Electronic Supplementary Information (ESI)

Efficient solar light driven H_2 production: A post-synthetic encapsulation of Cu_2O co-catalyst on metal-organic framework (MOF) for boosting the effective charge-carrier separation

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Content

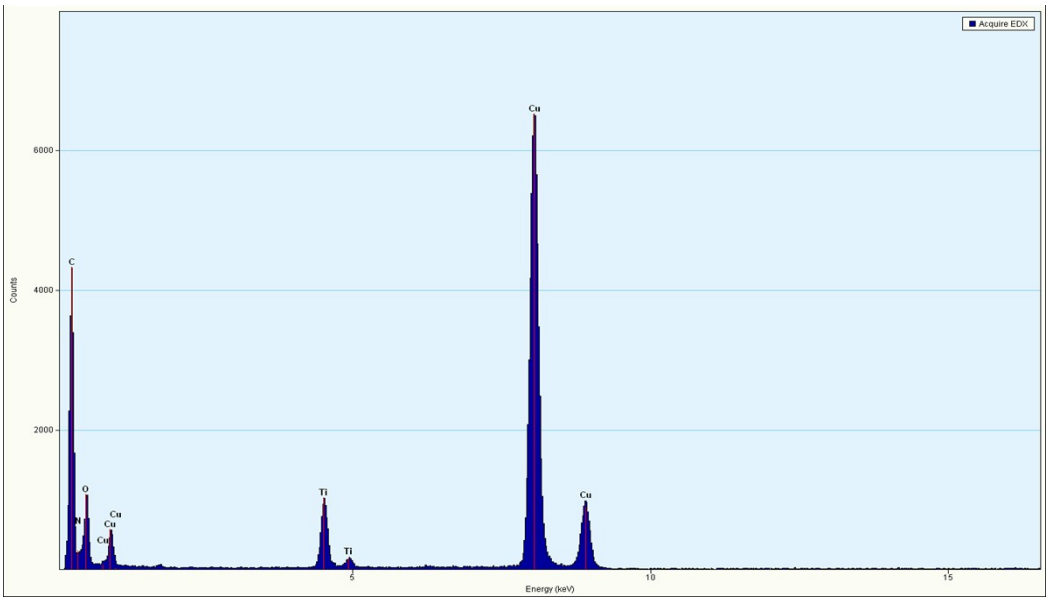

Figure S1.TEM-EDX of Cu_2O/ NH_2-MIL-125(Ti) MOF.

The EDX analysis shows the presence of all the elements such as C, N, O, Ti and Cu in the synthesized Metal-organic framework photocatalyst. The atomic and weight % of elements are tabulated in table S1.

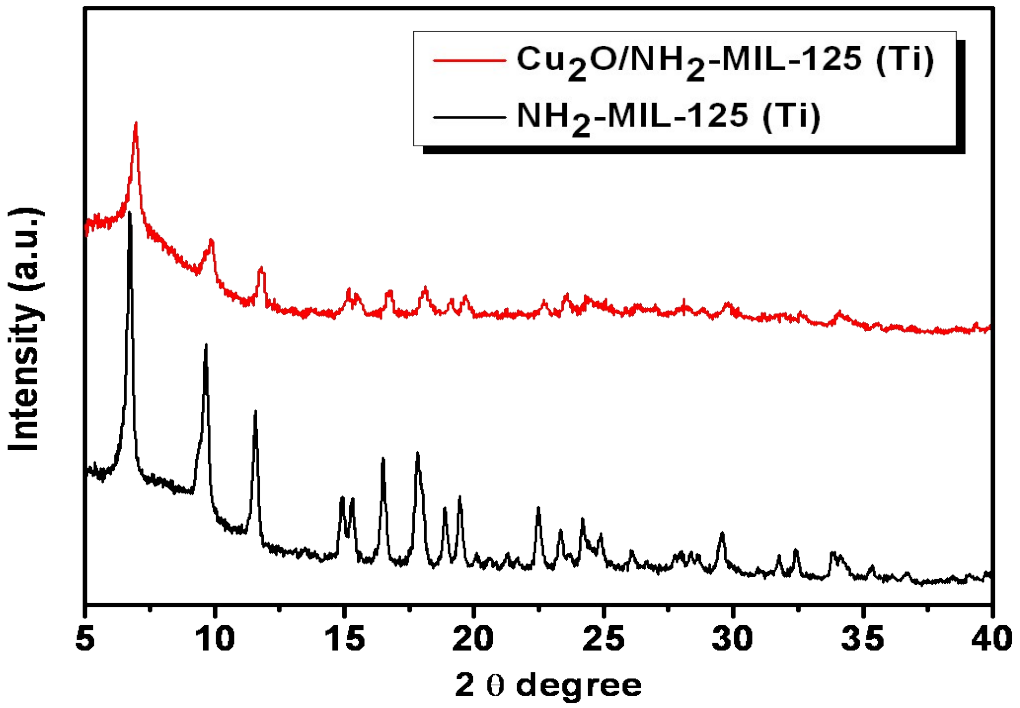

Figure S2. X-ray diffraction patterns of NH_2-MIL-125(Ti) and Cu_2O/ NH_2-MIL-125(Ti) MOFs.

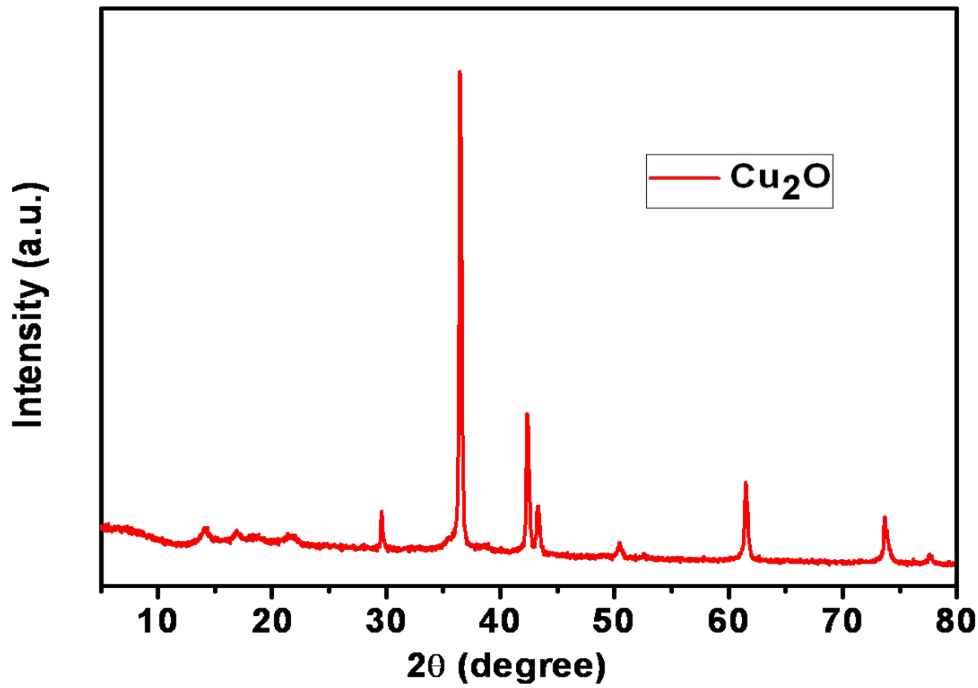

Figure S3. X-ray diffraction patterns of Cu_2O.

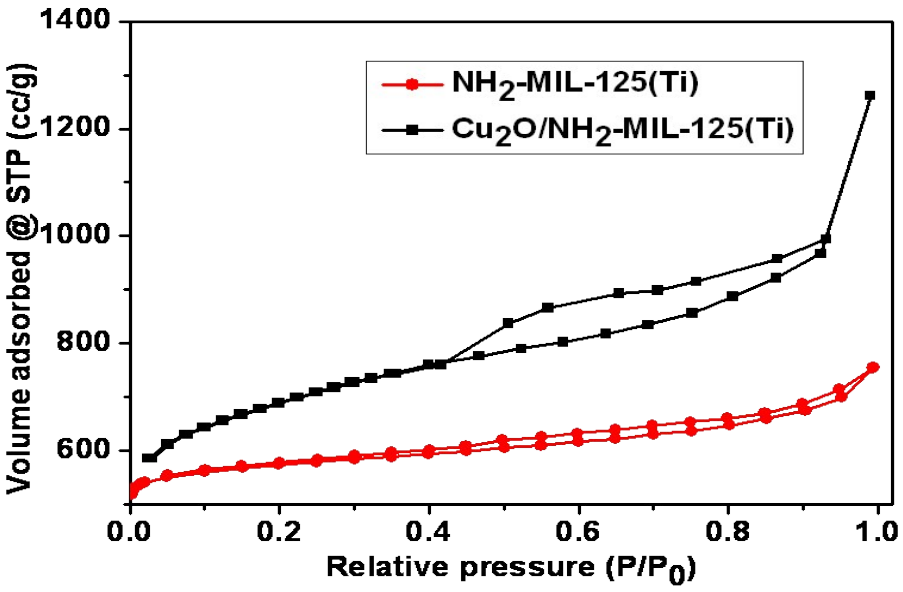

Figure S4. N_2 adsorption and desorption isotherms of NH2-MIL-125(TI) and Cu_2O/ NH_2-MIL-125(Ti) MOF.

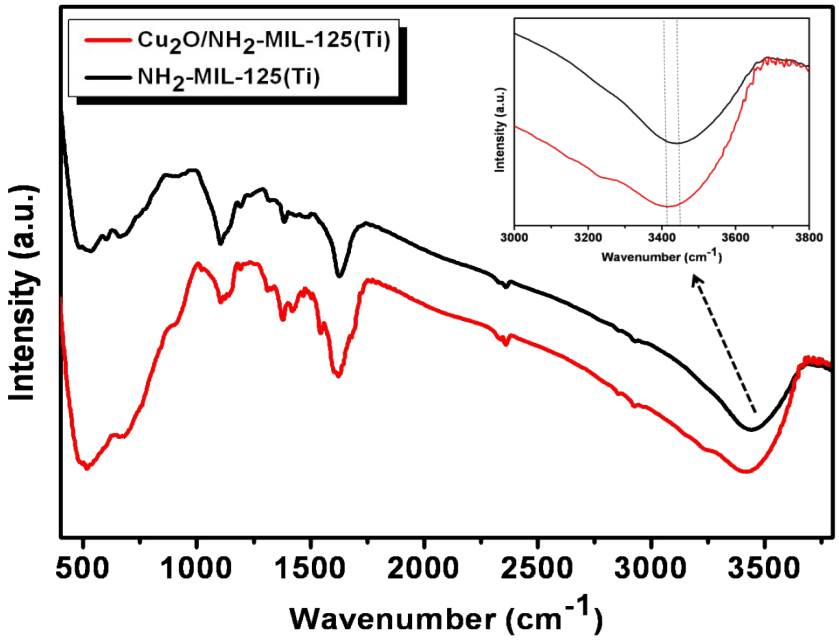

Figure S5. FT-IR spectra of NH_2-MIL-125(TI) and Cu_2O/ NH_2-MIL-125(Ti) MOFs.

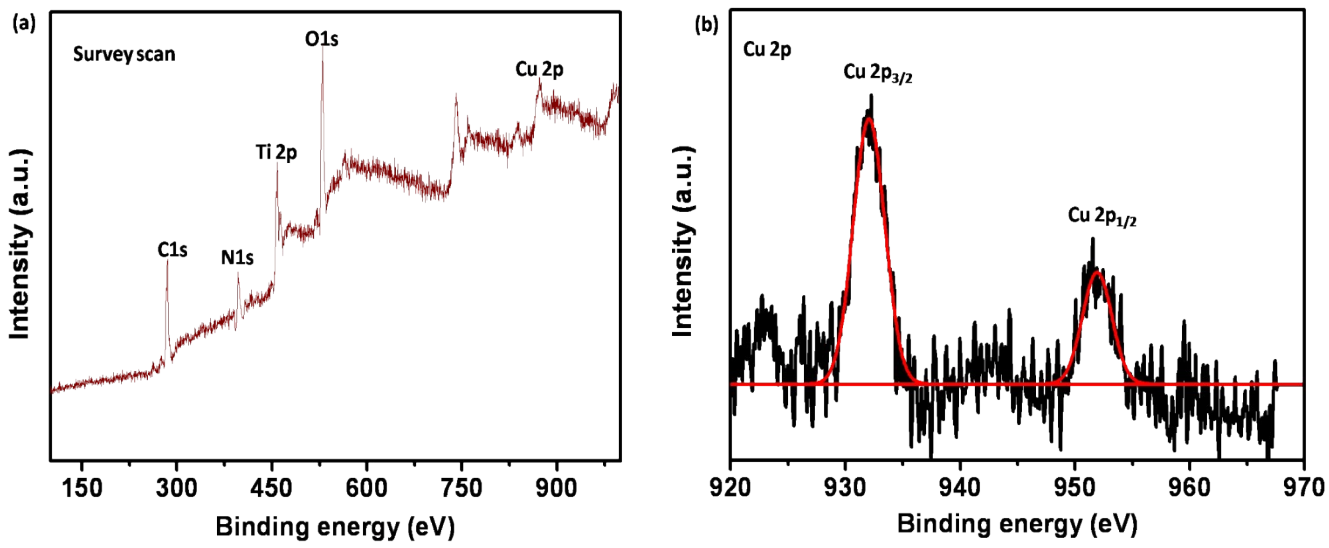

Figure S6. Survey scan and Cu2p spectra of Cu_2O/ NH_2-MIL-125(Ti) MOFs.

The chemical composition and valance states of Cu element were investigated by XPS spectra. The survey scan spectrum (Fig. S5a) clearly reveals the existence of Ti, Cu, O, N and C in the MOF composite. In addition, it is seen from the Cu2p core level spectrum of Cu, the two predominant binding energies such as 932.5 and 952.4 eV was observed related to Cu 2p3/2 and Cu 2p1/2, respectively and this obviously demonstrates the formation of Cu_2O.[1] However, the small peak appeared at 945.1 eV due to shake-up of outer electron in the Cu^+ state.[2]

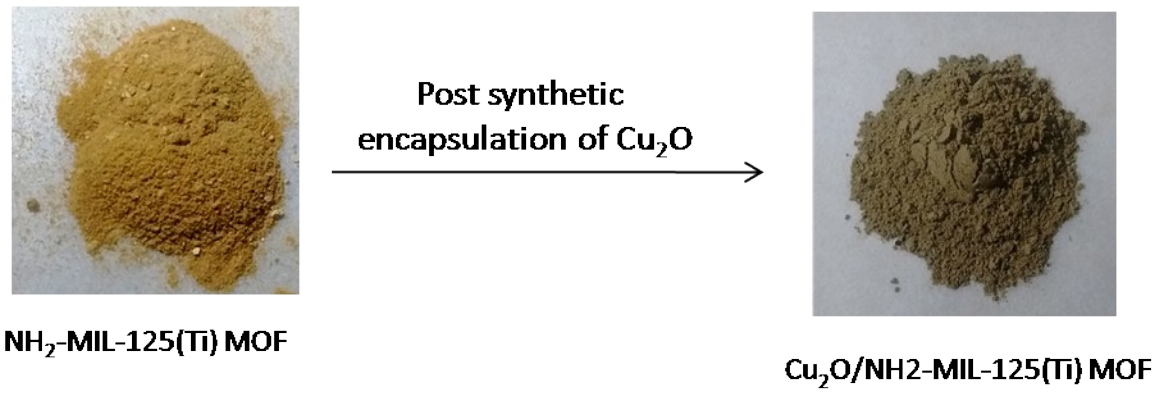

Figure S7. The photographs of pristine NH_2-MIL-125(Ti) MOF and (b) Cu_2O/NH2-MIL-125(Ti) MOF.

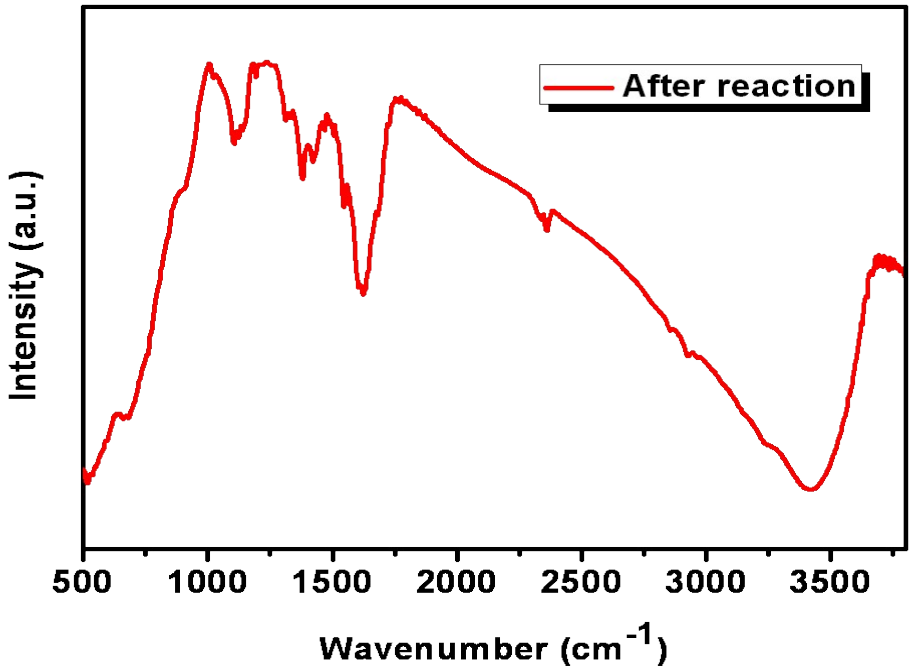

Figure S8. FT-IR spectra of after the photocatatlytic H_2 production.

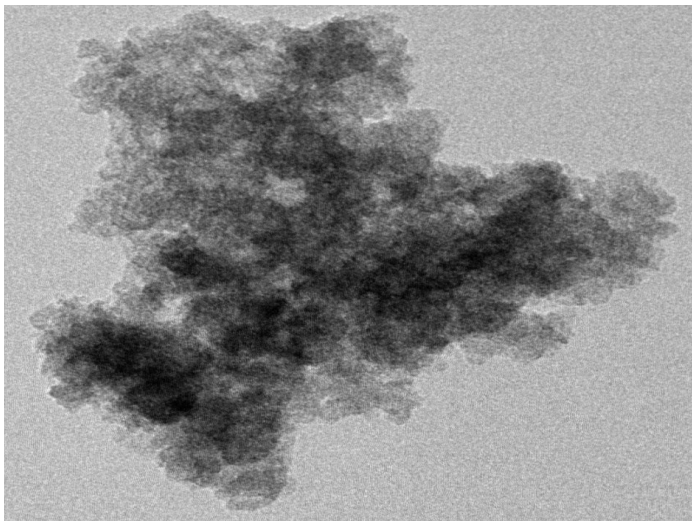

Figure S9. TEM image after the photocatatlytic H_2 production.

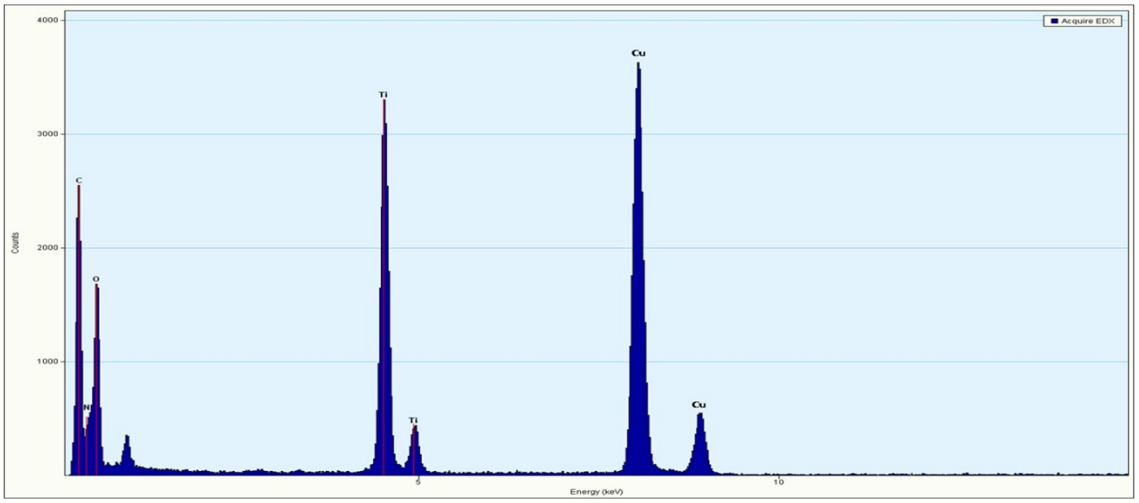

Figure S10. TEM-EDX of Cu_2O/ NH_2-MIL-125(Ti) MOFafter the photocatalytic reaction.

The superior stability of Cu_2O/ NH_2-MIL-125(Ti) MOF was further confirmed by the TEM-EDX analysis. It is clearly seen from the Fig. S10 and table S4, there is no significant change in the elemental composition Cu_2O/ NH_2-MIL-125(Ti) MOF after the photocatalytic H_2 production.

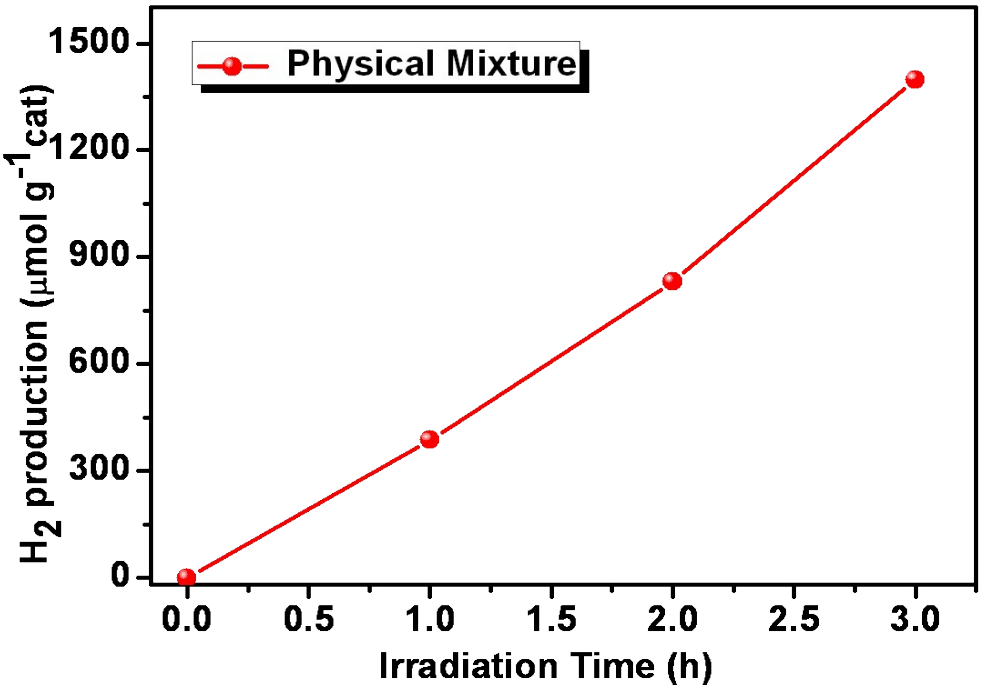

Figure S11. Photocatalytic H_2production using physical mixture of Cu_2O and NH_2-MIL-125 (Ti) MOF.

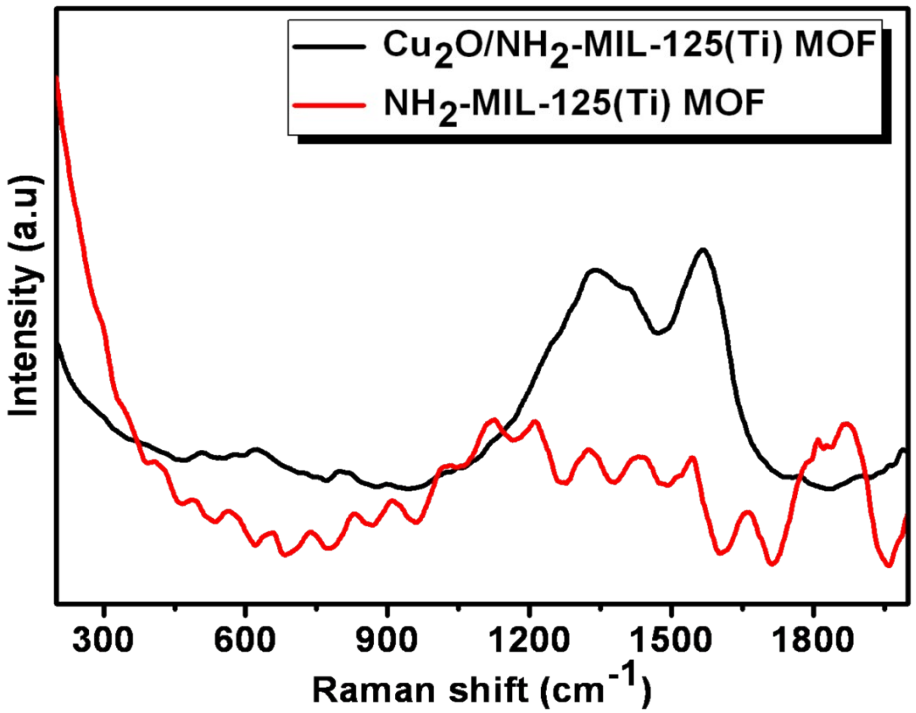

Figure S12. Raman analysis of NH_2-MIL-125(TI) and Cu_2O/ NH_2-MIL-125(Ti) MOFs.

Table S1. Elemental composition of Cu_2O/ NH_2-MIL-125(Ti) MOF.

Element	Weight %	Atomic %	Uncert. %	Correction	k-Factor
C(K)	37.98	71.18	0.29	0.26	3.94
N(K)	1.25	2.02	0.07	0.26	3.826
N(K)	1.25	2.02	0.07	0.26	3.826
Ti(K)	4.3	2.02	0.05	0.98	1.229
Cu(K)	51.92	18.39	0.21	0.99	1.667

Table S2. The BET surface area and pore volume data of pristine NH2-MIL-125(TI) and Cu_2O/ NH_2-MIL-125(Ti) MOF.

Entry	BET surface area (m^2/g)	pore volume (nm)
NH_2-MIL-125(Ti)	710	0.649
Cu_2O/NH_2-MIL-125(Ti) MOF	689	0.421

Table S3. Photocatalytic H_2 production comparison with existing MOF based catalysts.

MOF catalyst	Co-catalyst	Reaction conditions	H_2 evaluation rate	Quantum efficiency	Ref.
MOF-253-Pt	Pt	Light source : 300W Xe Lamp -Visible Sacrificial agent : TEOA	3000 µmol	1.63% at 440 nm	[3]
$H_2TCPP[AlOH]_2(DMF_3\text{-}(H_2O)_2)$	Colloidal Pt	Light source : 300W Xe Lamp -Visible Sacrificial agent : EDTA	200 µmol $g^{-1}h^{-1}$	0.1 %	[4]
$\{[Ln_2Cu_5(OH)_2(pydc)_6(H_2O)_8]\cdot I8\}$ (Ln: Tb)	-	Light source : 500W Hg Lamp –UV Sacrificial agent : aq. CH_3OH	2105 µmol $g^{-1}h^{-1}$	-----	[5]
RhB/UiO-66(Zr)-100*	Rh-B and Pt	Light source : 300W Xe Lamp –Visible Sacrificial agent : TEOA	116.0 µmol g^{-1} h^{-1}	-----	[6]
Pt-UiO-66-30	Pt	Light source : 300W Xe Lamp -Visible Sacrificial agent : CH_3OH	4.6 µmol	~0.25% at 420 nm	[7]
Pt/Ti-MOF-$Ru(tpy)_2$	Pt	Light source : 500W Xe Lamp -Visible Sacrificial agent : TEOA	5.1 µmol	------	[8]
Pt /$[Cu(en)_2]_4[PNb_{12}O_40(VO)_6]\cdot (OH)_5\cdot 8H_2O$	Pt	Light source : 125W Hg Sacrificial agent : aq.CH_3OH	44.35 µmol $g^{-1}h^{-1}$	-----	[9]
Pt@CdS/MIL-101(Cr)	Pt	Light source : 300W Xe Sacrificial agent : lactic acid	150 µmol $g^{-1}h^{-1}$	------	[10]
Co@NH_2-MIL-125(Ti)	Co	Light source : 500W Xe/Hg Sacrificial agent : TEOA	37 µmol	0. 5 % at 400 nm	[11]
Pt/NH2-MIL-125(Ti)	Pt	Light source : Xe lamp Sacrificial agent : TEOA	33 µmol	-----	[12]
Pt/MIL-125(Ti)	Pt	Light source : Xe lamp	38.68 µmol	-----	[13]

		(l=320-780 nm) Sacrificial agent : TEOA			
{[CuICuII 2-(DCTP)$_2$]NO_3·1.5DMF}n	Pt	Light source : 200 W Xe Sacrificial agent : CH_3OH	160 µmolh^{-1}	2.3% at 420 nm	[14]
[CoII(TPA)Cl][Cl]-MIL-125-NH_2	Co	Light source : 200 W Xe Sacrificial agent : CH3CN and TEOA	553 µmol $g^{-1}h^{-1}$	------	[15]
Pt@UiO-66-NH_2	Pt	Light source : 200 W Xe lamp Sacrificial agent : CH3CN and TEOA	257.3 µmolg^{-1} h^{-1}	-----	[16]
Cu_2O/ NH_2-MIL-125(Ti) MOF	**Cu_2O**	**Light source : Solar light Sacrificial agent : 5 %TEOA**	**11055.5 µmol $h^{-1}g^{-1}$**	**1.4 % at 420 nm**	**This work**

Table S4. Elemental composition of Cu_2O/ NH_2-MIL-125(Ti) MOF after the photocatalytic reaction.

Element	Weight %	Atomic %	Uncert. %	Correction	k-Factor
C(K)	35.37	48	0.34	0.26	3.94
N(K)	2.19	2.55	0.11	0.26	3.826
O(K)	43.79	44.61	0.29	0.49	1.974
Ti(K)	0.64	0.21	0.02	0.98	1.229
Cu(K)	17.98	4.61	0.16	0.99	1.667

Apparent Quantum Yield (AQY).

The AQY of photocatalytic H_2 production activity was calculated by using 420 nm band pass filter. The irradiation area was calculated as 0.00144 m^2

AQY Calculation details:

The energy of one photon (*E*photon) with wavelength of *λ*inc (nm) is calculated using the following equation.

$$E_{photon} = \frac{hc}{\lambda_{inc}}$$

Here,

h - Planck's constant (J·s)

c - Speed of light (m s^{-1})

λ_{inc}- wavelength of the incident monochromatic light (m)

Total energy of the incident light (*E* total) is can be calculated by following equation:

$$E_{total} = PSt$$

Where,

P - Power density of the incident monochromatic light *(*W·m^{-2})

S - Irradiation area (m^2)

t- Duration of the incident light exposure (s)

The number of incident photons can be obtained through the following equation

$$\text{Number of incident photons} = \frac{E_{total}}{E_{photon}} = \frac{PS\,\lambda_{inc}t}{hc}$$

Quantum yield (Q.Y.) which is widely used to evaluate the performance of photocatalysts for water splitting, is defined by the following equation

$$Q.Y.(\%) = \frac{\text{Number of reacted electrons}}{\text{Number of incident photons}} \times 100$$

Or

$$A.Q.Y.(\%) = \frac{2\,(\text{Number of } H_2 \text{ molecules evolved})}{\text{Number of incident photons}} \times 100$$

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