Supplementary Information (SI) for Materials Advances.

Supporting Information

In Situ Decorated Ni and Co in CuBTC MOF for Synergistic Photocatalytic Hydrogen Generation

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Experimental section

Materials

Copper nitrate trihydrate (Sigma Aldrich, Cu $(NO_3)_2.3H_2O$), trimesic acid (Sigma Aldrich, H_3BTC), Nickel nitrate hexahydrate (Sigma Aldrich, Ni $(NO)_3.6H_2O$), Cobalt nitrate hexahydrate (Sigma Aldrich Co $(NO_3).6H_2O$), Ethanol, Isopropanol, D.I Water, Methanol.

Preparation of CuBTC

The synthesis of CuBTC was performed by dissolving 1.75 g of Cu $(NO_3)_2{\cdot}3H_2O$ in 7.2 mL of deionized water and 0.840 g of 1,3,5-benzenetricarboxylic acid in 24 mL of ethanol. The two solutions were combined and stirred for 10 minutes, followed by the addition of 12 mL of isopropanol. The resulting mixture was transferred to a 100 mL Teflon-lined stainless-steel autoclave and heated in an oven at 120°C for 12 hours. The blue precipitate formed were washed three times with ethanol and dried overnight at 80°C.[1]

Preparation of Ni or Co-CuBTC

The synthesis of Ni-CuBTC/ Co-CuBTC was performed by dissolving 1.27 g of Cu $(NO_3)_2{\cdot}3H_2O$, 0.48 g of Co $(NO_3)_2{\cdot}6H_2O$ or 0.58 g of Ni $(NO_3)_2{\cdot}6H_2O$ in 7.2 mL of deionized water and 0.840 g of 1,3,5-benzenetricarboxylic acid in 24 mL of ethanol. The two solutions were combined and stirred for 10 minutes, followed by the addition of 12 mL of isopropanol. The two solutions were then transferred in to a Teflon-lined stainless-steel autoclave and heated in an oven at 120°C for 12 hours. The blue precipitate formed were washed three times with ethanol and dried overnight at 80°C.

Preparation of Co-Ni-CuBTC

The synthesis of Co-Ni-CuBTC was performed by dissolving 1.27 g of Cu $(NO_3)_2{\cdot}3H_2O$, 0.24 g of Co $(NO_3)_3{\cdot}6H_2O$, and 0.290 g of Ni $(NO_3)_2{\cdot}6H_2O$ in 7.2 mL of deionized water and 0.840 g of 1,3,5-benzenetricarboxylic acid in 24 mL of ethanol. The two solutions were combined and stirred for 10 minutes, followed by the addition of 12 mL of isopropanol. The two solutions were then transferred in to a Teflon-lined stainless-steel autoclave and heated in an oven at 120°C for 12 hours. The blue precipitate formed were washed three times with ethanol and dried overnight at 80°C.

Characterization

The structural phase analysis of the as-synthesized photocatalysts was performed by using Powder X-ray diffraction patterns (XRD) on a Bruker AXS diffractometer (D8 advance) at a generator voltage of 40 kV and current of 30 mA using Cu-Kα1 irradiation ($\lambda = 1.5406$ Å). The sample was scanned in the $2\theta = 5\text{-}80°$ range with a scan rate of 1 s/step. X-ray photoelectron spectroscopy (XPS) was performed via a Kratos (axis 165) analytical instrument with Mg Kα irradiation. About 10-9 Torr pressure was maintained in the spectrometer. The structural morphology of the photocatalysts was examined by using MIRA3 FEG-SEM (TESCAN) Scanning electron microscopy (SEM) at an accelerating voltage of 5 kV. Transmission electron microscopy (TEM) image of the representative photocatalysts was obtained by using a JEOL 2010EX TEM instrument equipped with the high-resolution style objective-lens pole piece at an acceleration voltage of 200 kV fitted with a CCD camera. N_2 adsorption-desorption isotherms of the photocatalysts were obtained on a Quanta chrome Nova 2200e gas adsorption analyzer at 77 K. The optical properties were characterized by using UV-Vis diffuse reflectance spectroscopy (DRS) Perkin Elmer Lambda 750 instrument using $BaSO_4$ as a reference. 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 transmitted by the sample has been recorded. The Photoluminescence (PL) spectra were recorded using a Fluorolog-3 spectrofluorometer (Spex model, JobinYvon) at their respective excitation (λex) wavelength. Fluorescence Lifetime decay measurements were carried out by using time-correlated singlephoton counting (TCSPC) setup (Fluorolog-3 Triple Illuminator, IBH Horiba Jobin Yvon). Briefly, the samples were excited at 375 nm, and the emission was observed at 425 nm. Thermogravimetric analyses (TGA) of the samples were carried out using the TA Instruments SDT Q500 apparatus to study the thermal treatment. Around 12-15 mg of the sample was placed in the TG pan and was heated at a scan rate of 10 °C min^{-1} within a temperature range of 25 to 800 °C under an inert atmosphere of N_2 gas flow of 50 ml min^{-1}.

Photo-electrochemical studies

The entire photo-electrochemical test was carried out in the electrochemical workstation. 0.25 M aqueous solution of Na_2SO_4 was used as an electrolyte for all experiments. Pt wire and calomel electrodes were used as counter and reference electrodes. The preparation of the working electrode is carried out using 20 μL of suspension (5 mg in 1mL ethanol) on ITO coated glass surface with a specific area of 2 cm^2. The light source is considered as an

Photoelectrochemical measurements at room temperature were recorded on the CH Instruments Inc., USA, CHI6005E, Electrochemical Workstation with Potentiostat using a three-electrode system with a standard three-electrode system with the photocatalyst-coated ITO as the working electrode, Pt wire as the counter electrode, saturated calomel electrode (SCE) as the reference electrode. The artificial solar simulator of AM 1G illuminator (100 mW cm^{-2}) was used as the light source during the measurement. The electrochemical cell was a conventional three-electrode cell with a 3 mm thick Pyrex glass eyelet. A 0.5 M Na_2SO_4 solution was used as the electrolyte. **Electrode Preparation:** To prepare the photoelectrode, 4 mg of each as-synthesized photocatalyst was dispersed into a suspension that contained 0.3 ml ethanol and 40 μmol Nafion by 30 min of ultrasonication. The as-prepared solution was dropped on the surface of Indium tin oxide (ITO) film of 3 × 2 cm^2 surface area to achieve uniform coverage and then dried in air at room temperature.

Photocatalytic Hydrogen Production

The photocatalytic hydrogen production by the water-splitting activity of CuBTC, Ni-CuBTC, Co-CuBTC and Co-Ni-CuBTC was investigated in a long-necked round bottom flask sealed with rubber septum in a nitrogen atmosphere at normal temperature. All samples were analysed in the same reaction condition. Over a typical experiment, 10 mg of catalyst was dispersed in 25 mL D.I water and 25 mL methanol of aqueous solution by ultrasonication. Before the irradiation reactor was evacuated, nitrogen purged in dispersion to ensure a complete nitrogen atmosphere. The suspension was stirred continuously for homogeneous distribution of the catalyst. 420W Xe lamp was used as a light source for the water-splitting reaction. A 100μL airtight gas syringe was used to take outgas from the reactor. The resultant gases evolved through the reaction using a gas chromatograph equipped with Thermal Conductivity Detector (TCD). The apparent quantum efficiency (AQE) was calculated at wavelength 420 nm (λ_{max} ± 420 nm) using a UV-vis cut-off filter. The experimental conditions of our work are considered, and we tend to use optical power meter (Newport, Model: 842-PE). The AQY (%) and the values of number of incident photons ($N_{photons}$) were calculated using the following equations

$$N_{photon} = \frac{P\lambda T}{hc}$$

Here, P = power of light (0.19 J s^{-1} cm^{-2}) over a specific area of 6 cm^2, λ = light wavelength (420 nm), t = irradiation time (4 h), h - Planck's constant (6.626 x 10^{-34} J s) and c = velocity of light (3 x 108 m s^{-1})

$$\text{AQE \%} = \frac{2 * No\ of\ evolved\ hydrogen\ molecule}{the\ no\ of\ incident\ photons\ (N\ photon)} * 100$$

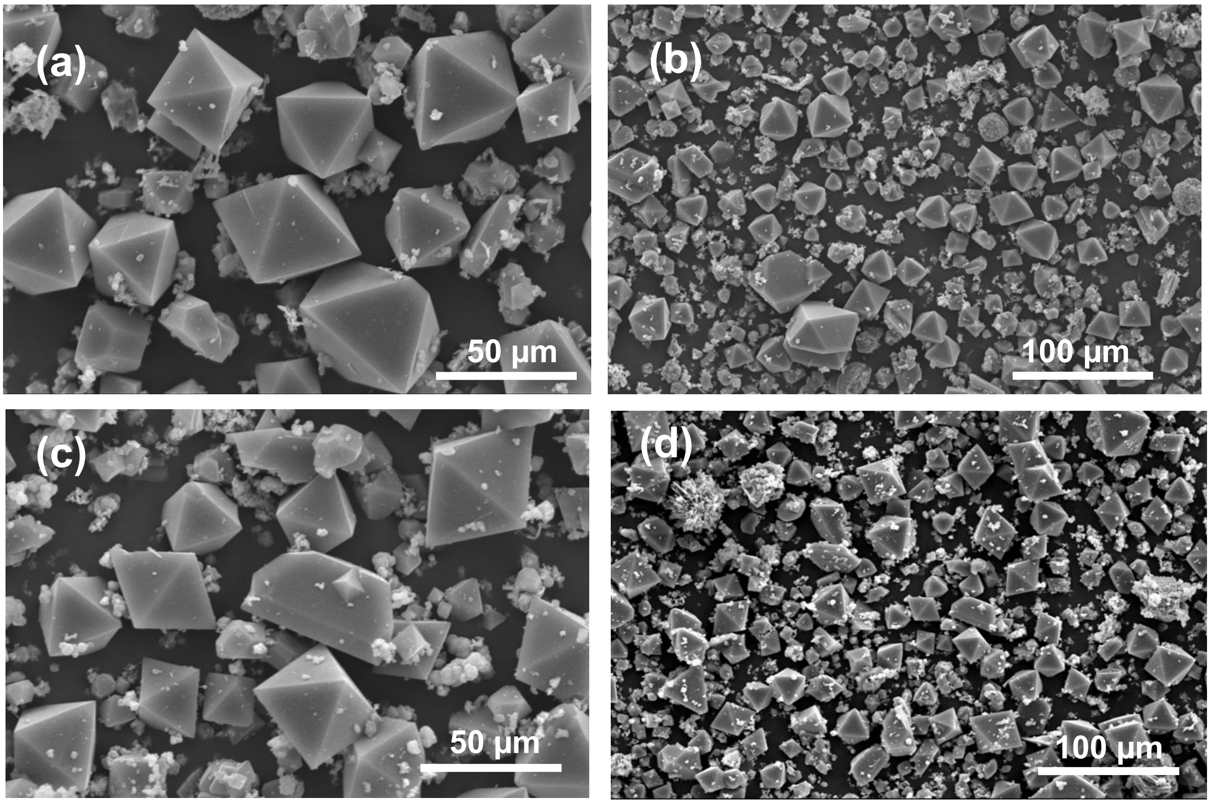
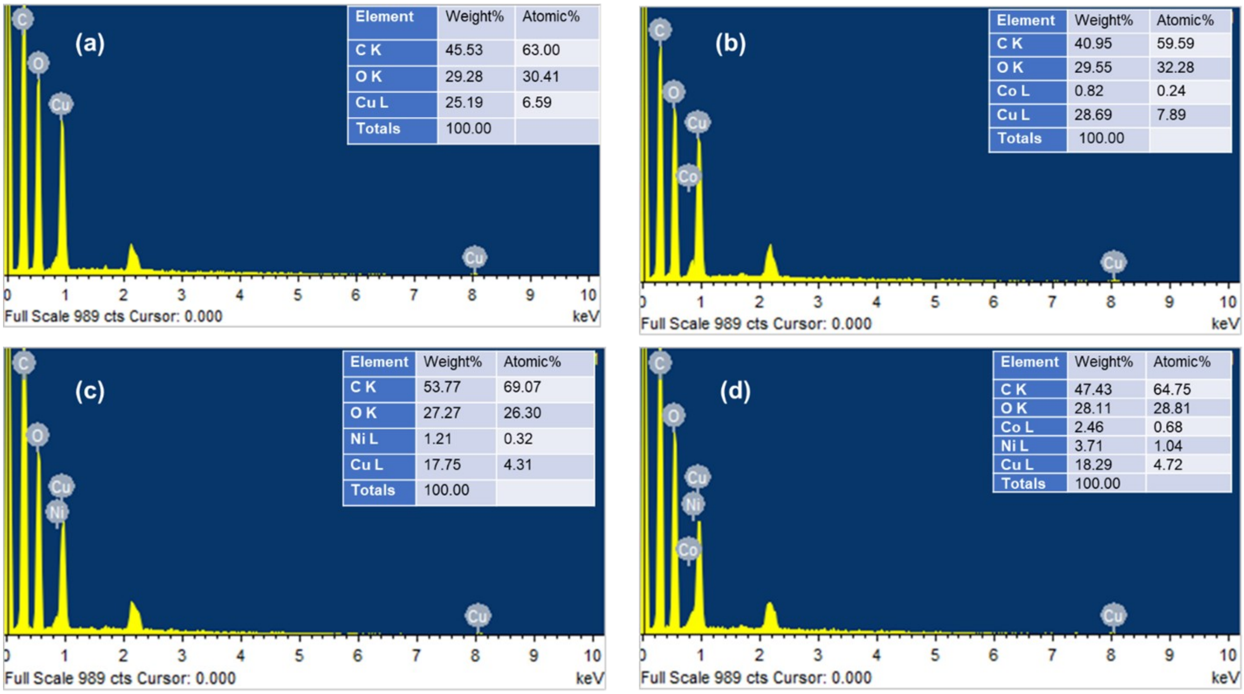


Fig. S1 SEM images of (a-b) Ni-CuBTC and (c-d) Co-CuBTC.



(a)

Element	Weight%	Atomic%
C K	45.53	63.00
O K	29.28	30.41
Cu L	25.19	6.59
Totals	100.00	

(b)

Element	Weight%	Atomic%
C K	40.95	59.59
O K	29.55	32.28
Co L	0.82	0.24
Cu L	28.69	7.89
Totals	100.00	

(c)

Element	Weight%	Atomic%
C K	53.77	69.07
O K	27.27	26.30
Ni L	1.21	0.32
Cu L	17.75	4.31
Totals	100.00	

(d)

Element	Weight%	Atomic%
C K	47.43	64.75
O K	28.11	28.81
Co L	2.46	0.68
Ni L	3.71	1.04
Cu L	18.29	4.72
Totals	100.00	

Fig. S2 EDS analysis of (a) CuBTC (b) Co-CuBTC (c) Ni-CuBTC and (d) Co-Ni-CuBTC

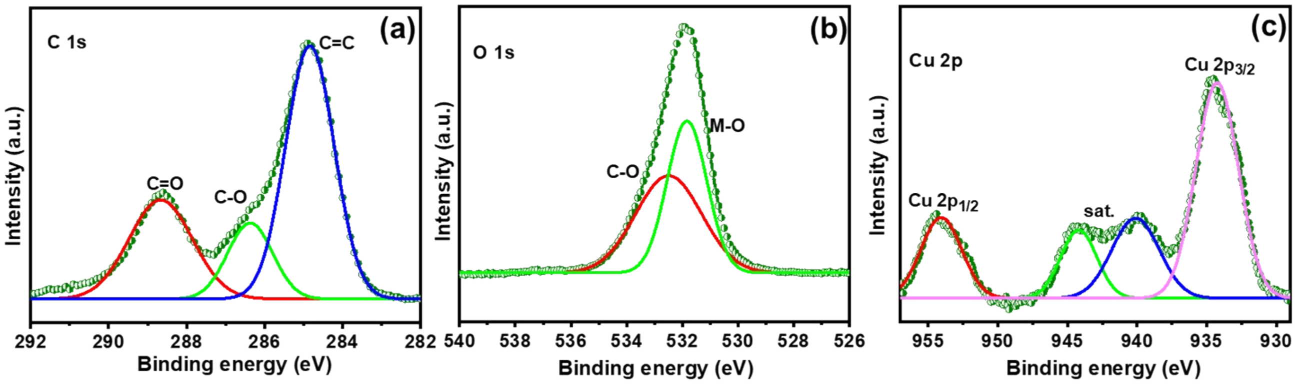


Fig. S3 XPS spectra of CuBTC (a) C 1s, (b) O 1s, (c) Cu 2p

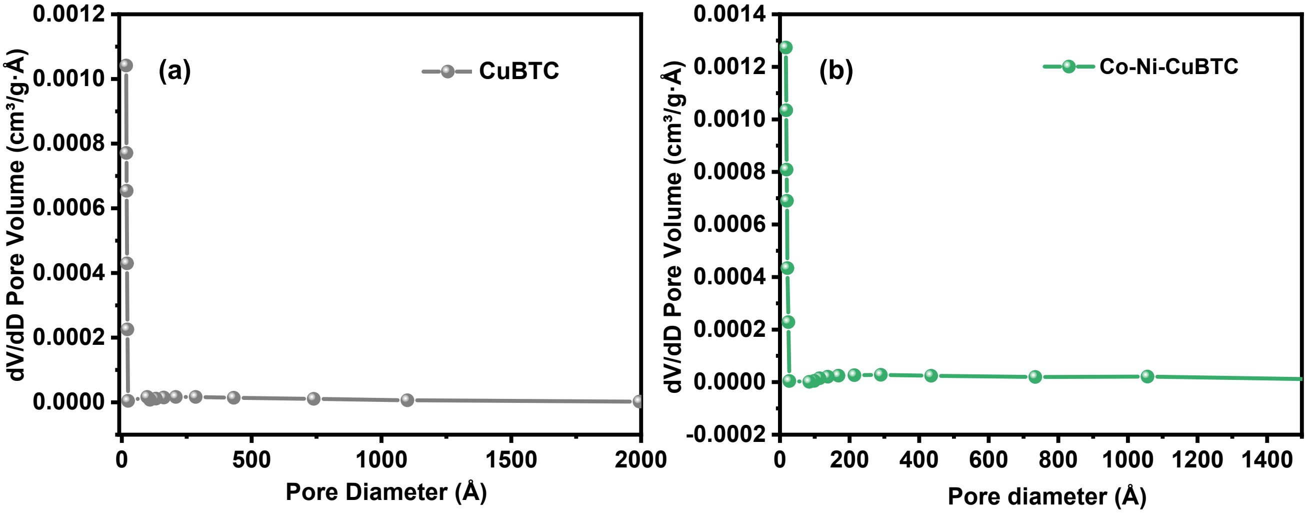


Fig. S4 Pore size distribution curves of (a) CuBTC and (b) Co-Ni-CuBTC

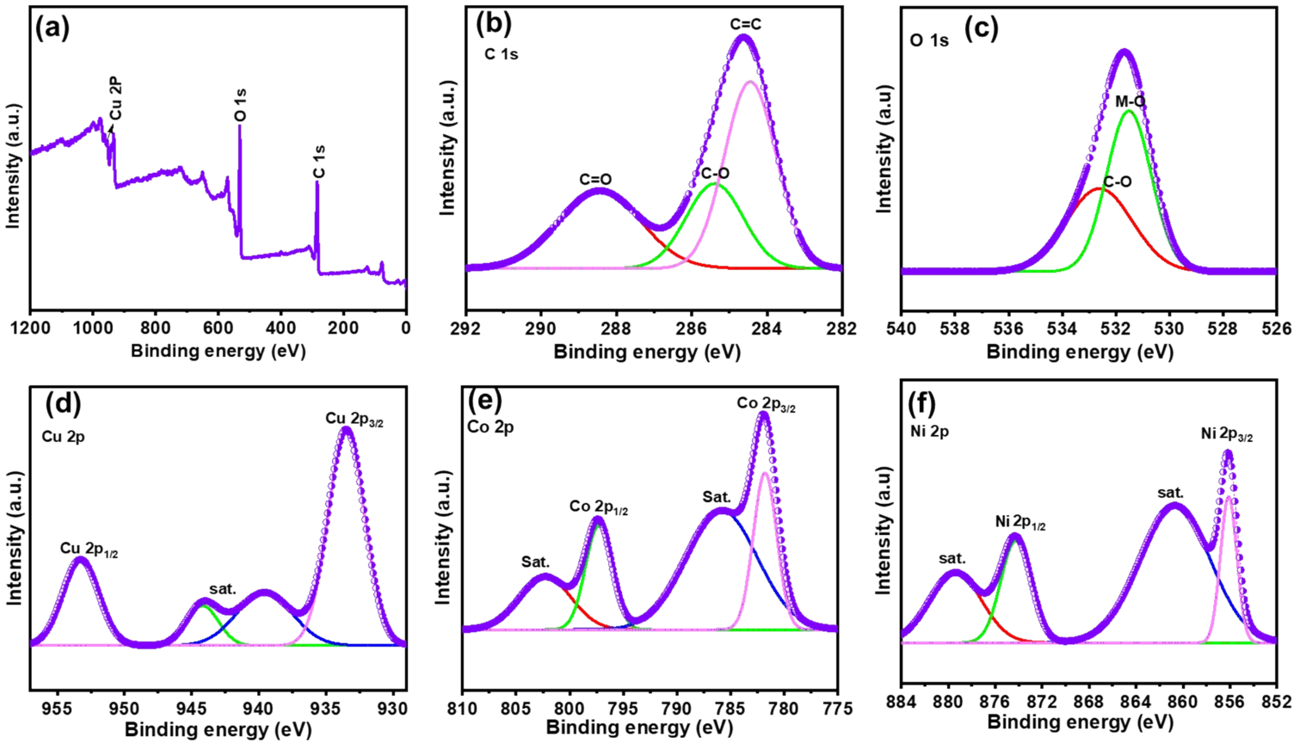


Fig. S5 XPS spectra of Co-Ni-CuBTC after photocatalytic reaction (a) Survey spectra, (b) C 1s, (c) O 1s, (d) Cu 2p, (e) Co 2p and (f) Ni 2p

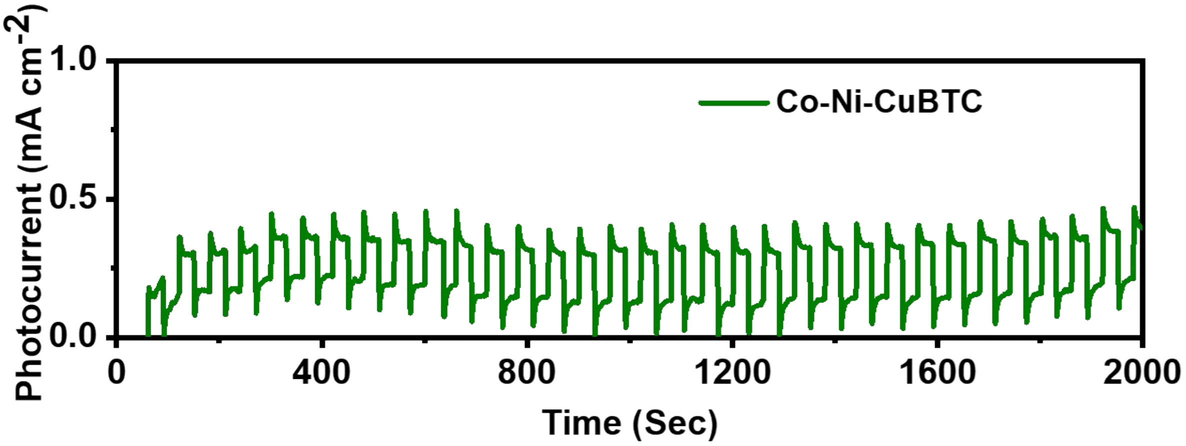


Fig. S6 Transient Photocurrent of Co-Ni-CuBTC extended to 30 minutes

Table. S1 Photocatalytic H_2 generation efficiency of the composites under visible light irradiation for 4 hrs

S. No.	Photocatalyst	H_2 Activity (mmol g^{-1} h^{-1})	AQE (%)
1.	CuBTC	3.6	8.6
2.	Co-CuBTC	8.4	20.1
3.	Ni-CuBTC	14.4	34.5
4.	Co-Ni-CuBTC	23.9	57.3
5.	Co-Ni-CuBTC(1)	13.4	32.1
6.	Co-Ni-CuBTC(2)	7.08	16.9

Table. S2 Comparative table of photocatalytic hydrogen evolution activity with CuMOF based catalysts.

S. No.	Photocatalyst	SED	HER Results (mmol g^{-1} h^{-1})	Reference
1.	Cu-BTC-FBA	TEOA	15.107	[2]
2.	Cu^{II}-MOF	TEA	1.36	[3]
3.	CuBTC/MoS_2	Methanol	0.62	[4]
4.	MOF-199/Ni	TEOA	8.00	[5]
5.	Ru/Cu–BTC	TEOA	15.81	[6]
6.	MET-Cu-D	Methanol	12.91	[7]
7.	Cu-I-bpy	TEA	7.09	[8]
8.	HKUST-1/TpPa-1	L-ascorbic acid	10.50	[9]
9.	15-ZCS/M	TEOA	11.62	[10]
10.	**Co-Ni-CuBTC**	**Methanol**	**23.9**	**This work**

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