Supporting information

Noble Metal-Free Integrated UiO-66-PANI-Co_3O_4 Catalyst for Visible-Light-Induced H_2 Production

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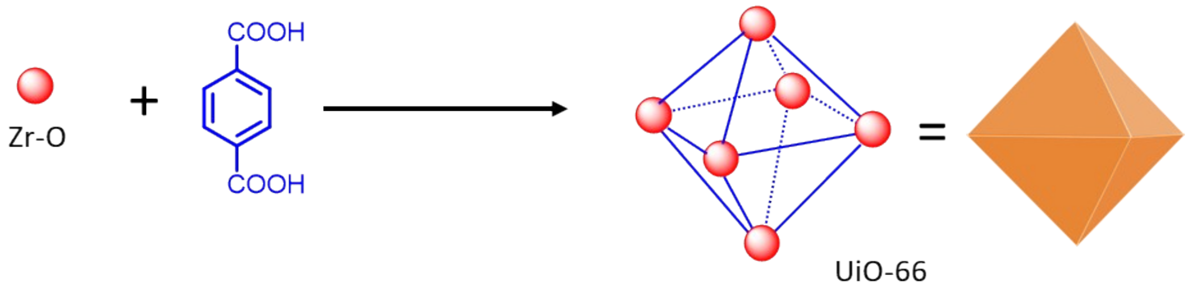
S1. Materials and methods

All chemicals were purchased from commercial sources and used without further purification: terephthalic acid (H_2BDC, Sigma-Aldrich), zirconium (IV) chloride ($ZrCl_{4,}$ Sigma Aldrich), Aniline (Avra Chemicals), SDS (Sigma-Aldrich), acetic acid, potassium persulfate ($K_2S_2O_{8,}$ Sigma-Aldrich) silver nitrate ($AgNO_{3,}$ Sigma-Aldrich), N, N-dimethylformamide (DMF, Finar Chemicals), tetrahydrofuran (THF, Finar chemicals), acetonitrile (ACN, Finar chemicals). Deionized water (18.2 mS conductivity) was used in all experiments. Sonication (Power Sonic 405) and centrifugation (Gyrogen 1236 MG) were used for re-dispersing and separation of the catalysts, respectively.

S2. Preparation of integrated photo-catalyst

Synthesis of UiO-66



UiO-66 was synthesized according to the reported procedure.[1] 0.35 g (1.5 mmol) of terephthalic acid and 150 µL of triethylamine were dissolved in 25 mL of DMF. Separately, 0.25 g (1.5 mmol) of $ZrCl_4$, and 6.9 mL of acetic acid were mixed with 25 mL of DMF. The solutions of terephthalic acid and $ZrCl_4$ were combined in 100 mL teflon coated autoclave, capped and placed in 85 ºC oven for a day. After cooling the reaction mixture to room temperature the solution was centrifuged at 4000 rpm for 10 min to collect the white crystalline powder of UiO-66. The white material was washed sequentially with DMF, deionized water, acetone and centrifuged. Then, the solids were suspended in ethanol for activation and dried under vacuum in oven at 60 ºC for 12 h.

Modification of the UiO-66 crystal: The following reaction condition has been followed for the integrating the highly efficient photo-catalyst.

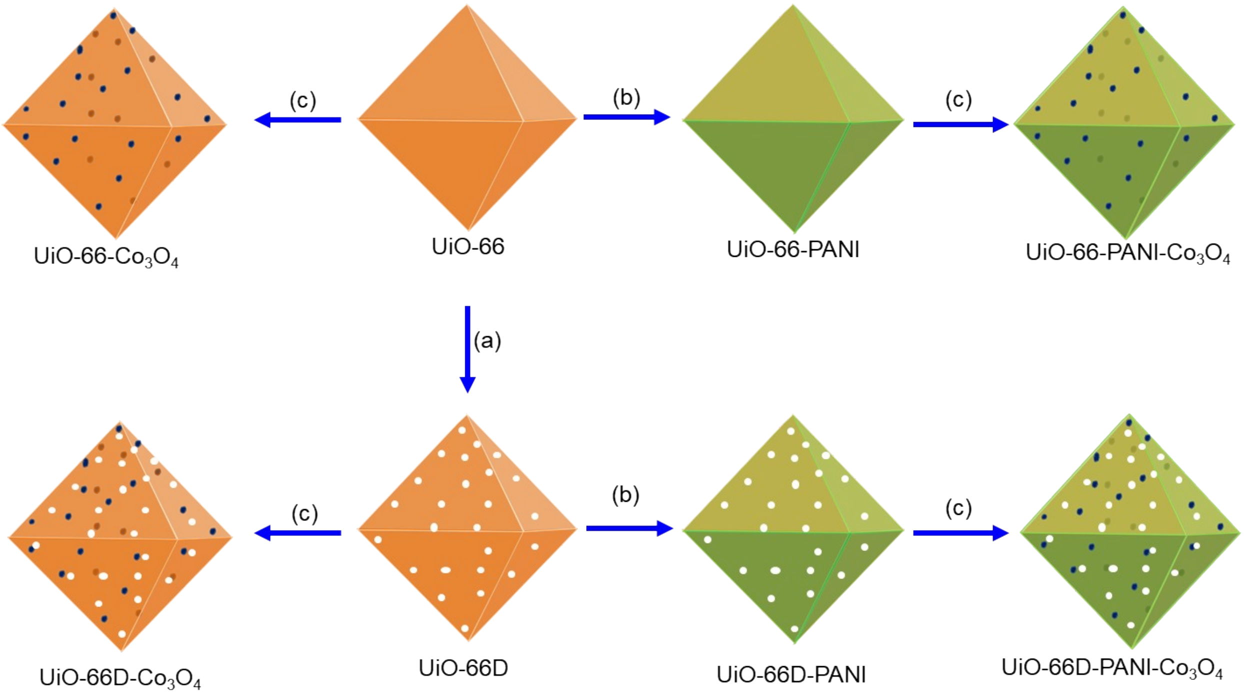
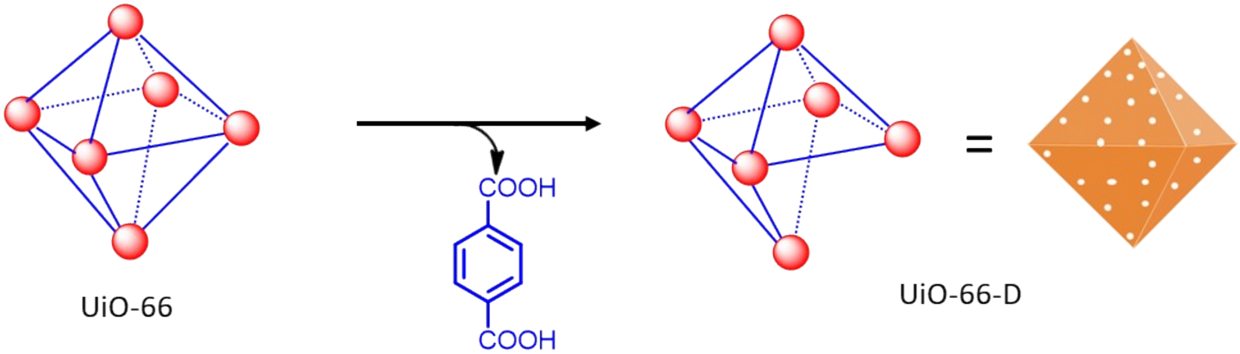


Fig. S1 Schematic presentation of the preparation of photo-catalyst (a) defect formation; (b) PANI coating; (c) Co_3O_4 deposition.

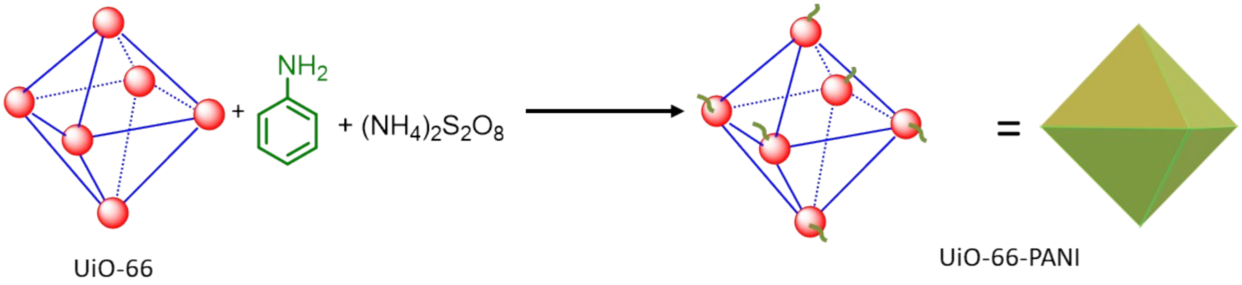
Reaction condition (a): Defect formation experiments



UiO-66D was synthesized according to the reported procedure.[1] 0.1 g of UiO-66 MOF, 0.135 mg of $K_2S_2O_8$, 0.05 g of $AgNO_3$ were mixed with 5 mL of MeCN in an auto-clave. The auto-clave was sealed, placed in an oven, and heated at 120 °C for 1 h. After cooling down to room temperature, the mixture was centrifuged and the white solid precipitate was collected. The resulting solid product was washed three times sequentially with water and acetone, and then dried at 120 °C under reduced pressure for 12 h.

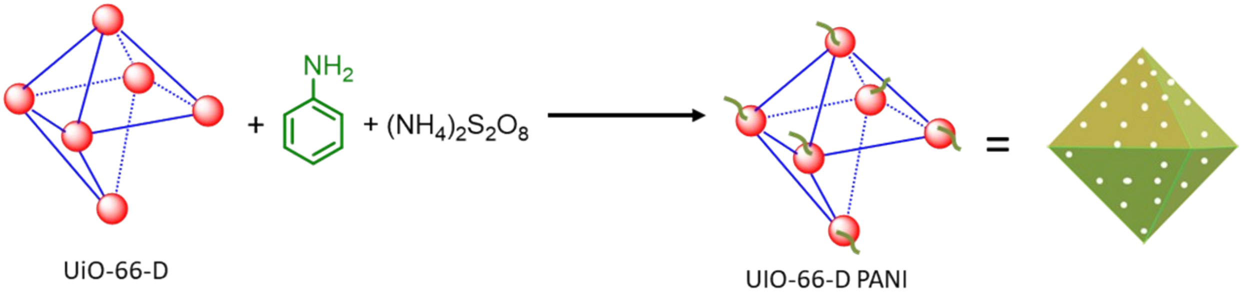
Reaction condition (b): PANI Coating

Synthesis of UiO-66-PANI



UiO-66-PANI was prepared by in-situ polymerization of aniline on UiO-66, using sodium dodecyl sulfate (SDS) as the surfactant to assist the dispersibility of aniline in water: firstly, 100 µL of aniline was added in 50 mL H_2O with 3 mg SDS, and then mixed together with 50 mL of aqueous UiO-66 dispersion (5 mg/mL), followed by ultrasonication for 15 min to form a homogeneous suspension. After sonication, the reaction mixture is kept in cooling condition (0-5 ^{o}C); and acidic solution of $NH_4S_2O_8$ (0.235 g in 25 mL, 1 M HCl) was added slowly and the mixture was vigorously stirred over night at 0-5 °C. Then, the resulting green suspension was centrifuged and washed with DI water for three times to afford UiO-66-PANI.

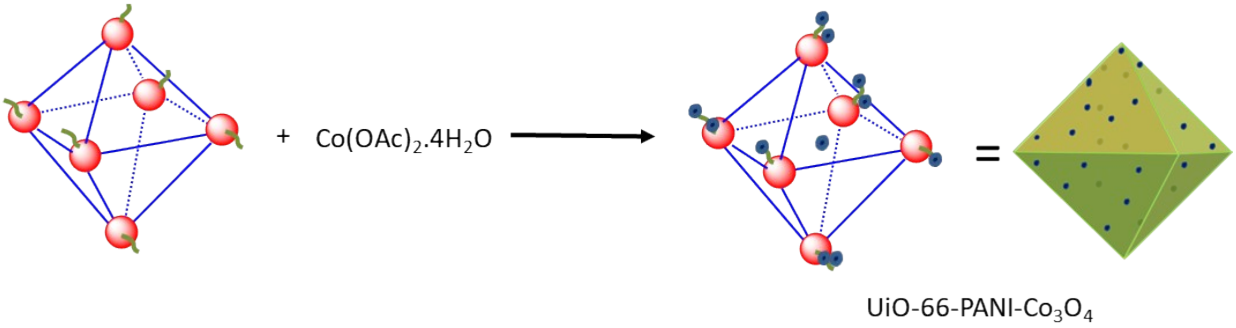
Synthesis of UiO-66-D-PANI



UiO-66D-PANI was prepared by in-situ polymerization of aniline on UiO-66D, using sodium dodecyl sulfate (SDS) as the surfactant to assist the dispersibility of aniline in water: firstly, 100 µL of aniline was added in 50 mL H_2O with 3 mg SDS, and then mixed together with 50 mL of aqueous UiO-66D dispersion (5 mg/mL), followed by ultrasonication for 15 min to form a homogeneous suspension. After sonication, the reaction mixture is kept in cooling condition (0-5 °C); and acidic solution of $NH_4S_2O_8$ (0.235 g in 25 mL, 1 M HCl) was added slowly and the mixture was vigorously stirred over night at 0-5 °C. Then, the resulting green suspension was centrifuged and washed with DI water for three times to afford UiO-66D-PANI.

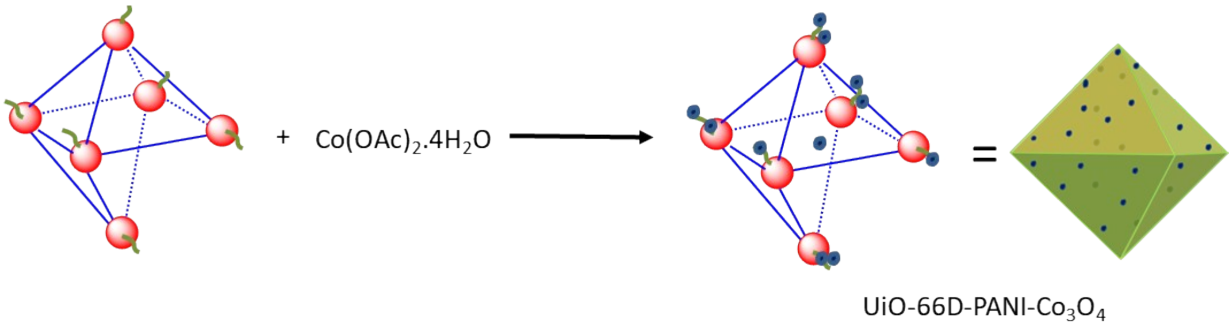
Reaction condition (c): Cobalt nanoparticle deposition

Synthesis of UiO-66-PANI-Co_3O_4



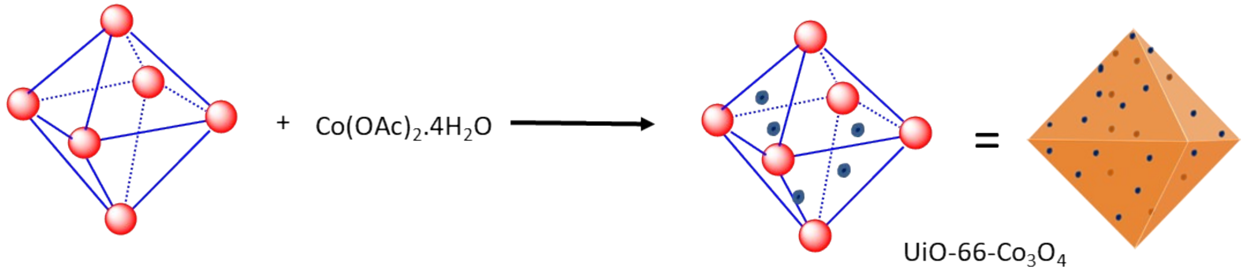
UiO-66-PANI-Co_3O_4 was prepared by in-situ hydrolysis of Co^{2+} in the presence of UiO-66 suspension. First, 100 mg $Co(Ac)_2 \cdot 4H_2O$ was dissolved in 50 mL H_2O, and then added into 50 mL solution of UiO-66-PANI (20 mg/mL). Then, the resulted mixture was added into 200 mL Teflon lined stainless steel autoclaves for hydrothermal treatment at 180 °C for 12 h to produce UiO-66-PANI-Co_3O_4 (10:1). The resulting solid product was washed three times sequentially with water and acetone, and then dried at 120 °C under reduced pressure for 12 h.

Synthesis of UiO-66-D-PANI-Co_3O_4



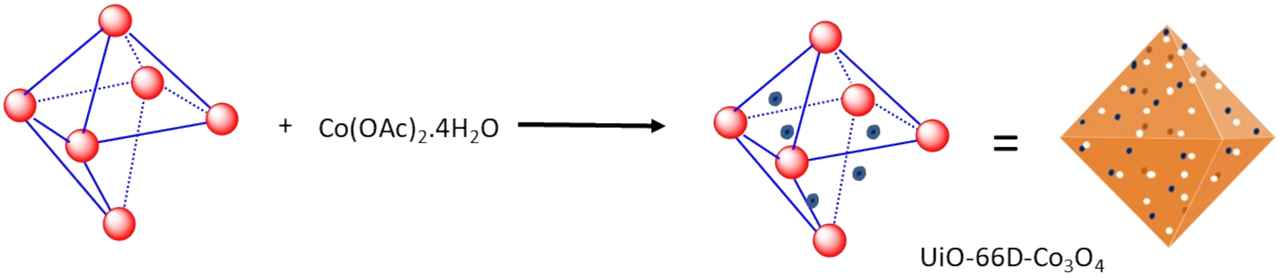
UiO-66-D-PANI-Co_3O_4 was prepared by in-situ hydrolysis of Co^{2+} in the presence of UiO-66 suspension. First, 100 mg $Co(Ac)_2 \cdot 4H_2O$ was dissolved in 50 mL H_2O, and then added into 50 mL solution of UiO-66-D-PANI (20 mg/mL). Then, the resulted mixture was added into 200 mL Teflon lined stainless steel autoclaves for hydrothermal treatment at 180 °C for 12 h to produce UiO-66-D-PANI-Co_3O_4 (10:1). The resulting solid product was washed three times sequentially with water and acetone, and then dried at 120 °C under reduced pressure for 12 h.

Synthesis of UiO-66-Co_3O_4



UiO-66-Co_3O_4 was prepared by in-situ hydrolysis of Co^{2+} in the presence of UiO-66 suspension. First, 100 mg $Co(Ac)_2 \cdot 4H_2O$ was dissolved in 50 mL H_2O, and then added into 50 mL solution of UiO-66 (20 mg/mL). Then, the resulted mixture was transferred into 200 mL Teflon lined stainless steel autoclaves for hydrothermal treatment at 180 °C for 12 h to produce UiO-66-Co_3O_4 (10:1). The resulting solid product was washed three times sequentially with water and acetone, and then dried at 120 °C under reduced pressure for 12 h.

Synthesis of UiO-66D-Co_3O_4



UiO-66D-Co_3O_4 was prepared by in-situ hydrolysis of Co^{2+} in the presence of UiO-66 suspension. First, 100 mg $Co(Ac)_2 \cdot 4H_2O$ was dissolved in 50 mL H_2O, and then added into 50 mL solution of UiO-66 (20 mg/mL). Then, the resulted mixture was added into 200 mL teflon lined stainless steel autoclaves for hydrothermal treatment at 180 °C for 12 h to produce UiO-66-D-Co_3O_4 (10:1). The resulting solid product was washed three times sequentially with water and acetone, and then dried at 120 °C under reduced pressure for 12 h.

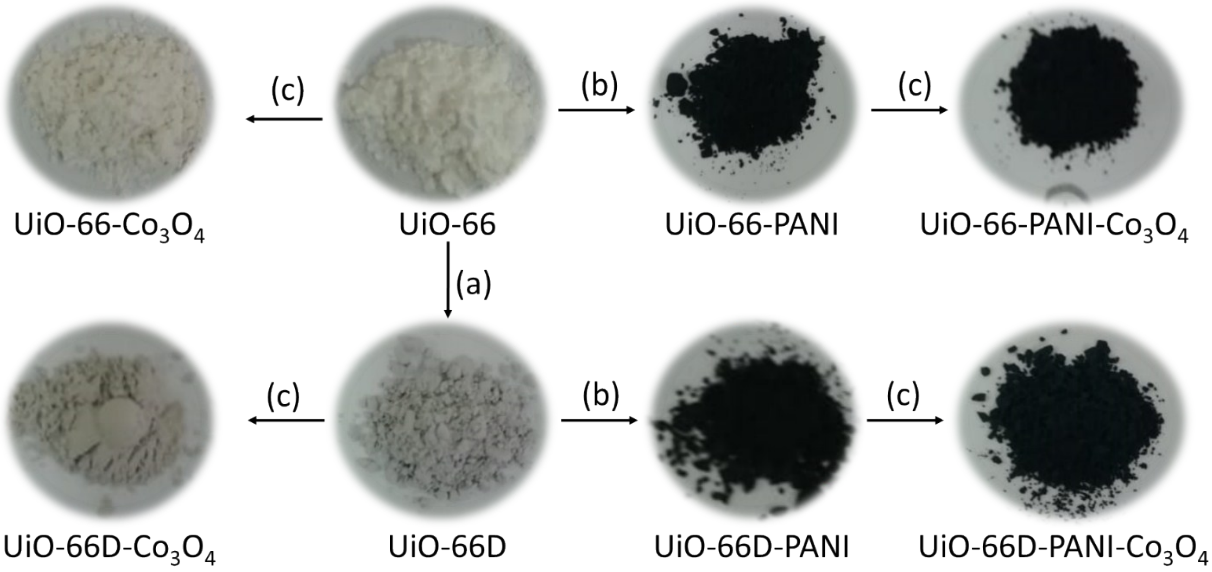


Fig. S2 Snapshot of the synthesized photo-catalyst.

Platinum loading procedure:

The Pt metals were evenly deposited on the photocatalysts using a simple deposition method. [2] 100 mg of the photocatalyst was dispersed in 20 mL of methanol. To the mixture calculated amount of H_2PtCl_4 (37.5µL, 1 wt%) was added in situ and stirred for 30 min under 400 W Hg lamp irradiation. Then the solution was further evaporated using reduced pressure in order to remove the solvent and dry the obtained product.

S3. Integrated photo-catalyst characterization and application details:

XRD Spectra: Powder X-ray diffraction patterns (XRD) of the photocatalysts were recorded on a Bruker AXS diffractometer (D8 advance) at a generator voltage of 40 kV and current 30 mA using Cu-Kα radiation (λ = 1.5406 Å). All the characteristic peak related to UiO-66 MOF are similar to our previous report.[1] Additionally, Co_3O_4 was confirmed by characteristic X-ray diffraction peaks the diffraction peaks at 17.2, 30.6, 35.4, 50.6, 60.3 and indexed to the (111), (220), (311), (422), and (511) planes, respectively as consistent with PDF No. 01-076-1802 (see Fig.S3).[2]

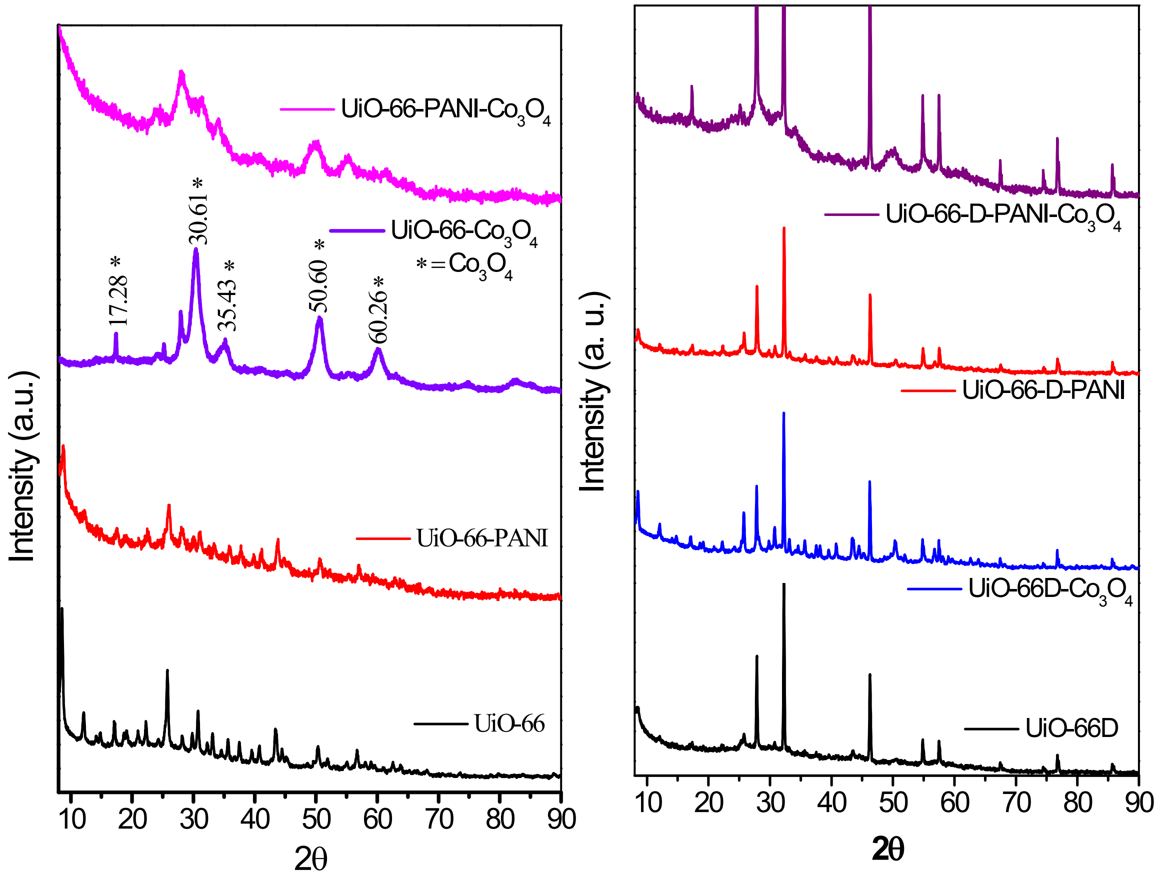


Fig. S3 X-Ray diffractometry analysis of the synthesized photocatalyst.

IR Spectra

ATR-IR spectroscopy was used to characterize the surface feature of the particles. The spectra were acquired using a Perkin Elmer ATR-IR spectrometer. A small drop of test sample was placed on smart gate surface over wave numbers ranging from 650 to 4000 cm^{-1}. The IR spectra of these four samples exhibit similar characteristic peaks as shown in Fig. S4. The broad peak at 3393 cm^{-1} in UiO-66 composite is due to C-H stretching vibrations which on the addition of PANI has resulted in the disappearance at that particular region and the formation of new sharp peak at 1134 cm^{-1} indicates the C-N stretching vibrations whereas the peak at 1496 cm^{-1} confirms the C-C vibrations of the Co_3O_4.[3] The peaks at 1410 cm^{-1} , 1565 cm^{-1}, and 1660 indicates the O-C-O asymmetric and symmetric stretching vibrations as shown in Fig. S4 (a & b).[3] The reduction of peak at stretching vibration 1660 cm^{-1} indicates the decarboxylation of the composites as shown in Figure S4b.

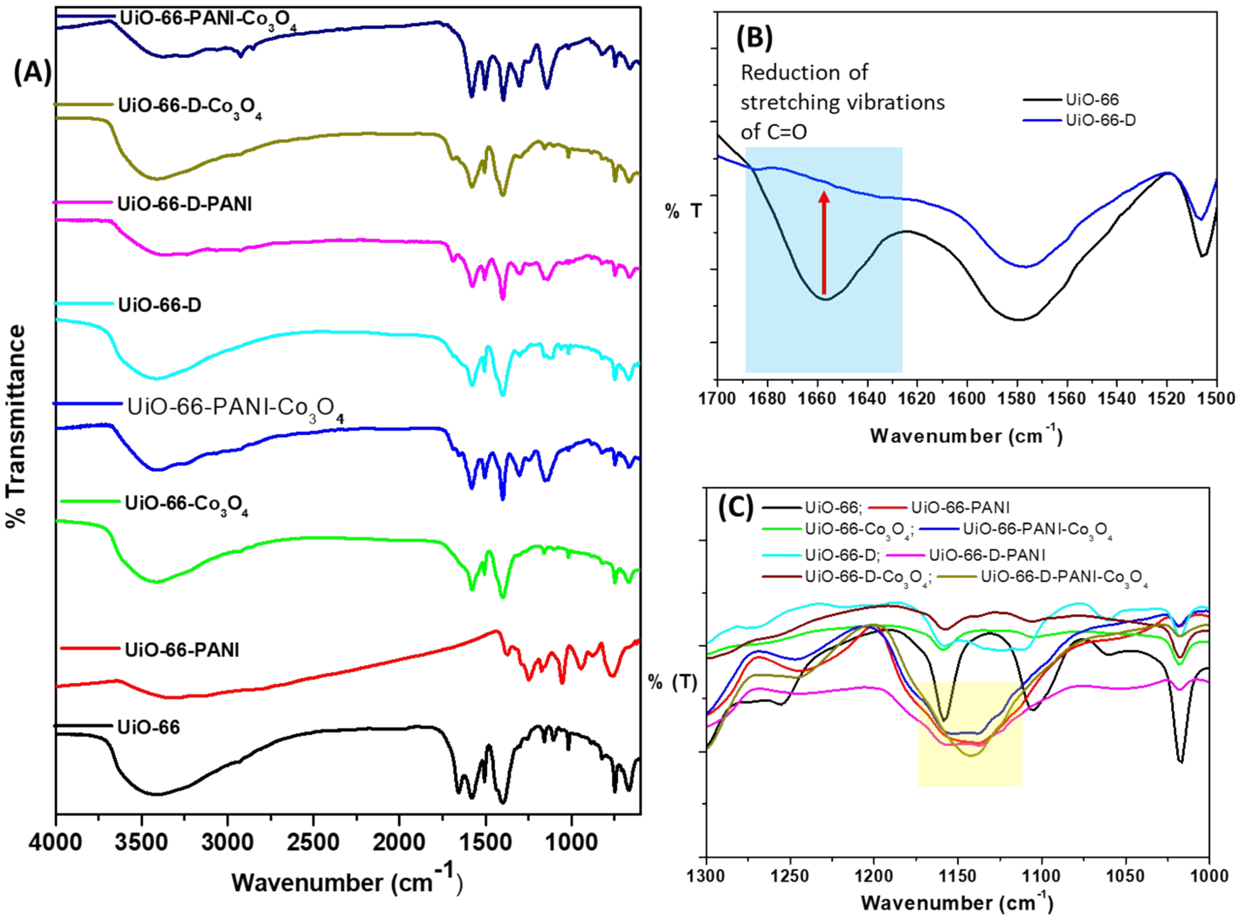


Fig. S4 Comparative ATR spectra of synthesized catalyst (a) synthesized composites, (b) determination of the particular spectral region, and (c) yellow highlight region representing -C=N of quinoid of PANI coating**.**

Thermo-gravimetric analysis: The Thermogravimetric analysis (TGA) of the samples were performed using TA Instruments SDT Q600 apparatus to optimise the thermal stability of the synthesized molecules. An amount of 15-20 mg was loaded in the TG pan and subjected to heating at a rate of 10 °C/min in an inert atmosphere (under N_2). The weight loss of the samples has been recorded by heating the sample from 25 °C to 900 °C.

The TGA analysis shows a two-step decomposition process in the temperature range of 25-150 °C which can be attributed due to the loss of H_2O adsorbate and HOAc modulator and the second decomposition is due to the loss of the linkers in the PANI resulting in the decomposition.

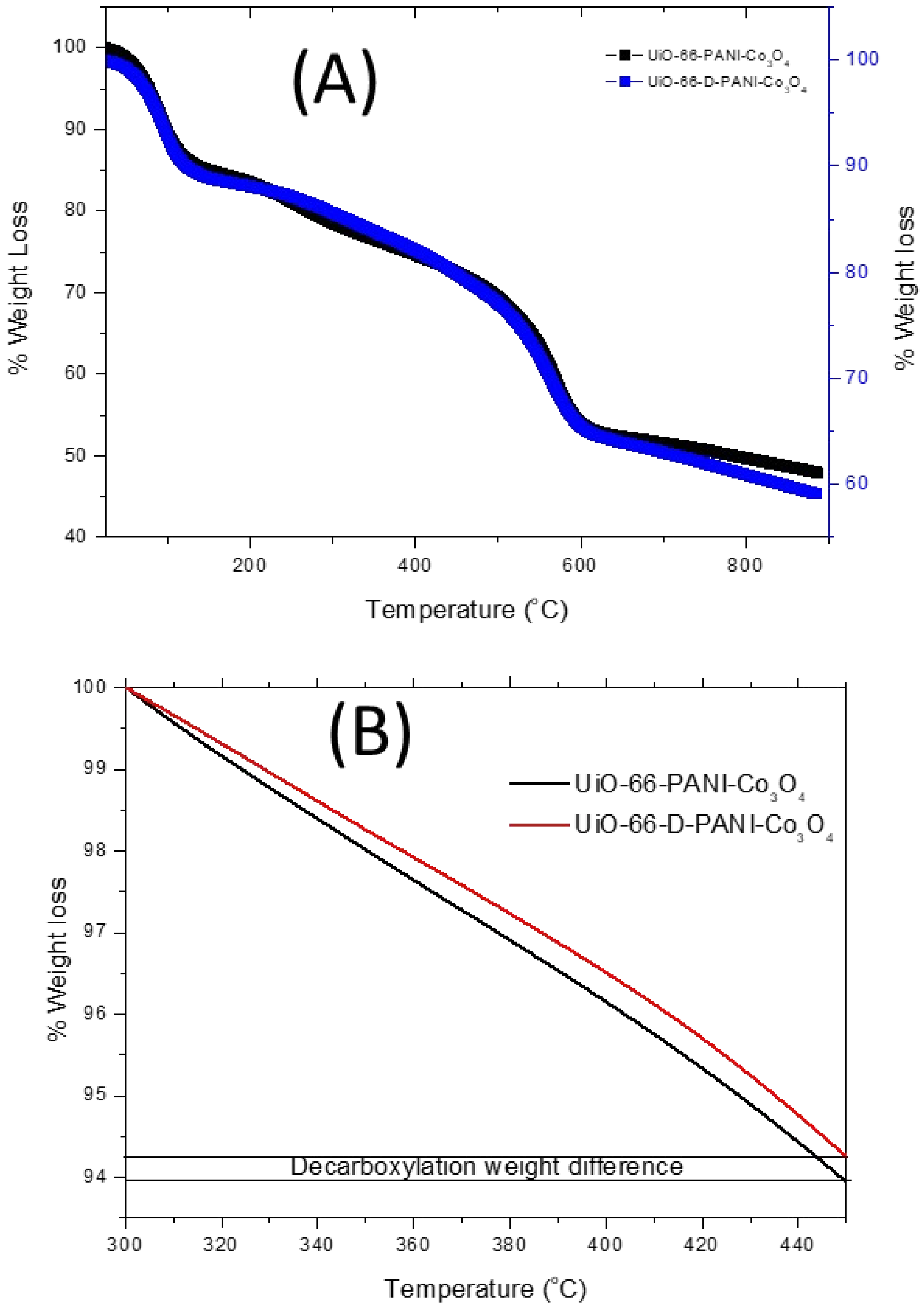


Fig. S5 Comparative TGA graph of synthesized catalyst; (a) synthesized composites, (b) comparative decarboxylation graph.

Total amount of carboxylic acid in UiO-66-PANI-Co_3O_4 estimated through the TGA analysis = 6.06 wt%.

Total amount of carboxylic acid in UiO-66-D-PANI-Co_3O_4 estimated through the TGA analysis = 5.75 wt%.

$$\%\ decarboxylation\ during\ the\ silver\ assisted\ oxidation = 100 - \left[\frac{5.75}{6.06}\right] x\ 100$$

= 5.1 %

X-ray photo-electron spectroscopy (XPS) of highly efficient integrated photocatalyst UiO-66-PANI-Co_3O_4:

XPS measurements were performed with an AXIS SUPRA XPS System (Shimadzu group company) using monochromated Al Ka radiation. The X-ray Photoelectron Spectroscopy (XPS) analysis of the UiO-66-PANI-Co_3O_4 composite has been carried out (Fig. S6). The deconvolution of the high resolution XPS spectra determine that there is no deviation from the raw C, the peak at 284.5 eV is due to the C- atoms present in the composites. 284.4 eV is due to the C-C bonding,[4] 285.1 eV is due to COO (Fig. S6a). The peaks at 529.8eV, 528.3 eV and 531.2 eV are due to O2s, O1s and O3s respectively (Fig. S6b).[5] The peaks at 399.9 eV, 398.7 eV and 398.8 eV are due to –NH-, =NH- respectively (Fig. S6c), Zr3d3/2 shows peak at 182.6 eV and that of the Zr 3d5/2 shows peak at 180.57 eV (Fig. S6d). Finally, the cobalt composite possesses peaks at 780.8 eV, 788.04 eV and 793.0 eV, 800.12 eV for the Co 2p3/2 and Co2p1/2 respectively (Fig. S6e).[6]

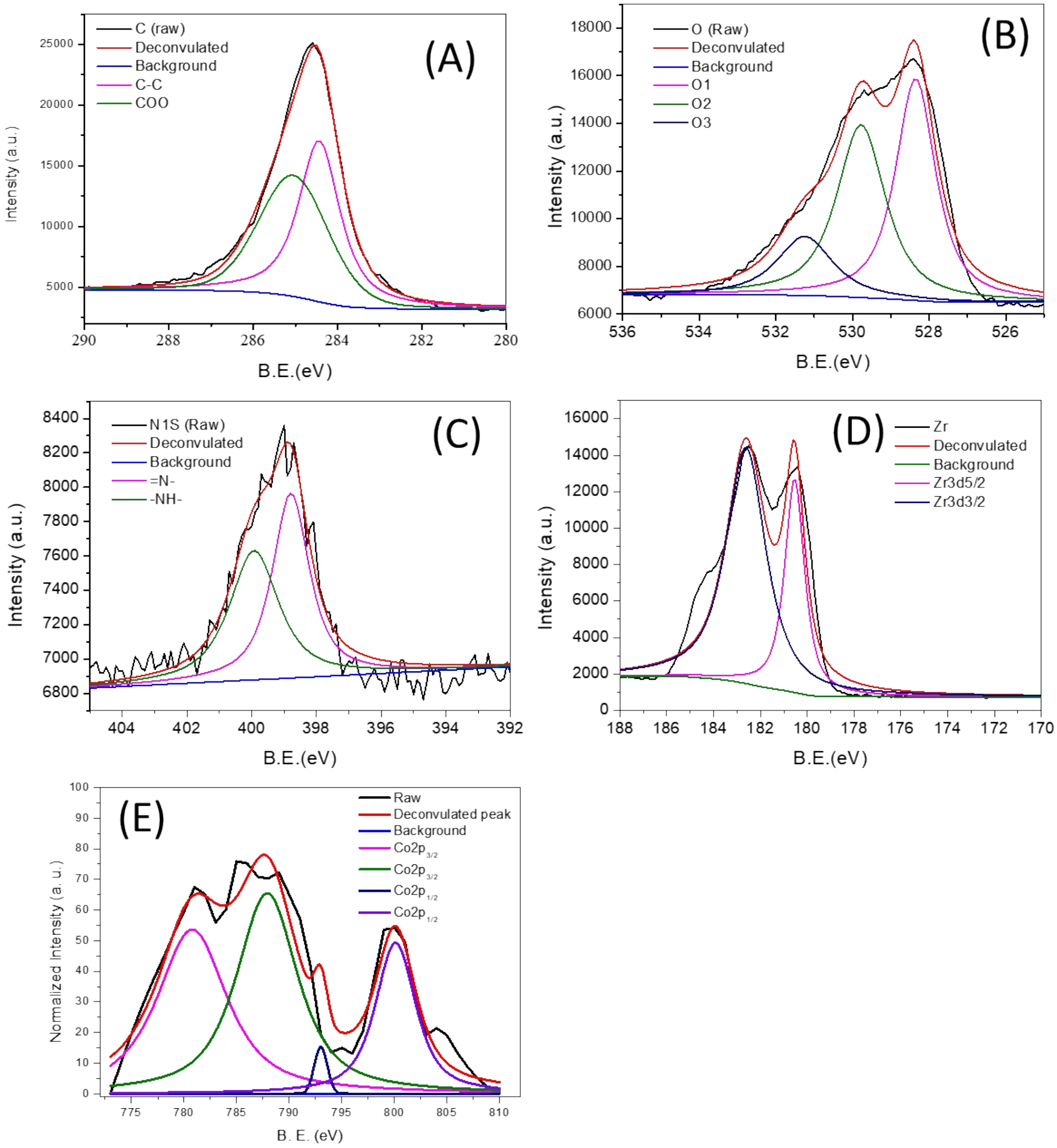


Fig. S6 XPS data of the synthesized the catalyst UiO-66-PANI-Co$_3$O$_4$, (a) C1 spectra, (b) O1s spectra, (c) N1s spectra, (d) Zr 3d spectra and (e) Co 2p spectra.

Photocatalytic experiments

The photocatalytic experiments were carried out under external light source using a 450 W Xenon arc lamp (Newport, USA). GC analysis was performed by gas chromatograph TCD detector (Perkin Elmer Clarus 590 GC containing molecular Sieve/5Å column) using Nitrogen as carrier gas. Typically, 80 mL of Quartz reactor has been taken to carry out the photocatalytic reactions. The photocatalyst (15 mg) was dispersed in 18 mL of deionized water and 2 mL of Triethanolamine (TEOA) under ultrasonication, the pH of the suspension was maintained at 7 by adjusting the pH using Conc. HCl, then the suspension was subjected to high evacuation to remove any dissolved gases followed by-purging nitrogen (N_2) gas in order to maintain inert atmosphere. The photoreactor was finally subjected to light irradiation using 450 W Xenon lamp under stirring conditions, the collection of gas samples has been carried out at regular intervals of time and is analyzed using Gas chromatography (GC) (Perkin Elmer Clarus 590 GC containing molecular Sieve/5Å column) equipped with thermal conductivity detector using nitrogen as carrier gas.

Table S1. Parameters and values of the H_2 gas analysis experimental details.

S. No	**Parameters**	**Value**
1	Sample injection volume	100 µL
2	Carrier gas flow rate	10 mL/min
3	Detector (TCD) temperature	125 °C
4	Oven temperature	200 °C
5	Injection port temperature	300 °C

Table S2: Photocatalytic H_2 generation efficiency of the composites.

Entry	Photocatalyst	Activity (µmolg^{-1})	AQY (%)
1	UiO-66	115	0.38
2	UiO-66/Pt	357	1.18
3	UiO-66-PANI	605	2.01
4	UiO-66-PANI/Pt	1242	4.13
5	UiO-66-D-PANI	861	2.86
6	UiO-66-D-PANI/Pt	1003	3.33
7	UiO-66-D	175	0.58
8	UiO-66-D/Pt	399	1.32
9	UiO-66-Co_3O_4	378	1.25
10	UiO-66-Co_3O_4/Pt	260	0.86
11	UiO-66-D-Co_3O_4	158	0.52
12	UiO-66-D-Co_3O_4/Pt	303	1.00
13	**UiO-66-PANI-Co_3O_4**	**2841**	**9.44**
14	UiO-66-PANI-Co_3O_4/Pt	1041	3.46
15	UiO-66-D-PANI-Co_3O_4	1290	4.28
16	UiO-66-D-PANI-Co_3O_4/Pt	1262	4.19

Table S3 Comparative table of H_2 generation

Entry	**Catalyst**	**Incorporated component**	**Solvent**	**Xe Lamp (W)**	**Activity $\mu mol^{-1}g^{-1}$**	**Ref.**
1	UiO-66-PANI-Co_3O_4	Co_3O_4	Water	450	710	This work
9	Pt@UiO-66	Pt	Water	300	3.9	7
10	Pt-CdS:Ru	Pt	Water	450	11	8
3	CdS@NU1000/1% RGO	Pt	Water	300	12	9
4	CdS/UiO-66	Pt	Water	300	235	10
6	ZrT-1-NH_2	Cp	Water	300	510	11
7	PW_{12}@UiONH_2	---	Water	500	72.7	12

Optical properties measurements

UV-Vis Spectrum of catalyst

The solid state diffuse reflectance spectroscopy (DRS) measurements of the samples have been measured using Perkin Elmer Lambda-6000 instrument using $BaSO_4$ as a reference. 100 mg of the sample has been placed in the sample holder for the measurement and the light is allowed to pass through the sample which leads to the absorption of the light and the light emitted by the sample has been recorded. The UV-vis diffuse reflectance spectrum (DRS) (Fig. S7a) shows that UiO-66 (Zr) has an absorption band-edge at 335 nm which could be attributed due to the π-π* transitions in the inorganic ligands. We were used the Xe-lamp as model light source for the for the photo-catalytic application. (Fig. S7b), light interaction with photo-catalysts are clearly showing that the only PANI coated composite photo-catalyst able to absorb the Xe-lamp output spectrum (visible light).[13]

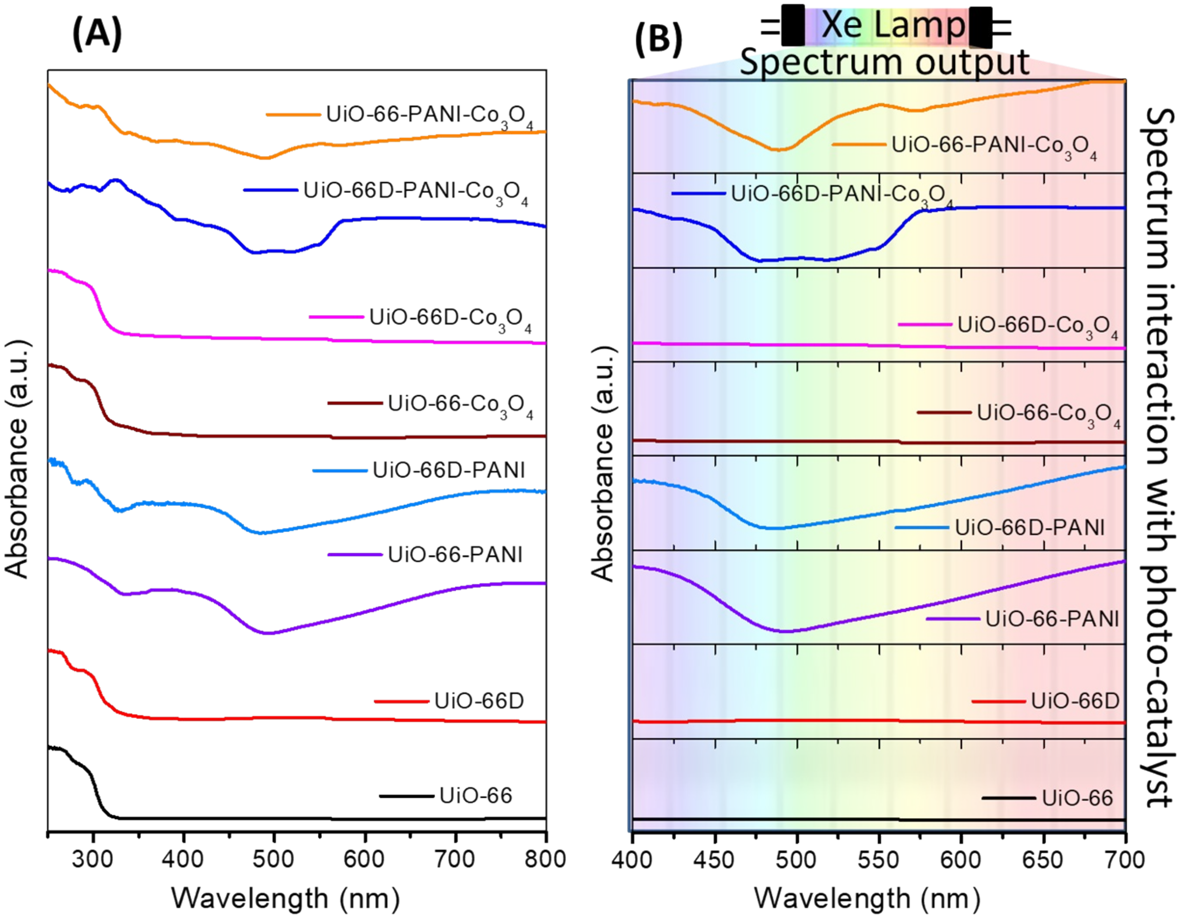


Fig. S7 Comparative UV-Vis DRS of the photo-catalyst, (a) full range; (b) Xe lamp output spectrum interaction behavior of photo-catalyst.

Band Gap calculation:

The band gap calculations of the solid samples have been mainly carried out using the absorbance obtained from the UV-vis DRS spectra. The indirect band gap calculation of the samples has been carried out so far using the kubelk-Maunk Plot or Tauc Plot.[14]

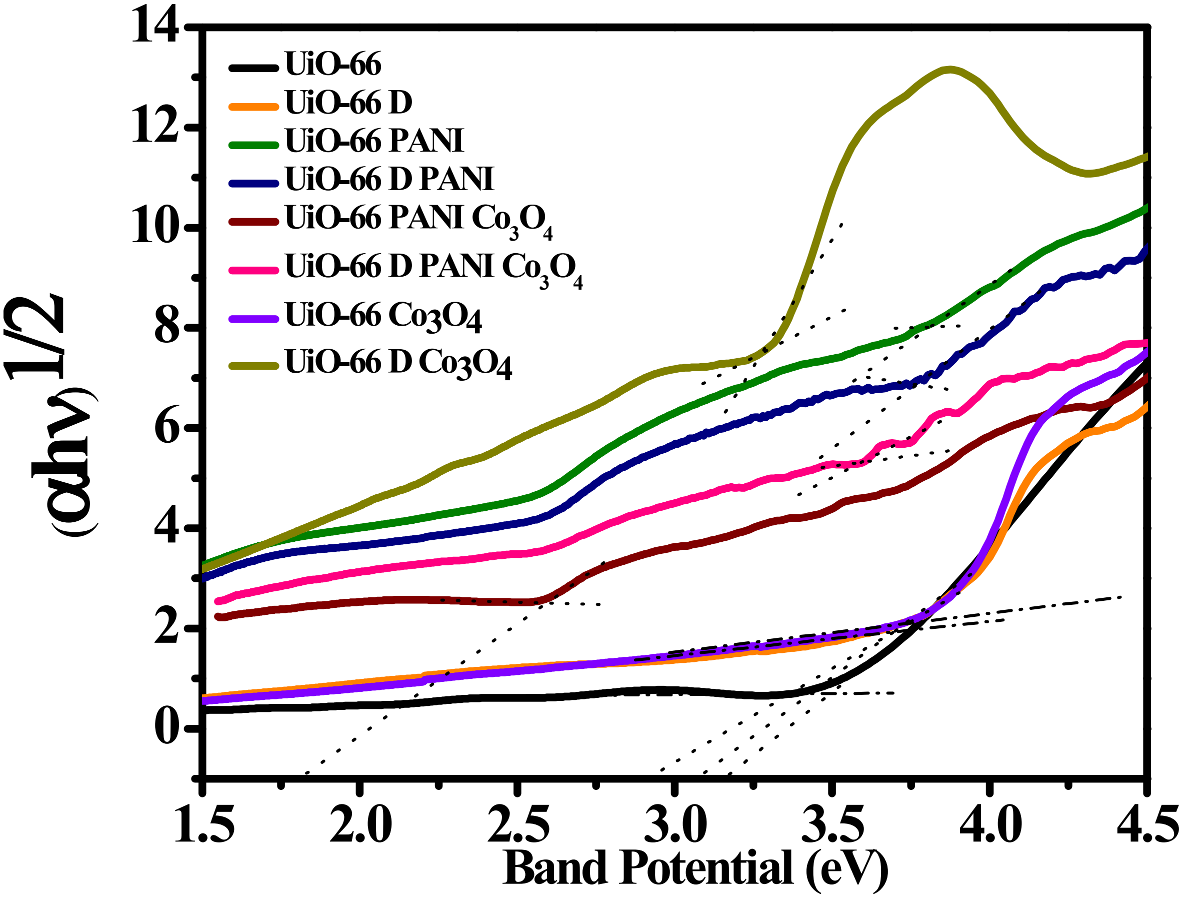


Fig. S8 Band gap potential of the as synthesized photocatalysts.

Photo-electrochemical Measurements:

Photoelectrochemical measurements were performed at room temperature using a three electrode system with Pt wire as counter electrode, AG/AgCl as reference electrode and Glassy carbon electrode coated with the sample as the working electrode in a CH Instruments Inc., USA CHI6005E electrochemical work station with Potentiostat. A 0.5M Na2SO4 solution was used as the electrolyte, the as synthesized sample (1mg) was dispersed in 1 mL of water and sonicated for 5 min later on, 15 μL of the solution is coated on metal tip of the glassy carbon electrode, which is allowed to dry, and then the 10 μL of Nafion and 1 mL ethanol mixed solution was drop casted on to the metal tip and allowed to dry. The initial electrode potential values have been obtained from the Open Circuit Potential Measurements and have been used.

Lifetime measurements

Fluorescence lifetime measurements were carried out using a ps time-correlated single photon counting (TCSPC) setup (FluoroLog3-Triple Illuminator, IBH Horiba JobinYvon) employing a ps light emitting diode laser as excitation source. The decay curves were recorded by monitoring the fluorescence emission maxima of the (λem = 420 nm, the intensity was normalized). 5 mg of the sample is dispersed in 5 mL of the methanol and is subjected to sonication for a period of 10 min, then the solution is put aside in order to let the particles settle at the bottom of the sample vials. The supernatant liquid is used for the measurements and is carried out using a ps time-correlated single photon counting (TCSPC) setup (FluoroLog3-Triple Illuminator, IBH Horiba JobinYvon) employing a ps light emitting diode laser as excitation source.

Table S4: Time resolved photoluminescence spectra and their average lifetime.

Entry	**Sample**	**Wavelength (λ) nm**		**Lifetime in ns (% decay)**			
		Excitation	**Detection**	**τ_1**	**τ_2**	**τ_3**	**Average τ**
1	UiO-66	305	460	1.63 (36.79%)	7.39 (17.83%)	2.11 (45.38%)	2.87
2	UiO-66-D-PANI-Co_3O_4	355	420	1.56 (74.03%)	5.50 (25.97%)	------	2.58
3	UiO-66-PANI	355	420	1.46 (71.01%)	7.04 (28.99%)	-------	3.07
4	**UiO-66-PANI-Co_3O_4**	**355**	**420**	**1.66 (68.78%)**	**6.98 (31.22%)**	**-------**	**3.32**

Scanning electron Microscopic analysis of highly efficient photo-catalyst (UiO-66-PANI-Co_3O_4): Field emission scanning electron microscopy (FESEM) was performed on a Carl Zeiss SIGMA HD field-emission scanning electron microscope.

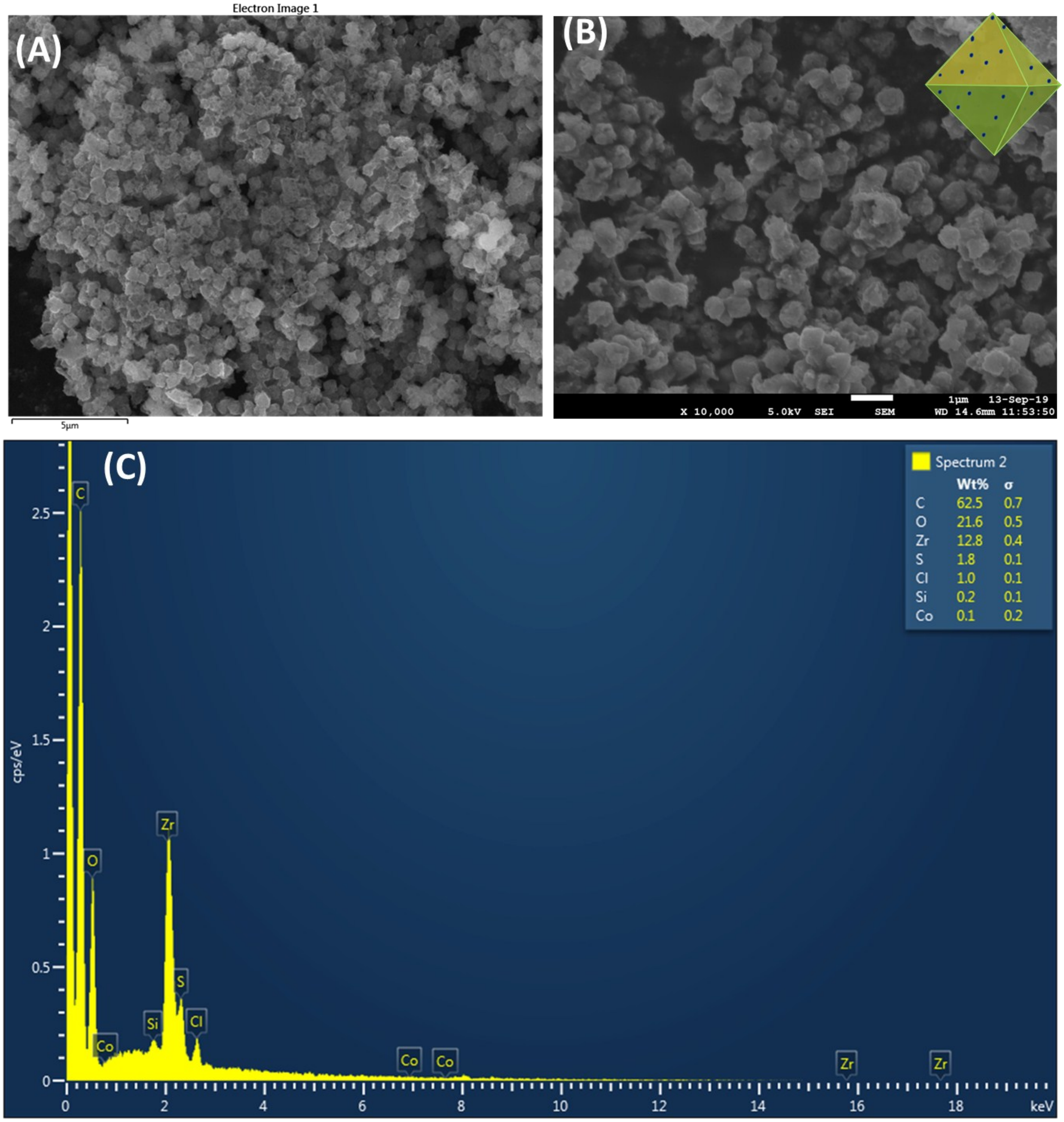


Fig. S9 Microscopic view of the highly efficient catalyst UiO-66-PANI-Co_3O_4; (a&b) Low and high resolution SEM image; (c) EDX spectra.

BET surface area analysis:

Nitrogen adsorption/desorption isotherms were measured using NOVA 2200e apparatus to determine the textural properties such as surface area (S_{BET}), total pore volume (V_{TOTAL}) and mean pore volume (V_{MEAN}). The catalysts were initially degassed for 3 h at 523 K under liq. nitrogen as adsorbent and then subjected to stepwise N_2 gas for the adsorption-desorption studies. The porosity of the catalysts was studied by the adsorption studies of N_2 at 77 K. The obtained BET surface areas were 553, and 491 m^2 g^{-1} for UiO-66-PANI-Co_3O_4, UiO-66-D-PANI-Co_3O_4 respectively with total pore volume of 0.41 and 0.382 cm^3 g^{-1} and average pore diameter of 1.50, and 1.55 nm. The decrease in the surface area has been observed compared to the UiO-66 in the synthesized UiO-66-PANI-Co_3O_4 and UiO-66-D-PANI-Co_3O_4 composite respectively similar to the our previously reported UiO-66.

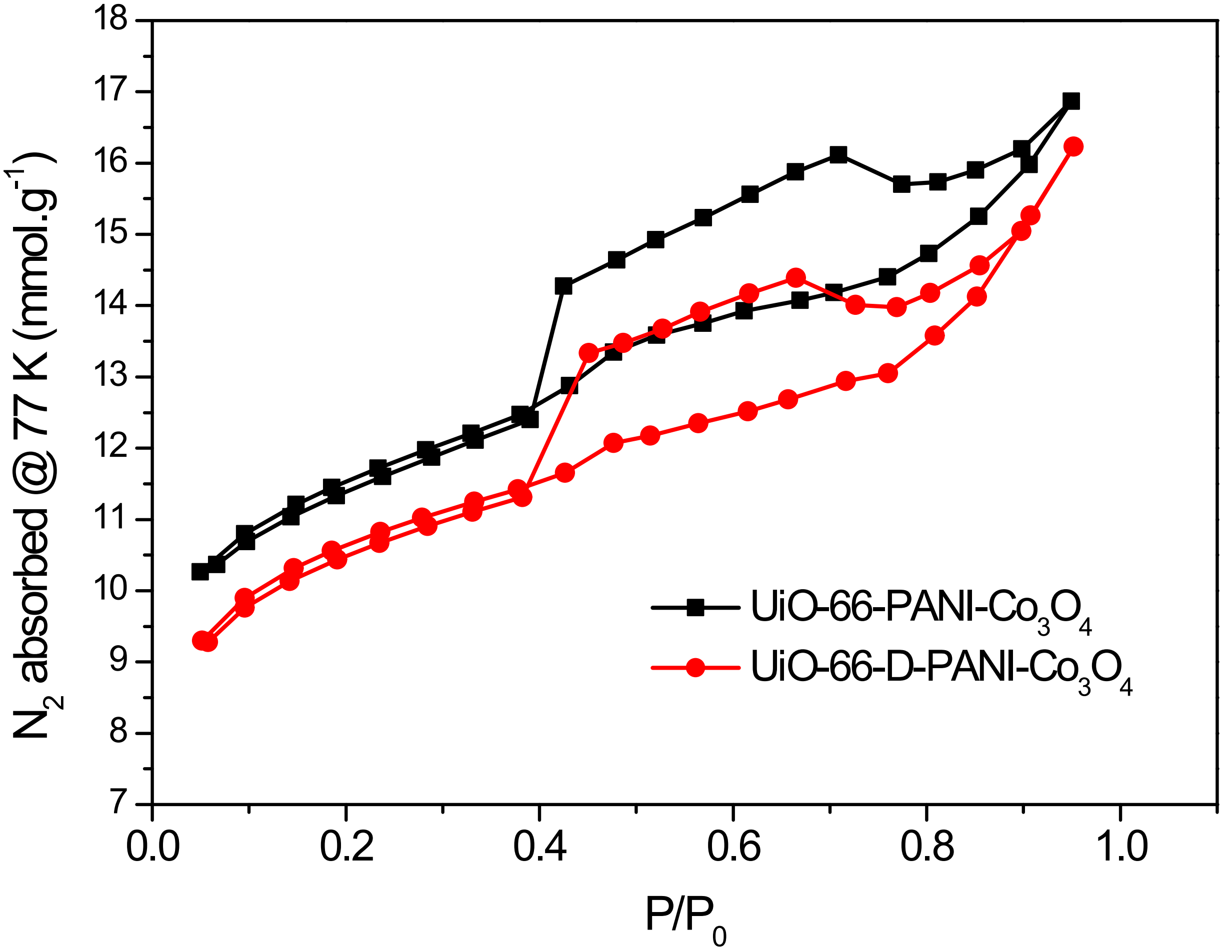


Fig S10. N_2 adsorption distributions for the photo-catalyst.

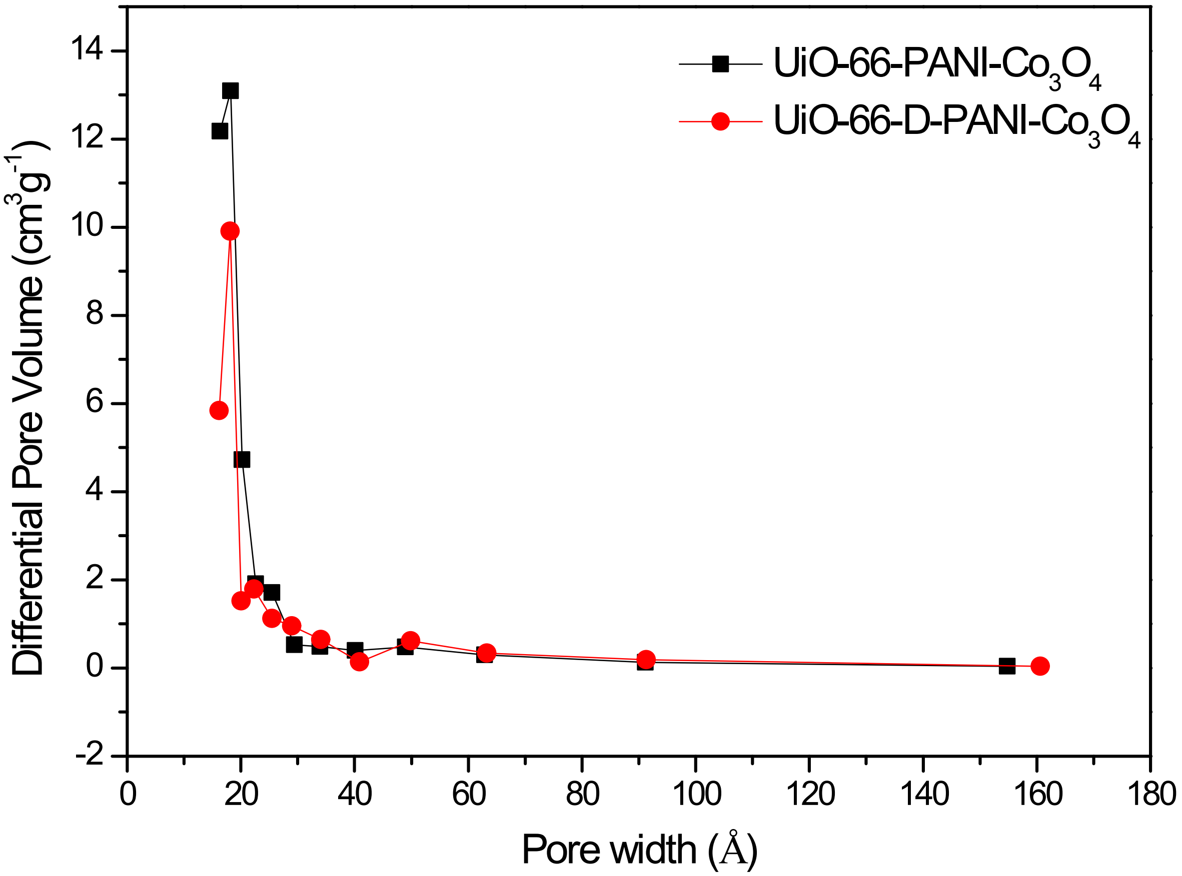


Fig. S11 Pore size distributions for the photo-catalyst.

Table S5. Comparative surface area and pore distribution analysis of photo-catalyst.

S. No.	Catalyst	BET surface area [$m^2 g^{-1}$]	Vt [$cm^3 g^{-1}$]	Average Pore radius [nm]	Reference
1	UiO-66-PANI-Co_3O_4	553	0.41	1.50	This study
2	UiO-66-D-PANI-Co_3O_4	491	0.382	1.55	This Study
3	UiO-66	1720	0.77	1.4	[1]

Supporting Video S1: The preparation of the film has been carried out manually using a rectangular glass plate of dimension 2x3 cm^2. In which, 20 mg of the catalyst has been made into suspension using 2 mL ethanol and then 50 μL of the Nafion solution was added and ultrasonicated for 5 min. The film has been prepared by dropping this evenly dispersed suspension onto the glass plate and is allowed to dry overnight. Then the photocatalytic experiment has been performed similar to our standard procedure. The evolution of the H_2 gas has been observed in the form of bubbles during photo irradiation over the stipulated time as shown in the supporting video.

Supporting Video S1

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