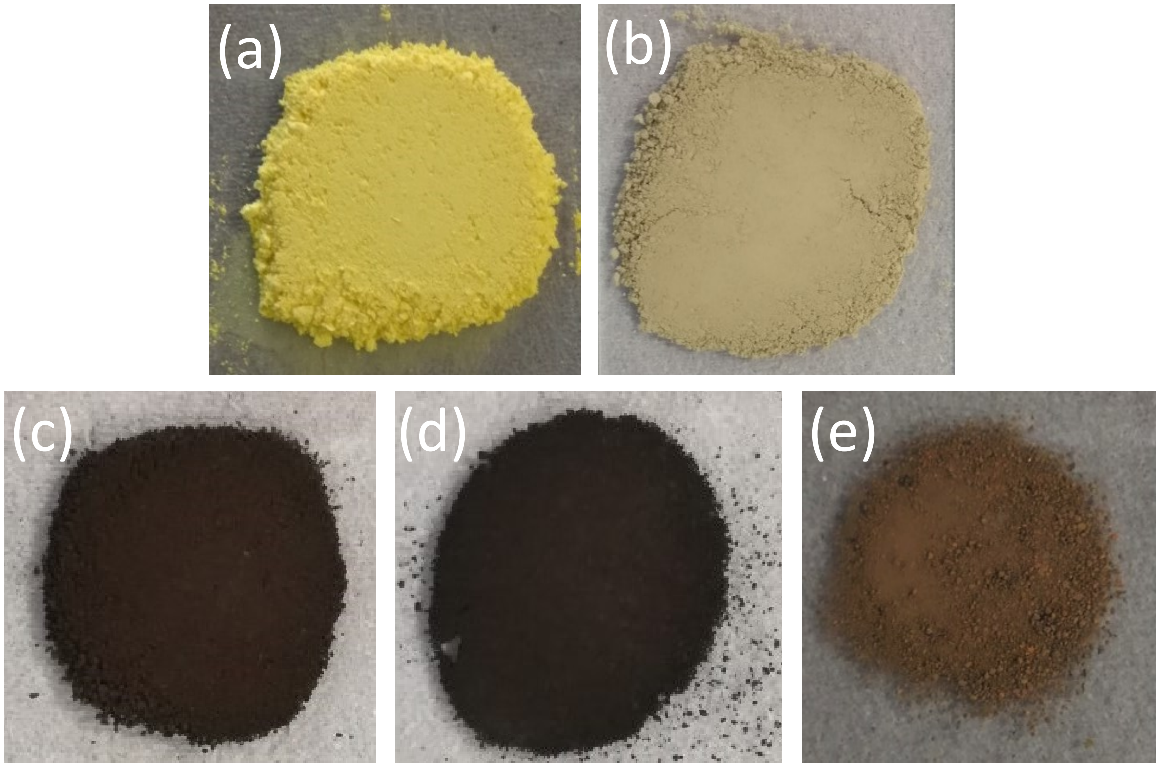

Fig. S8 Photos of (a) NH_2-MIL-125(Ti), (b) NH_2-MIL-125(Ti/Cu) and derived composites (c) TiCuC550, (d) TiCuC700 and (e) TiCuC800.

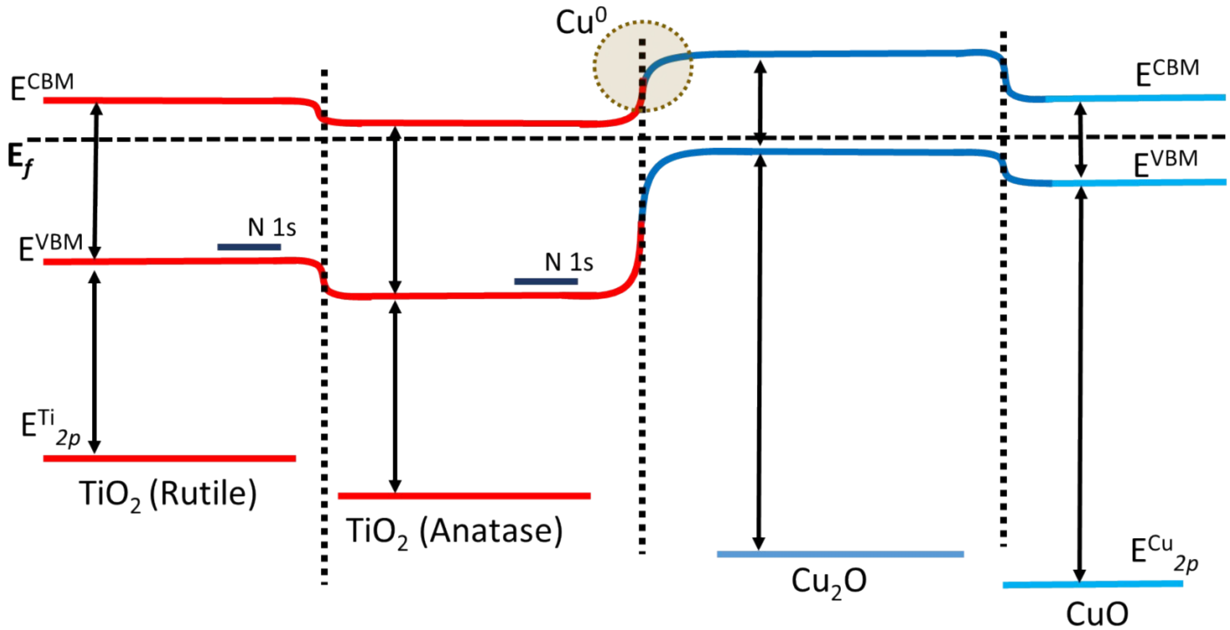

Fig. S9 The proposed schematic of energy band alignments of NH_2-MIL-125(Ti/Cu) derived nanocomposite TiCuC700. The anatase and rutile TiO_2 polymorphs and Cu_2O/CuO form phase junctions whereas p-n heterojunction is formed between n-type TiO_2 and p-type Cu_2O/CuO causing band bending. The presence of Cu^0 nanoparticles may facilitate a quick charge transfer from Cu_2O/CuO to anatase TiO_2 and/or functionalized carbon matrix.

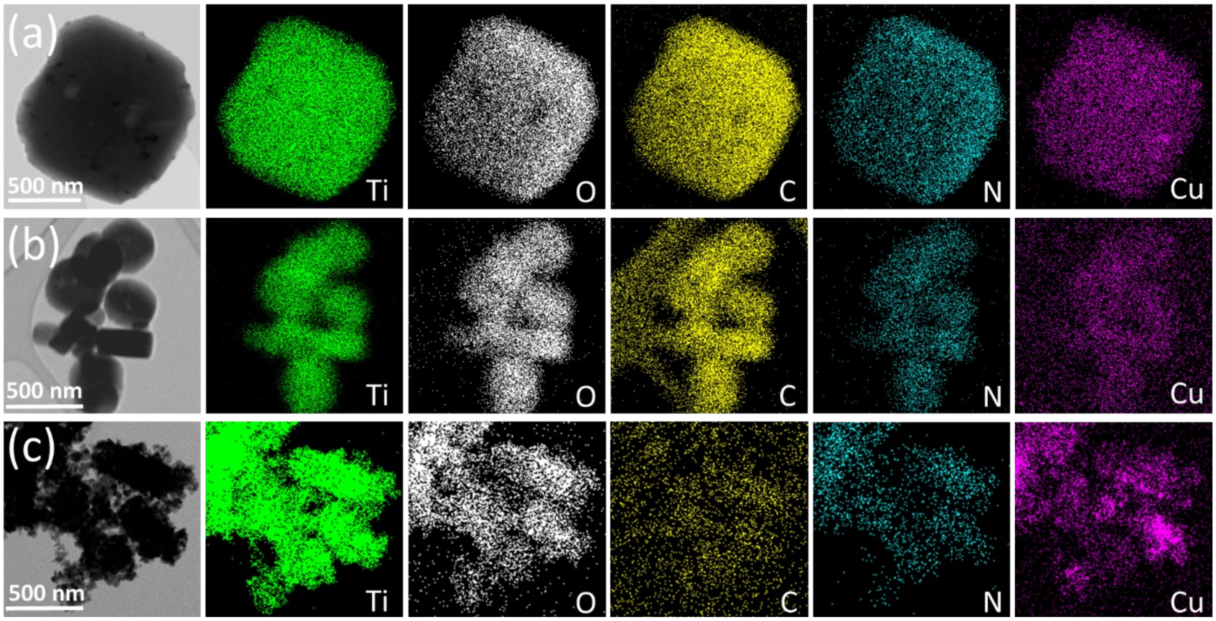

Fig. S10 Representative EDX elemental maps of Ti, O, C, N and Cu for sample (a) NH_2-MIL-125(Ti/Cu), (b) TiCuC550 and (c) TiCuC800.

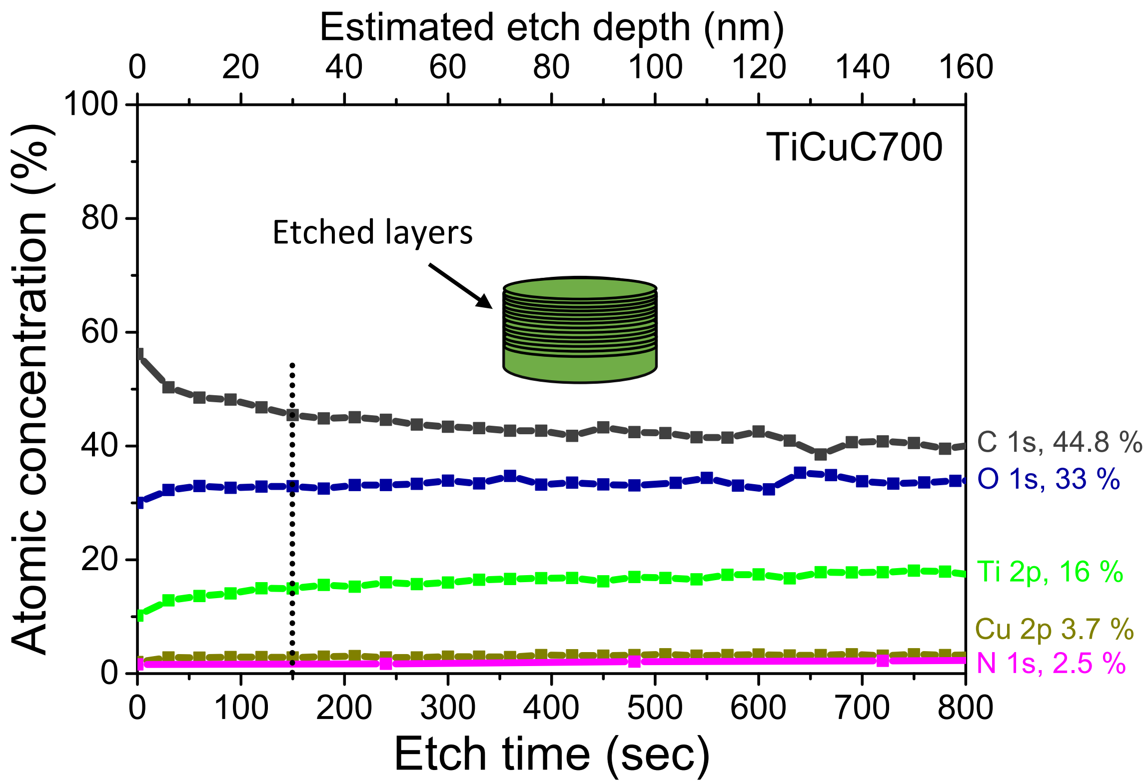

Fig. S11 TXPS depth profiles of the selected sample TiCuC700.

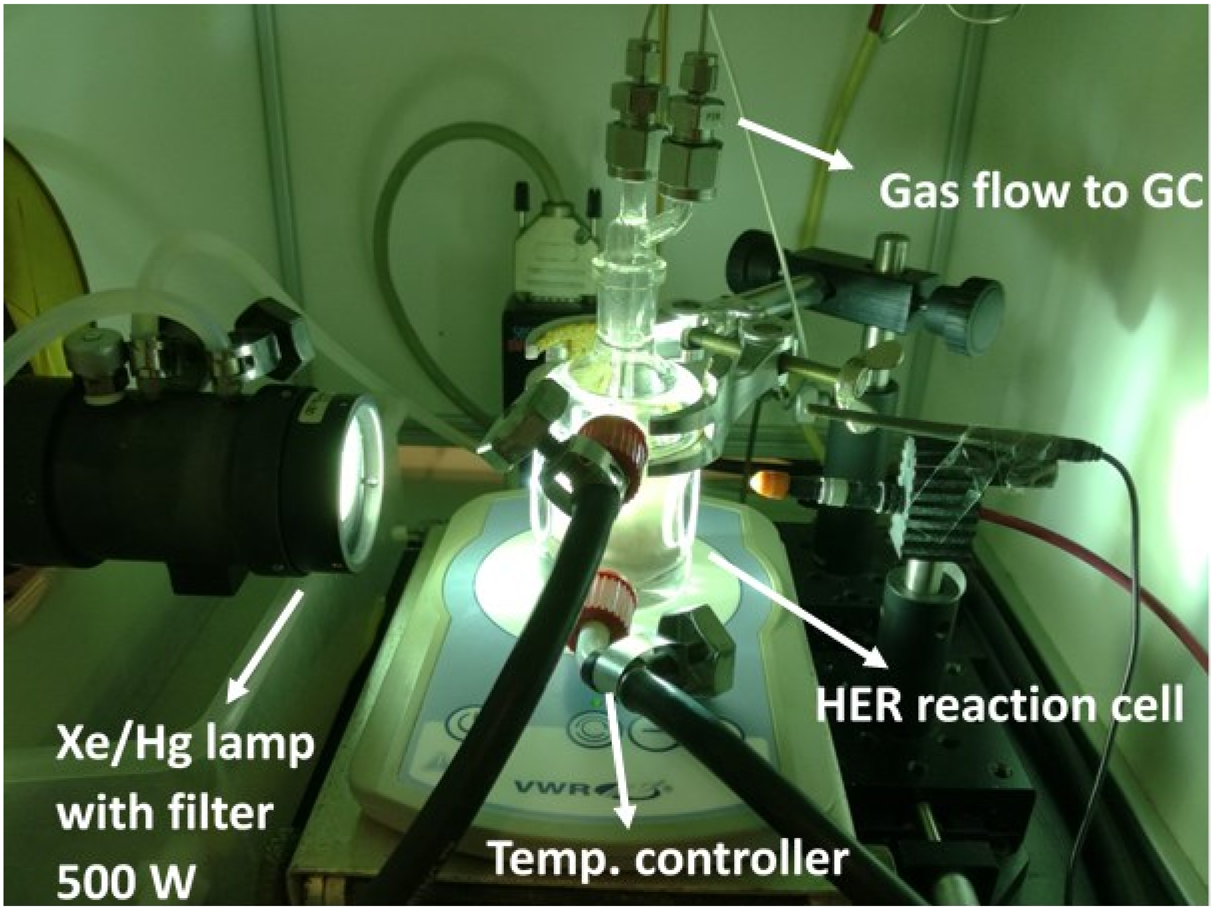

Fig. S12 Photocatalytic setup with HER reaction cell with temperature controller and magnetic stirrer. The HER reaction cell is connected to GC. On the left side, there is a Xe/Hg lamp (500 W) with 285 nm cut-off filter.

Calculation of apparent quantum yield (%) for photocatalytic H_2 evolution

The apparent quantum yield (AQY_λ) can be calculated from the following equation:

$$AQY_\lambda = \frac{2 \times number\ of\ evolved\ H_2\ molecules}{Total\ number\ of\ incident\ photons} \times 100\ \%$$

And Energy of photon $_{(435\ nm)}$ = $E = \frac{h \times c}{\lambda}$ = 4.56×10^{-19} J/photon

where E is the energy of the photon, h is Planck's constant (6.63×10^{-34} J.sec^{-1}) and c is the speed of light (3×10^{8} m/sec). The light source is 500 W Xe/Hg lamp (66983, Newport). The light beam is focused with the spot size of 2.23 cm^2 reaching the reactor window) and an H_2O filter (61945, Newport). The photon count was determined with the help of a photon counter. The absolute irradiance at wavelength λ = 435 nm in the test facility is 28994.1 µWcm^{-2}nm^{-1}.

Total no. of photons $_{(435\ nm)}$ = $\frac{Absolute\ Irradiance}{Energy\ of\ photon} = \frac{28994.1\ \mu J sec^{-1} cm^{2} nm^{-1}}{4.56 \times 10^{-19} J}$

Total no. of photons $_{(435\ nm)}$ = 6.35×10^{22} µs^{-1}cm^{2}nm^{-1}

Total no. of photons in moles = $\frac{No.\ of\ photons\ (\mu s^{-1} cm^{2} nm^{-1}) \times (100 \times 10^{2})}{N_A}$

where N_A is Avogadro's number = 6.02×10^{23} mol^{-1}

Total No. of photons in moles = **1055 µmols^{-1}m^{-2}nm^{-1}**

Photon count within the irradiated area (2.23 cm^2) = 1055 µmols^{-1}m^{-2} × 0.000223 m^2

Total number of incident photons in irradiated area = **0.235 µmols^{-1}**

The total amount of evolved H_2 molecules for sample **TiCuC700** = 3298 µmolg^{-1}h^{-1}

Number of evolved H_2 molecules by the catalyst used (10 mg) = 32.98 µmolh^{-1} = 0.0092 µmols^{-1}

$$AQY_{(435\ nm)} = \frac{2 \times 0.0092\ \mu mols^{-1}}{0.235\ \mu mols^{-1}} \times 100\ \%$$

$AQY_{(435\ nm)}$ = 7.79 %

The same calculation was followed to determine the AQY (%) of other samples at 435 nm.

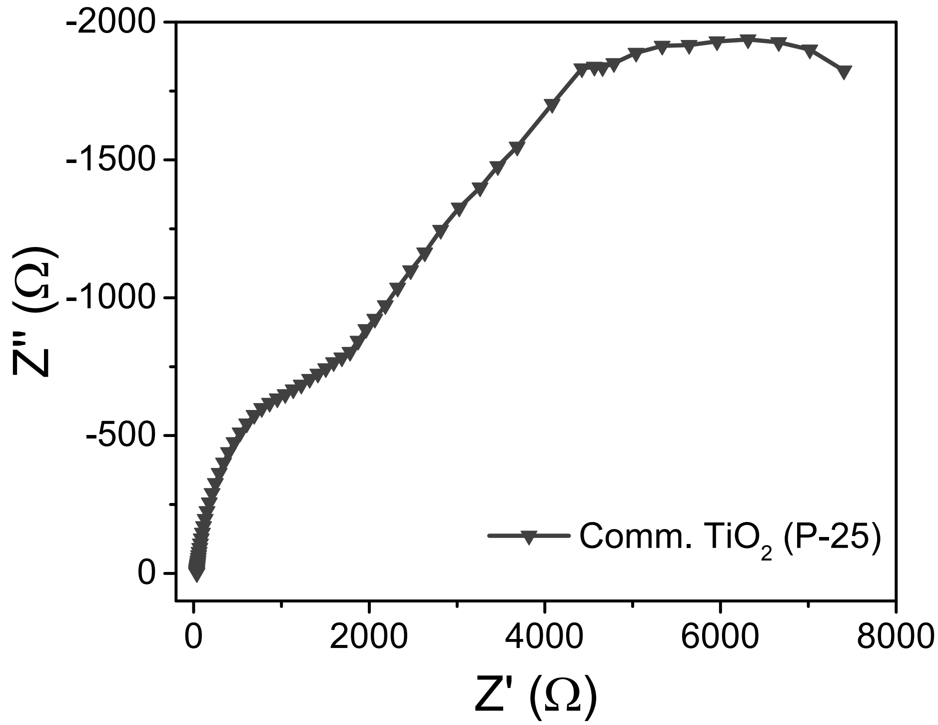

Fig. S13 EIS Nyquist plots of commercial TiO_2 (P-25) under the same potential in 0.5 M H_2SO_4.

Table S2 The photocatalytic HER performance of the selected similar materials reported in the literature.

Photocatalyst	Morphology	Sacrificial electron donor	Light source	H_2 evolution ($\mu mol\ g_{cat}^{-1}h^{-1}$)	Stability test Decrease in H_2 activity (%)	Ref.
0.5Fe/TiO_2	Disc-like	methanol	500 W Xe/Hg lamp (UV light)	230	NA	1
TiO_2@ZIF-8	Hollow nanospheres	methanol	300 W Xenon lamp (UV-light)	261.7	5 cycles (9 %)	2
Cu/TiO_2	Octahedral shell	methanol	300 W Xe lamp (UV light)	62.16	NA	3
Mixed phase TiO_2	Disc-like	methanol	300 W Xe lamp (UV-Vis light)	1394	3 cycles (~ 0 %)	4
CuO@MTs (MT = Mesoporous TiO_2)	Mesoporous tablets	methanol	1000 Wcm^{-2} (Xe lamp)	4760	NA	5
1-D TiO_2	Nanorods	glycerol	Sun light (10 AM-3 PM)	707	5 cycles (16 %)	6
High pressure hydrogenated TiO_2	Nanoparticles	methanol	100 $mWcm^{-2}$ (Xenon lamp)	220	5 cycles (~ 0 %)	7
Cu-(Ti-MOF)	Disc-like	TEOA	Sun light (88500 lux)	1583.5	5 cycles (56 %)	8
Ternary TiO_2/CuO/Cu	Mesoporous nanofibers	methanol	Xenon lamp	851.3	3 cycles (~ 8 %)	9
NiS/CdS/h-TiO_2	Disc-like	Na_2SO_3/ Na_2S	300 W Xenon lamp	2149.15	4 cycles (~ 20 %)	10
Cu_2O/TiO_2 composite	Microcubes	methanol	300 W Xenon lamp	500.4	3 cycles (8 %)	11
NH_2-MIL-125(Ti)	Disc-like	CH_3CN/ TEA	500 W Xe/Hg lamp (UV-Vis light)	49.3	NA	12
TiO_2-Ag-Cu_2O	Nanotubes	methanol	350 W Xe arc lamp (UV-Vis light)	874.7	NA	13
Graphene/TiO_2	Nanosheets	methanol	350 W Xe arc lamp	736	NA	14
TiO_2/Cu_2O/Cu/C multi-heterojunction	Disc-like	methanol	500 W Xe/Hg lamp (UV-Vis light)	3298	5 cycles (15 %)	This work

*NA = Not available

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