Supplementary Information

for

Enhancing Formate Yield through Electrochemical CO_2 Reduction Using BiOCl and g-C_3N_4 Hybrid Catalyst.

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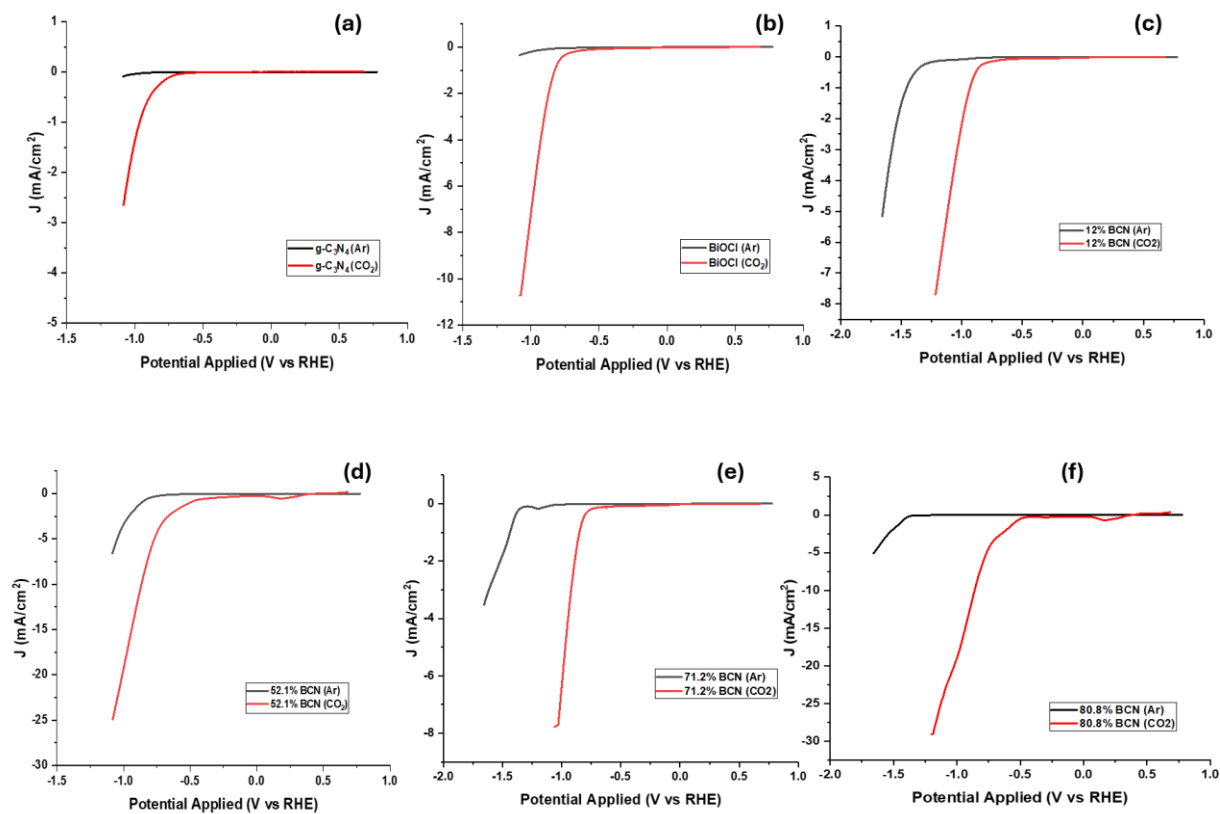
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Figure S1| LSV curves in CO_2 and Ar atmosphere from the potentials range of 0V to -1.06V (vs RHE) for (a) g-C_3N_4 (b) BiOCl, (c) 12% BCN, (d) 52.1% BCN, (e) 71.2% BCN, and (f) 80.8% BCN. RDE rotation speed: 1600 rpm. Scan Rate: 5mV/s.

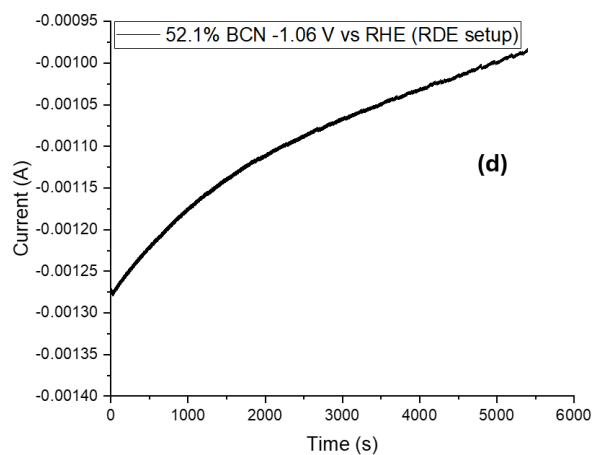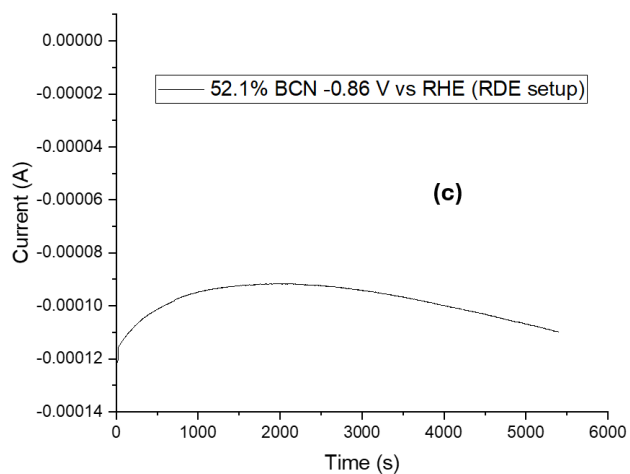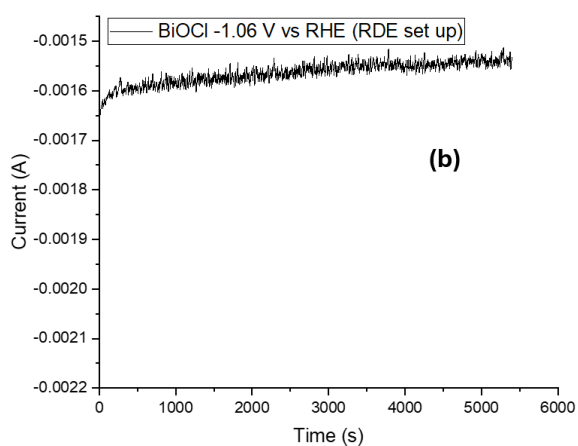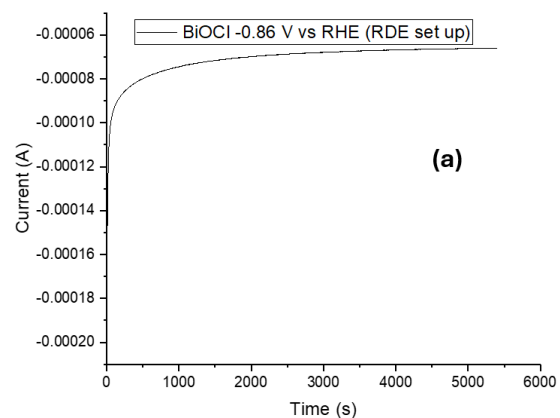Figure S2| CA curves in CO_2 saturated 0.1 M $KHCO_3$ for BiOCl at (a) -0.86 V vs RHE, (b) -1.06 V vs RHE, and for 52.1% BCN at (c) -0.86 V vs RHE, (b) -1.06 V vs RHE. RDE rotation speed: 1600 rpm. Scan Rate: 5mV/s.
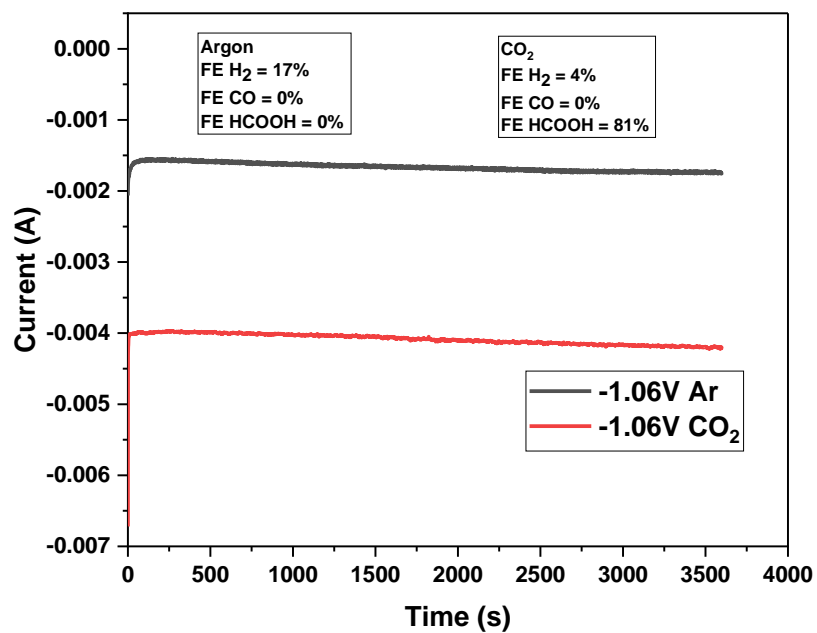
Figure S3| 52.1% BCN in CO_2 and Argon saturated 0.1M $KHCO_3$ with CA recorded for 3600 s in a gas-tight cell applying -1.06 V vs RHE. Gaseous products were evaluated at 2500s and HCOOH was evaluated at 3600s.
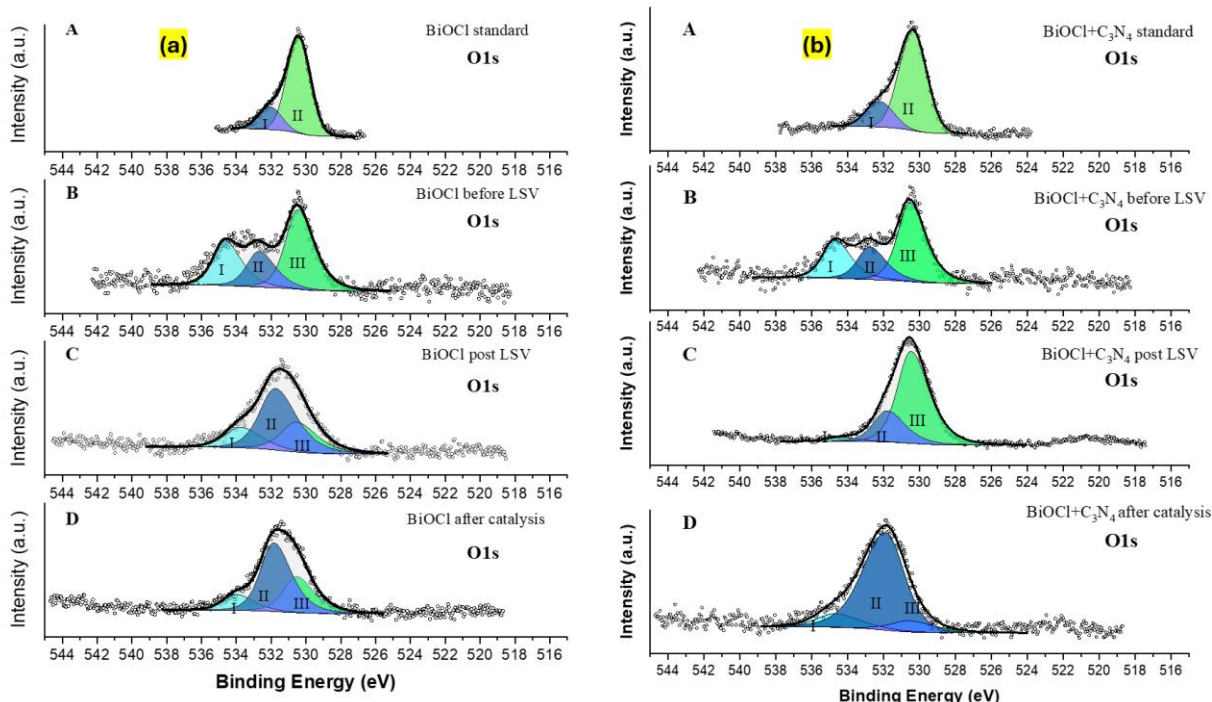
Figure S4| XPS analysis of Cl 2p spectra of (a) BiOCl and (b) 52.1% BCN in the different stages of eCO₂RR including (A) powdered catalyst, (B) dropcasted on carbon paper before LSV measurement, (C) post LSV, and (D) post catalysis.
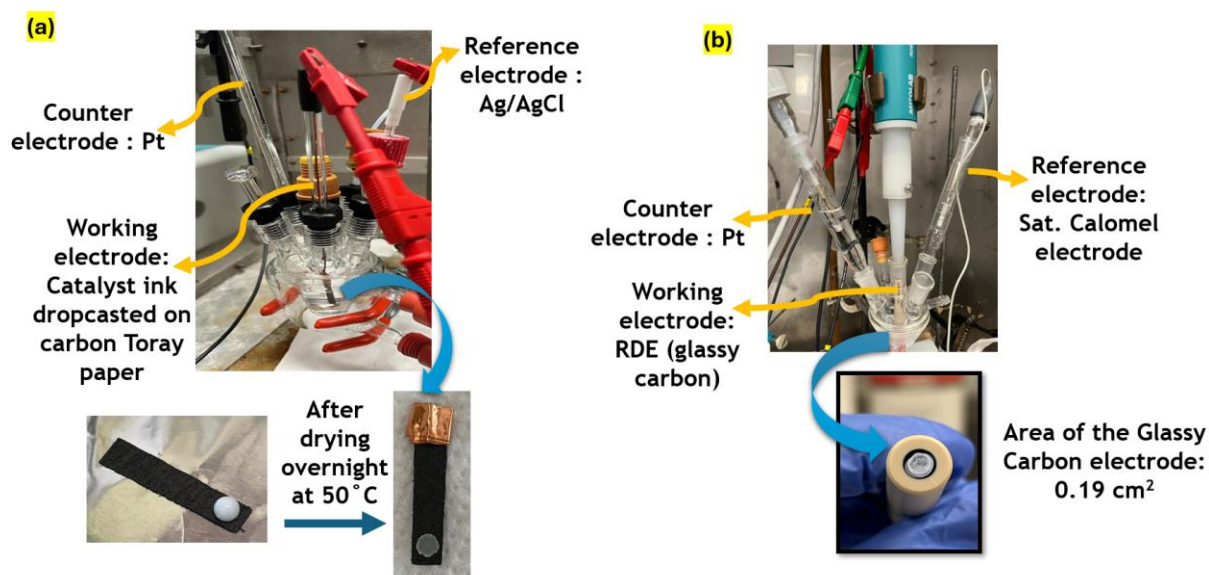

Figure S5| Types of electrochemical cells used. (a) Ho me-made prototype of Dr. Bob™ cell and (b) Rotating Disc Electrode based electrochemical cell.
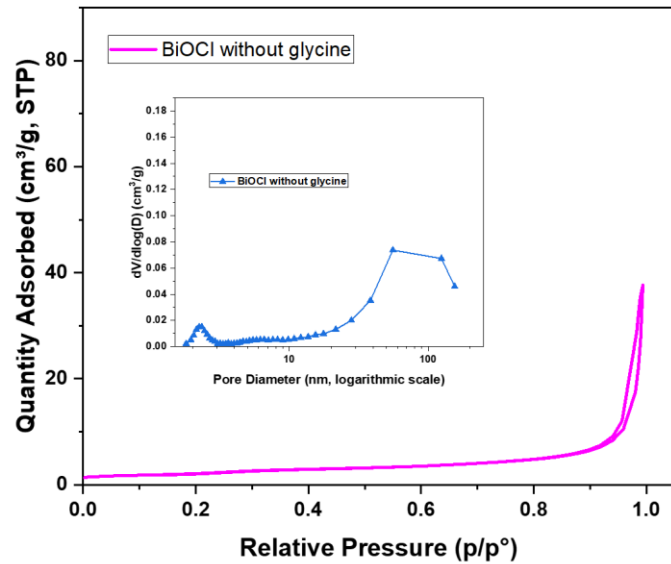
Figure S6| N$_2$-physisorption isotherm and BJH pore-size distribution (inset) of BiOCl synthesized without glycine.
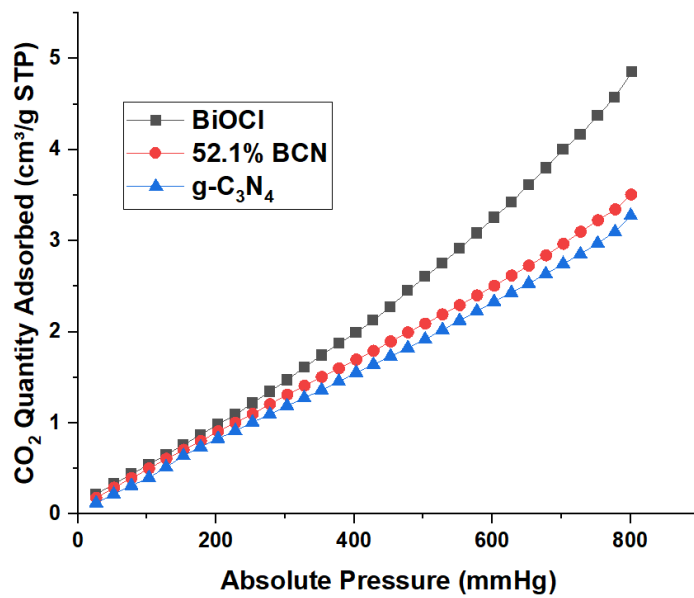

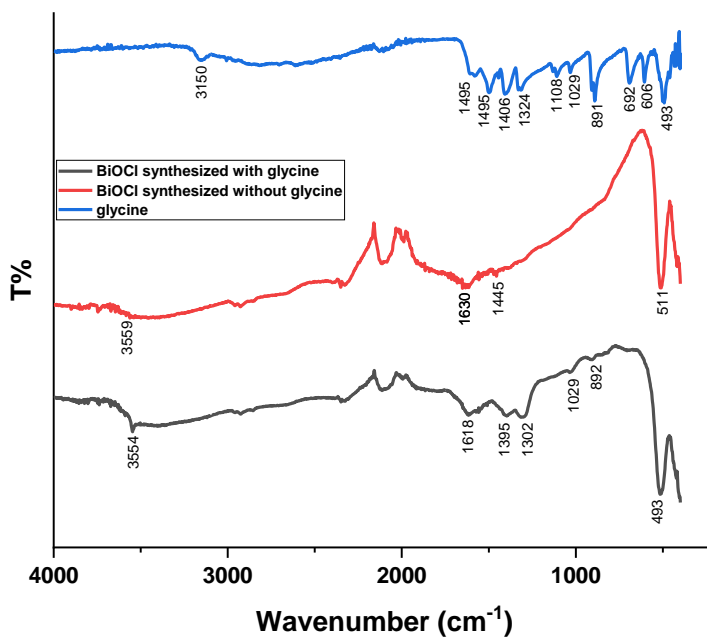Figure S7| CO$_2$ adsorption isotherms at 304K for BiOCl (black), 52.1 BCN (red) and g-C$_3$N$_4$ (blue).

Figure S8| ATR-IR spectra for pure glycine, BiOCl synthesized with glycine, and BiOCl synthesized without glycine.

Materials and methods

Electrochemical tests:

Ink and electrode preparation (carbon paper electrode): 5 mg of catalyst was weighed and added to 50 µl of Nafion^{TM} 117 with the addition of 100 µl of iPrOH and 900 µl H_2O. The above was ultra-sonicated and then 25 µl of ink was drop cast on the carbon electrode on each side with the electrode placed on a hot plate at 50˚ C. After an interval of 2 hours, the ink was deposited similarly on the other side of the carbon electrode.

Ink and electrode preparation (glassy carbon electrode): 5 mg of catalyst was weighed and added to 50 µl of Nafion^{TM} 117 with 950 µl of iPrOH:H_2O (1:3). The above was ultra-sonicated for 2 hours and then 5 µl of ink was deposited on the glassy carbon electrode and was then dried under vacuum for more than 2 hours.

The pH of the CO$_2$-saturated electrolyte of 0.1 KHCO$_3$ was measured to be 7.45 and that of Ar saturated was found to be 9.07. The measurements performed with Ag/AgCl(KCl$_{SAT}$) and SCE as reference were converted to RHE(Reversible Hydrogen Electrode) using equation (1) and (2):

$$E_{RHE}(V) = E_{SCE}(V) + 0.244V + (0.0591 * pH) \qquad (1)$$

$$E_{RHE}(V) = E_{Ag/AgCl(KClSAT)}(V) + 0.198 + (0.0591 * pH) \qquad (2)$$

The FE was calculated by the following formula :

$$FE = (n_e * F * n)/Q \qquad (3)$$

where n$_e$ is the number of electrons involved in the reaction, n is the moles of product, F is the Faraday constant (96485 Cmol^{-1}) and Q is the charge obtained from integration of the CA curve (as an absolute value).

XPS analysis:

XPS analysis was carried out employing an in-house built apparatus consisting of an analysis chamber, a hemispherical analyzer (VSW-HA100) equipped with a 16-channel detector which is served by a differential pumping system. The employed source is a non-monochromatic Al Kα (1486.7 eV, VSWTA10). The analysis chamber pressure during the measurements was around 1x10^{-9} mbar. Samples were insulated to avoid differential charging using Kapton foils [1]. The analysis was carried out cooling down the system to 160 K using liquid nitrogen to minimize the thermal degradation of the samples. Surveys have been registered using a pass energy of 44 eV and a step of 0.4 eV; the regions of interest (ROI) have been registered using a pass energy of 22 eV and a step of 0.05 eV. The presented ROI are relatives to the Bi 4f, Cl 2p, O 1s; all the spectra have been recorded using a normal incidence. Data was fitted using the CasaXPS software (V2.36) employing LF(a,b,c,d) curves, parameters are adjusted depending on the orbital's nature while a Shirley type background subtraction was adopted. The reference powders' spectra were calibrated using the Cu 2p peak (932.7 eV) [2]. The electrodes' spectra were calibrated, depending on the sample, using the C 2p (198.3 eV) peak that was previously detected in the referencing powder, and the most intense component of the F 1s peak (688.9 eV)2 was used in case of absence of the Cl 2p signal. The area correction and the semiquantitative analysis have been carried out using the cross-sections taken from the literature [3].

References:

[1] American Society for Testing and Materials *(ASTM) guide E 1523 to the methods to charge control and charge referencing techniques in x-ray photoelectron spectroscopy* by ASTM [Annual Book of ASTM Standards Surface Analysis (American Society for Testing and Materials, West Conshohocken, PA, 2004), Vol. 03.06].

[2] Chastain J, King Jr RC. Handbook of X-ray photoelectron spectroscopy. Perkin-Elmer

Corp. 1992;40:221.

[3]   J.J. Yeh, I. Lindau, Copyright 0 1985 by Academic Press, Inc., At. Data Nucl. Data Tables 32 (1985) 1–155. http://linkinghub.elsevier.com/retrieve/pii/0092640X85900166.