Supporting Information

Co-MOF as sacrificial template: Manifesting new Co_3O_4/TiO_2 system with *p-n* heterojunction for photocatalytic hydrogen evolution

Molecular formula

Co-SA: $\{[Co(H_2MDP)(SA)_2].(H_2O)\}_n$
Co-TA: $\{[Co(H_2MDP)(TA)]\}_n$
Co-DHTA: $\{[Co(H_2MDP)(DHTA)]\}_n$
Co-PA: $\{[Co_2(H_2MDP)_2(PA)_2].(H_2O)_2\}_n$

H_2MDP: Methylene bis (3,5-dimethylpyrazole)

Synthesis of MOFs:

(a) Synthesis of $[Co(SA)(H_2MDP)]_n$ (Co-SA):

0.0204 g (0.1 mmol) of H_2MDP,0.0249 g (0.1 mmol) of $Co(OAc)_2.4H_2O$ and 0.0138 g (0.1 mmol) of salicylic acid (SA) were dissolved in 1:1 mixture of water, methanol and heated to 75 ^{0}C in a sealed container for 3 days. Afterwards, the container was cooled to room temperature slowly. Purple block shaped crystals were obtained, which were filtered, washed with methanol and dried in air (77% yield based on H_2MDP). Elemental analysis for $C_{25}H_{26}CoN_4O_7$ calcd (%): C 54.2, H 4.69, N 10.12, Found: C 55.72, H 4.83, N 10.56. IR (KBr cm^{-1}): 3353(b), 1587(s), 1485(s), 1450(s), 1392(s), 1251(s).

(b) Synthesis of $[Co(TA)(H_2MDP)]_n$ (Co-TA):

To a mixture of $Co(NO_3)_2.6H_2O$ (0.0291 g, 0.1 mmol) H_2MDP (0.0204 g, 0.1 mmol), terephthalic acid (TA) (0.0244 g, 0.1 mmol), 1 ml of distilled water, 1 ml of DMF and 3 ml of methanol were added. Then the mixture was heated to 120^{0}C for 72 h in a 25 ml sealed Teflon-lined autoclave. Afterward, the autoclave was slowly cooled down to room temperature and cube shaped purple crystals were obtained (73% yield based on H_2MDP). Elemental analysis for $C_{19}H_{20}CoN_4O_4$.calcd (%): C 42.6, H 3.92, N 10.47 Found: C 42.68, H 3.56, N 11.19. IR (KBr cm^{-1}): 3404(b), 2974(ms), 1568(s), 1359(s), 1296(s), 1193(s), 1080(s),1014(s).

(c) Synthesis of $[Co(DHTA)(H_2MDP)(H_2O)]_n$ (Co-DHTA):

0.204 g, (0.1 mmol) of H_2MDP and 0.0198 g, (0.1 mmol) of 2,5-dihydroxyterephthalic acid (DHTA) were dissolved in a mixture of solution containing 3ml methanol, 1 ml water and 1 ml DMF and then 0.0291g,(0.1 mmol) of $Co(NO_3)_2$. $6H_2O$ was added to the mixture and heated to 75 ^{0}C in a sealed container for 3 days. Afterwards, the container was cooled to room temperature slowly. Purple block shaped crystals were obtained, which were filtered, washed with methanol and dried in air (75% yield based on H_2MDP). Elemental analysis for $C_{19}H_{20}CoN_4O_6$ calcd (%): C 49.63, H 4.35, N 12.19, Found: C 49.38, H 4.27, N 11.94. IR (KBr cm^{-1}):3431(b), 3195(b), 1575(s), 1490(s), 1413(s), 1232(s).

(d) Synthesis of $[Co(PA)(H_2MDP)]_n$ (Co-PA):

0.0204 g, (0.1 mmol) of H_2MDP and 0.0388 g, 0.1 mmol of pamoic acid (PA) were dissolved in a mixture of solution containing 3 ml DMF, 1 ml methanol ,1 ml water and then 0.1 mmol of $Co(NO_3)_2$. $6H_2O$ was added to the mixture and heated to 75 ^{0}C in a sealed container for 3 days. Afterwards, the container was cooled to room temperature slowly. Purple block shaped crystals were obtained, which were filtered, washed with methanol and dried in air (79% yield based on H_2MDP). Elemental analysis for $C_{68}H_{64}Co_2N_8O_{14}$ calcd (%): C 61.28, H 4.96, N 9.06, Found: C 60.64, H 5.31, N 9.53. IR (KBr cm^{-1} :3353(b), 1660(s), 1554(s), 1456(s), 1394(s).

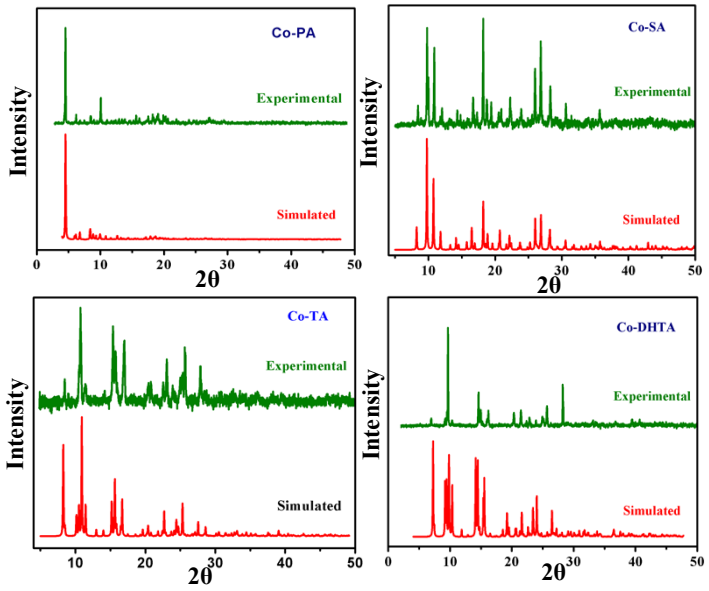

Fig. S1 Simulated and experimental powder XRD pattern of the Co-MOF's.

Table S1. Crystal data and structure refinements for Co-MOFs.

	Co-SA	**Co-TA**	**Co-DHTA**	**Co-PA**
empirical formula	$C_{25}H_{26}Co_{N4}O_7$	$C_{19}H_{20}CoN_4O_4$	$C_{19}H_{20}CoN_4O_6$	$C_{68}H_{64}Co_2N_8O_{14}$
formula weight	553.43	427.32	459.32	1335.13
crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
space group	*P2(1)/n*	*C2/c*	*C2/c*	*C2/c*
a/Å	10.4589(14)	19.2342(13)	19.2106(11)	38.226(7)
b/Å	13.3445(17)	13.4738(10)	13.5093(7)	13.456(2)
c/Å	18.115(2)	18.5923(13)	18.6918(16)	33.945(7)
α/°	90	90	90	90
β/°	90.25	116.139(2)	116.602(2)	110.132(11)
γ/°	90	90	90	90
V/Å³	2528.2(6)	4325.6(5)	4337.4(5)	16394(5)
reflections collected	36122	30203	24928	93123
unique reflection	7810	6133	4681	14029
observed reflections[I>2σ(I)]	6637	2955	2824	5685
R1	0.0406	0.1240	0.1249	0.0803
wR2	0.1201	0.2969	0.3020	0.1887
CCDC no.	**1407122**	**1407123**	**1407120**	**1407121**

Table S2 Selective bond lengths and bond angles.

Co-SA			
Bond lengths		**Bond angles**	
Co_1-O_4	1.9603(12)	O_4-Co_1-O_1	110.39(5)
Co_1-O_1	1.9961(12)	O_4-Co_1-N_3	19.70(5)
Co_1-N_3	2.0049(13)	O_1-Co_1-N_3	114.64(5)
Co_1-N_1	2.0174(13)	O_4-Co_1-N_1	108.45(5)
		O_1-Co_1-N_1	95.84(5)
		N_3-Co_1-N_1	104.65(5)
Co-TA			
Co_1-O_{2B}	1.897(5)	O_{2B}-Co_1-$O2_A$	110.7(3)
Co_1-O_{2A}	1.922(6)	O_{2A}-Co_1-N_2	113.7(3)
Co_1-N_2	1.982(5)	$O2_B$-Co_1-N_3	112.1(3)
Co_1-N_3	2.021(6)	O_{2A}-Co_1-N_3	104.7(3)
		N_2-Co_1-N_3	106.1(2)
Co-DHTA			
Co_1-O_4	1.877(12)	O_4-Co_1-O_1	106.3(4)
Co_1-O_1	1.950(5)	O_4-Co_1-N_3	108.7(4)
Co_1-N_3	1.994(5)	O_1-Co_1-N_3	113.6(2)
Co_1-N_1	1.997(6)	O_4-Co_1-N_1	119.2(4)

Co_1-$O_{5'}$ 2.122(14) Co_1-$O_{4'}$ 2.351(15)	O_1-Co_1-N_1 101.3(2) N_3-Co_1-N_1 107.7(2) O_4-Co_1-$O_{5'}$ 24.6(4) O_1-Co_1-$O_{5'}$ 118.8(4) N_3-Co_1-$O_{5'}$ 116.3(4) N_1-Co_1-$O_{5'}$ 95.0(4) O_4-Co_1-$O_{4'}$ 32.3(5) O_1-Co_1-$O_{4'}$ 92.9(4) N_3-Co_1-$O_{4'}$ 88.5(4) N_1-Co_1-$O_{4'}$ 151.5(4) $O_{5'}$-Co_1-$O_{4'}$ 56.5(5)
Co-PA	
Co_1-O_{1C} 1.951(4) Co_1-O_{1B} 1.987(4) Co_1-N_{1A} 1.999(5) Co_1-$N7_A$ 2.009(5) Co_2-$N5_A$ 2.036(5) Co_2-N_{3A} 2.040(5) Co_2-O_{5C} 2.077(4) Co_2-O_{5B} 2.161(4) Co_2-O_{4B} 2.200(4) Co_2-O_{4C} 2.289(4)	O_{1C}-Co_1-O_{1B} 113.52(18) O_{1C}-Co_1-N_{1A} 111.3(2) O_{1B}-Co_1-N_{1A} 101.8(2) O_{1C}-Co_1-N_{7A} 111.4(2) O_{1B}-Co_1-N_{7A} 112.7(2) N_{1A}-Co_1-N_{7A} 105.3(2) N_{5A}-Co_2-N_{3A} 97.69(19) N_{5A}-Co_2-O_{5C} 108.84(19) N_{3A}-Co_2-O_{5C} 96.7(2) N_{5A}-Co_2-O_{5B} 97.50(19) N_{3A}-Co_2-O_{5B} 103.76(19) O_{5C}-Co_2-O_{5B} 144.04(17) N_{5A}-Co_2-O_{4B} 156.93(18) N_{3A}-Co_2-O_{4B} 86.54(17) O_{5C}-Co_2-O_{4B} 93.06(17) O_{5B}-Co_2-O_{4B} 59.56(16) N_{5A}-Co_2-O_{4C} 94.20(17) N_{3A}-Co_2-O_{4C} 156.74(19) O_{5C}-Co_2-O_{4C} 60.47(16) O_{5B}-Co_2-O_{4C} 94.37(16) O_{4B}-Co_2-O_{4C} 90.31(15)

Table S3 Experimental amount (wt %) of element in the different photocatalyst nanocomposites (FESEM-EDX analysis)

Nanocomposite	**Elements (wt %)**		
	Co	Ti	O
NC-PA	1.03	54.72	44.25
NC-SA	0.82	45.47	53.71
NC-DHTA	1.00	57.27	41.73
NC-TA	0.80	53.89	45.31

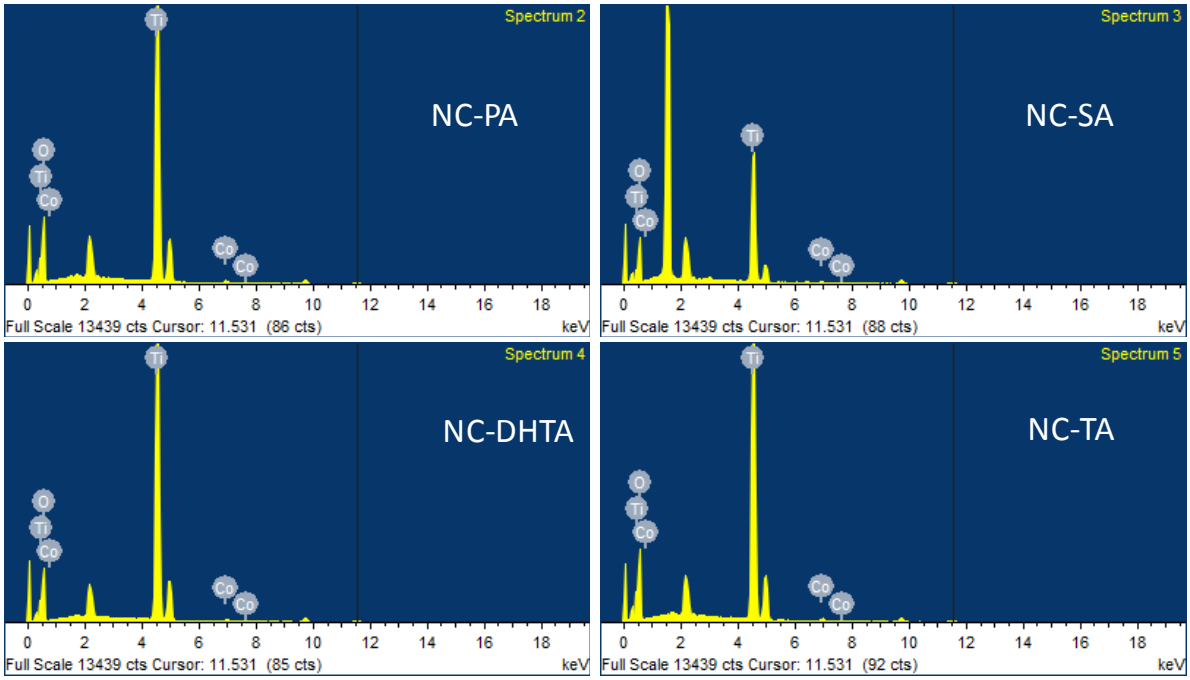

Fig. S2 FESEM-EDX pattern of different photocatalyst nanocomposites.

Thermal properties of MOFs

Thermo gravimetric analysis (TGA) of **Co(PA-TA)** were performed under N_2 atmosphere in an aluminium crucible at a rate of 10 ºC min^{-1}. All these data were collected in the temperature range 30-700 °C. For **Co-SA** two identifiable weight loss occurred. First weight loss 2.503% (calcd: 3.25%) in the temperature range 70-295 °C for the removal of lattice water molecule and at 325 °C , **Co-SA** has lost its weight about 25.32 % (calcd: 24.75%) for the removal of one salicylic acid molecule and then it was completely decomposed. **Co-TA** showed a weight loss of about 6% (calcd: 7.07%) for the removal of one methanol molecule at about 315 °C and then decomposed completely. **Co-DHTA** was stable up to ~380 °C and no such weight loss showed and then it was decomposed. For **Co-PA** first break occurred at 137 °C and weight loss was 2.8% (calcd: 2.6%) for the removal of two non coordinate water molecule and then lost its weight about 8.051% (calcd: 8.37%) at 210 °C for the removal of one DMF molecule and then the compound was completely decomposed at 395 °C.

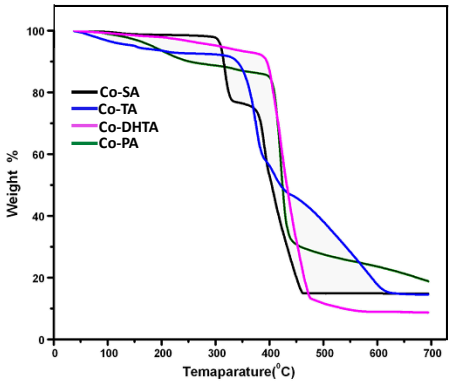

Fig. S3 TGA of different cobalt MOFs.

Gas Adsorption studies of MOFs

The presence of distinct solvent filled channels and pores inside the above-mentioned frameworks prompted us to evaluate their absorbent potentials. We report herein N_2, H_2, and CO_2 gas sorption of all compounds. Gas adsorption measurements for all compounds were performed at 77 K for N_2 in a Quantachrome Autosorb-1 instrument at lower pressures ranging from 0 to 1 atm. For compound 4, N_2 and H_2 uptake measurements were performed at 77 K within the same pressure range in a Quantachrome Quadrasorb automatic volumetric instrument. However, CO_2 adsorption measurements for the same were performed at 273 K temperature. In all measurements, ultrahigh-purity adsorbents (N_2, H_2, and CO_2) were obtained by using calcium aluminosilicate adsorbents to remove trace amounts of moisture and other impurities present in these gases prior to introducing them into sample. In order to achieve partial or complete removal of solvent molecules (as observed from single crystal structures), the crystals were soaked in a 1:1 mixture of methanol and dichloromethane for 48 h. The resultant solvent-exchanged crystals were then heated at 60 °C under high vacuum for 12 h and at 150 °C for 24 h in order to remove the solvent molecules from the frameworks. After thermal activation of samples, retention of the framework integrity, an essential prerequisite for gas sorption experiments, was confirmed by PXRD patterns. After this treatment, a 100 mg sample of each of the compounds was loaded for gas adsorption studies, and validity of the N_2, H_2, and CO_2 adsorption isotherms obtained was confirmed by repeating the data collection at least three times.

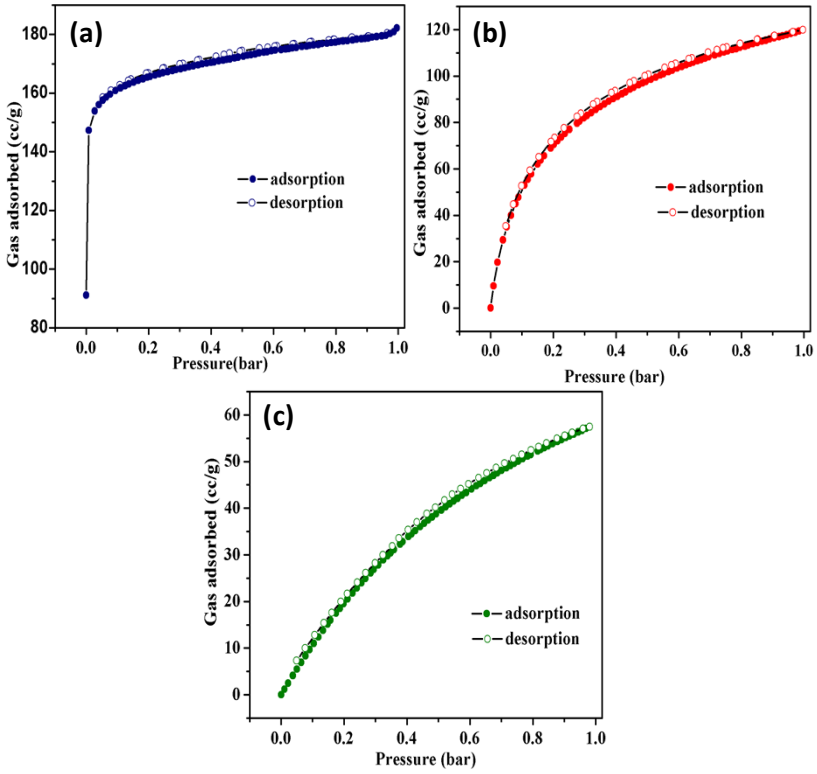

Fig. S4 (a) N_2 gas (b) H_2 gas and (c) CO_2 gas adsorption isotherm of **Co-PA**.

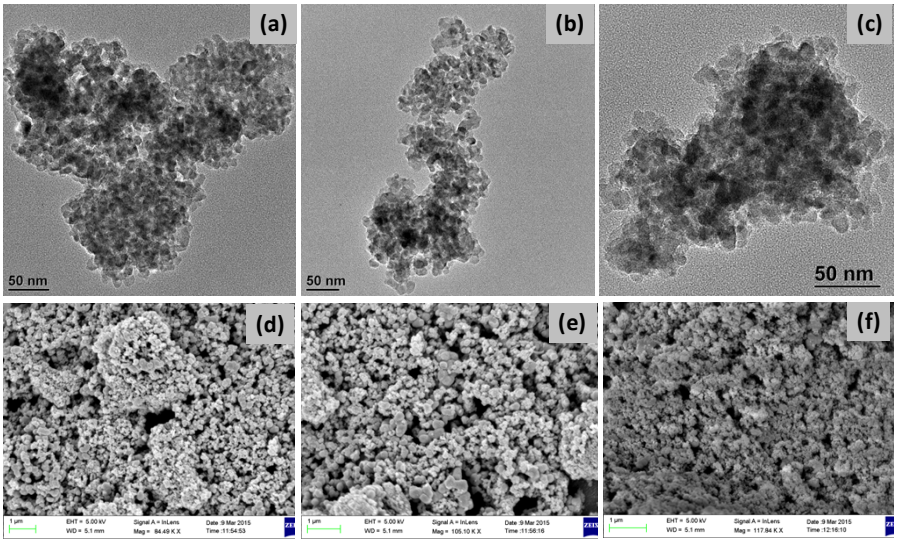

Fig. S5 TEM images of (a) **NC-SA**, (b) **NC-DHTA**, (c) **NC-TA** and FESEM images of (d) **NC-SA**, (e) **NC-DHTA** and (f) **NC-TA**.

Gas Adsorption studies of nanocomposites

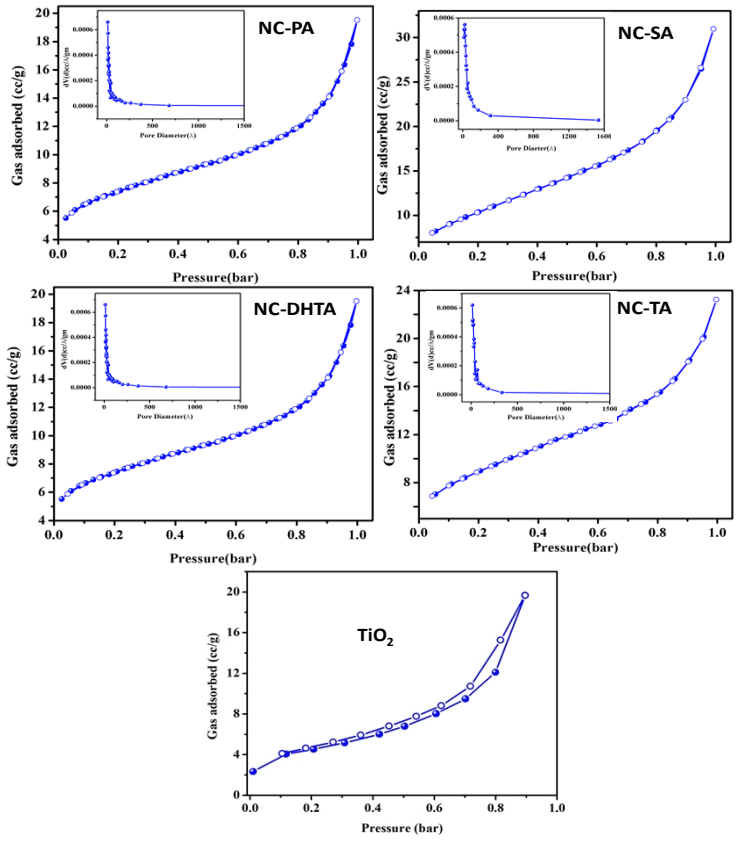

Fig. S6 N_2 adsorption isotherm and pore size distribution of different Co_3O_4/TiO_2 nanocomposites and bare TiO_2.

Table S4 Gas adsorption data of different nanocomposites

	Co-PA	NC-SA	NC-TA	NC-PA	NC-DHTA
N_2Gas Adsorbed(cc/g)	182.2	30.96	11.48	19.51	23.23
BET surface area(m^2/g)	520.3	35.2	18.03	30.16	24.31
Pore diameter (nm)	-	2.8	2.5	3.3	3.2

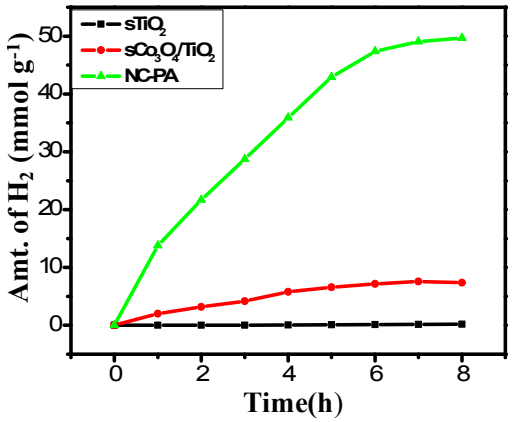

Fig. S7 Time courses for photocatalytic H_2 production over bare TiO_2, conventional Co_3O_4/TiO_2 nanocomposite and NC-PA nanocomposite.

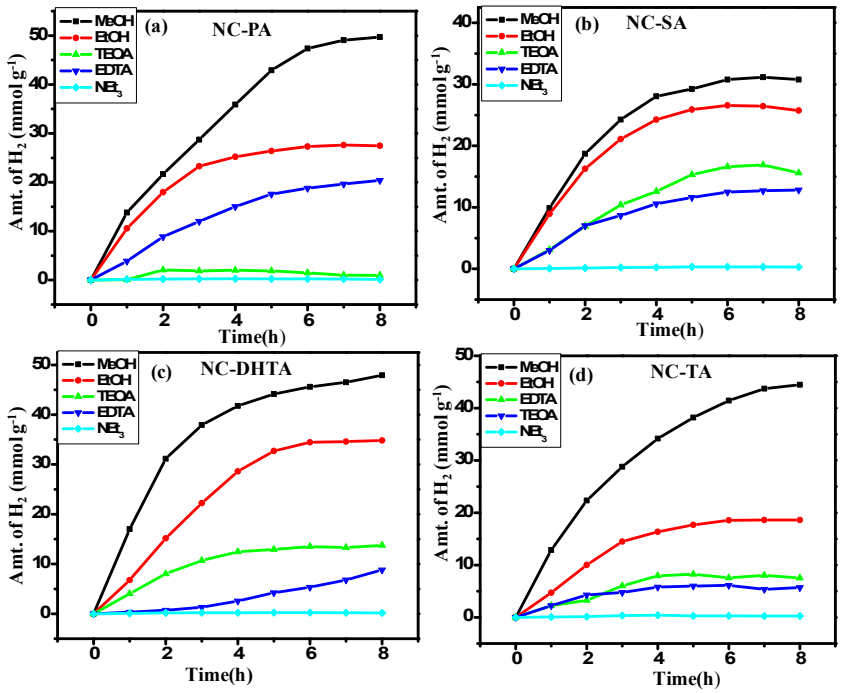

Fig. S8 Time courses for photocatalytic H_2 production over different photocatalyst composite. Reaction condition: 20 ml of 15 vol% aqueous SED solution containing 20 mg photocatalyst, pH 7 and room temperature.