



Enhancing formate yield through electrochemical CO₂ reduction using BiOCl and g-C₃N₄ hybrid catalyst

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ABSTRACT

Electrochemical carbon dioxide (CO₂) reduction with bismuth-based catalysts has been widely investigated in the recent few years. This is due to bismuth's ability to perform selective electrochemical CO₂ reduction reaction (eCO₂RR) to an important C₁ product, the formate (HCOO⁻). However, boosting the performance of such catalysts is a continuous investigation. In this work, enhancing the active sites for eCO₂RR is investigated by forming nanocomposites with graphitic carbon nitride (g-C₃N₄). BiOCl is synthesized by a simple wet-chemical approach in the presence of glycine as size-controlling agent and formed into nanocomposites, which were characterized by Scanning Electron Microscopy (SEM), X-ray diffraction (XRD), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), Infrared (IR) Spectroscopy and N₂ physisorption. Linear Sweep Voltammetry (LSV) in argon and CO₂-saturated atmosphere showed higher current values in the case of CO₂. Chronoamperometries (CA) were recorded at -1.06 V vs Reversible Hydrogen Electrode (RHE) for 5400 s obtaining Faradic Efficiencies (FE) varying in the range of 70–77 % depending on the nanocomposites' composition. In fact, 52.1 wt% BiOCl/g-C₃N₄ formed the highest yields for formate (with also the highest rate of formation of formate) together with a minimal production of H₂ and CO. The effect of nano-structuration induced by glycine, used as a size-controlling agent, to form nanoplates was crucial: microplates of BiOCl produced without glycine showed an FE of 4 %, reaching 85 % in the case of the nanoplates. Post-electrocatalysis characterization revealed the possible role of Bi₂O₂CO₃ as the active phase for eCO₂RR.

1. Introduction

There has been a lot of research ongoing to find an efficient, selective, durable, and low-cost catalyst for electrochemical CO₂ reduction reaction (eCO₂RR) to other carbon-based products [1–3]. In recent years, the value of formic acid has increased due to the world's inclination toward the hydrogen economy [4–6]. It can be attributed to the fact that formic acid is a viable and suitable H₂ carrier. This is due to its high volumetric capacity of 53 g H₂/L given by its high density of 1.22 g·cm⁻³ in addition to low toxicity and flammability [7,8]. Moreover, the distribution cost of H₂ is reported to have been cut by 12 % by eCO₂RR obtaining formic acid in comparison with the thermocatalytic process

[8]. This benefits us in reducing excessive CO₂ emissions as well as obtaining a Liquid Hydrogen Carrier (LHC) that brings us closer to a carbon-neutral economy.

Product selectivity is an essential parameter necessary to understand the performance of the catalyst. It was reported in 2020 by Yang et al. that the *p*-block metal-based electrocatalysts were responsible for selectively reducing CO₂ to HCOO⁻. The characteristic oxophilicity of *p*-block metals leads to the formation of *OCHO over *COOH, which has been shown to be the key intermediate in the formation of formate or formic acid [9]. Amongst recent literature, eCO₂RR, leading to formate using gas-diffusion electrodes, using these *p*-block metals was reported. It was shown in the study that indium, tin, and bismuth had FE values of

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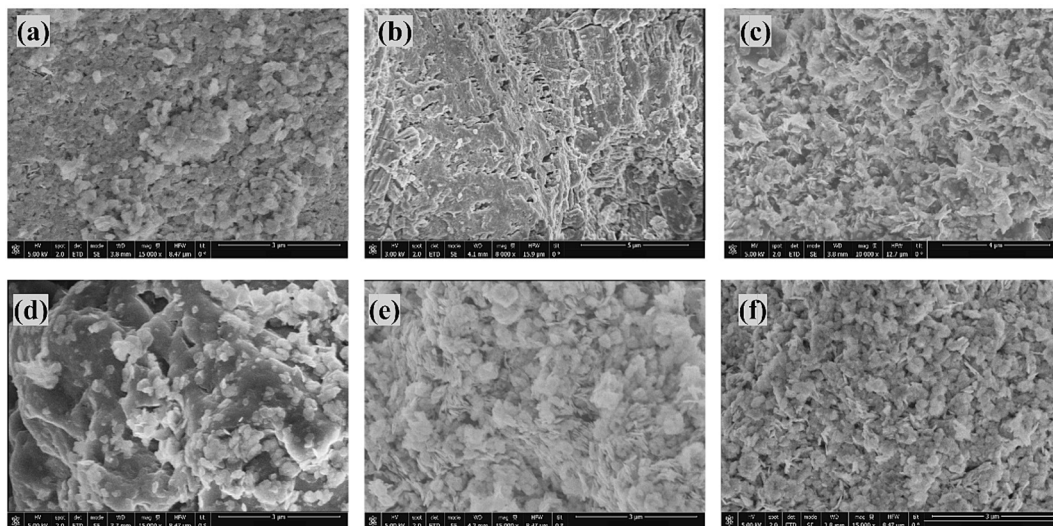


Fig. 1. Representative SEM images of (a) BiOCl (b) $g-C_3N_4$ (c) 52.1 % BCN (d) 12 % BCN (e) 71.2 % BCN (f) 80.1 % BCN.

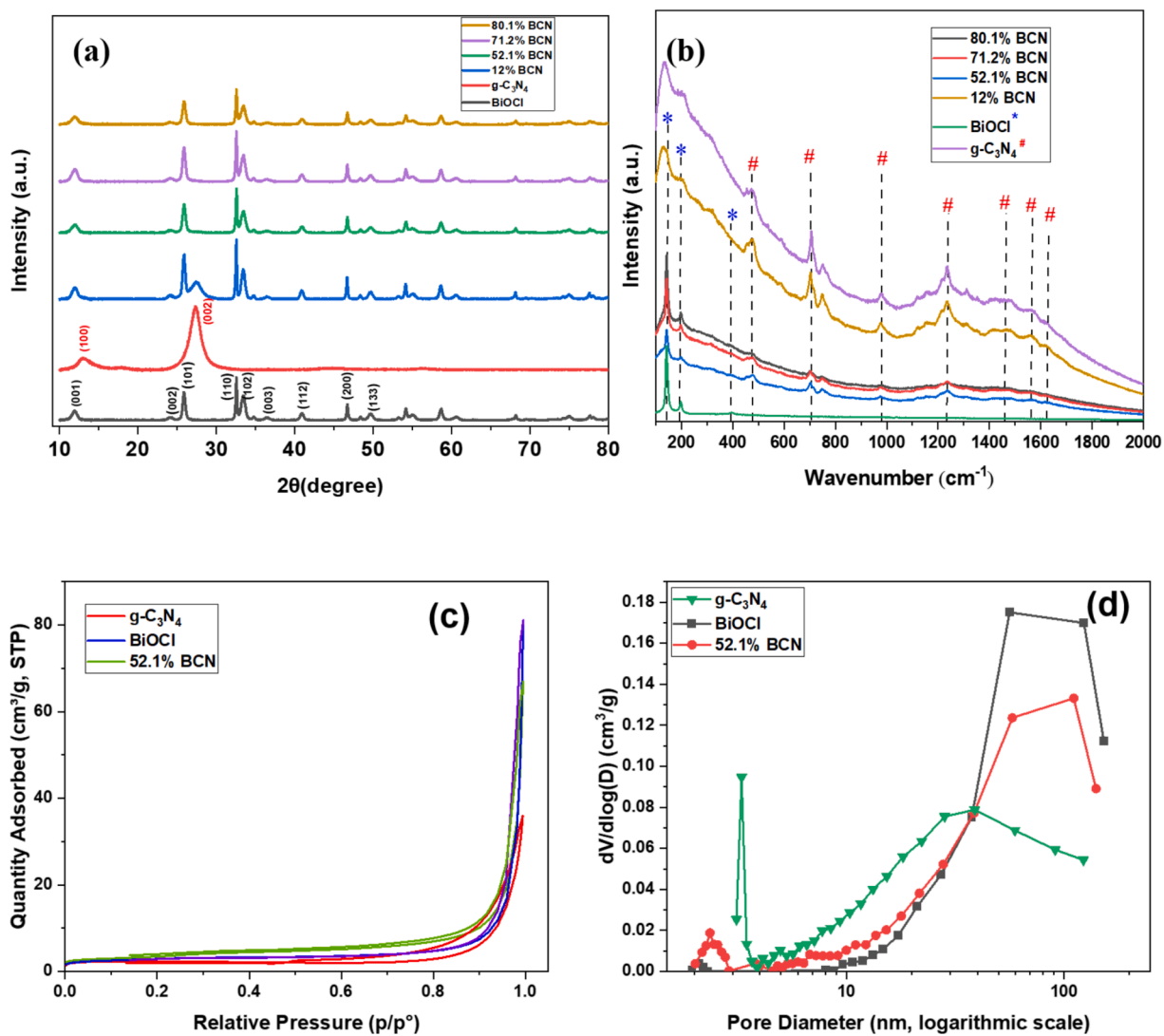


Fig. 2. Characterization of the synthesized materials: (a) XRD patterns, (b) Raman spectra of all the materials; (c) N_2 sorption isotherm, and (d) BJH pore-size distribution of $g-C_3N_4$, BiOCl and 52.1 % BCN.

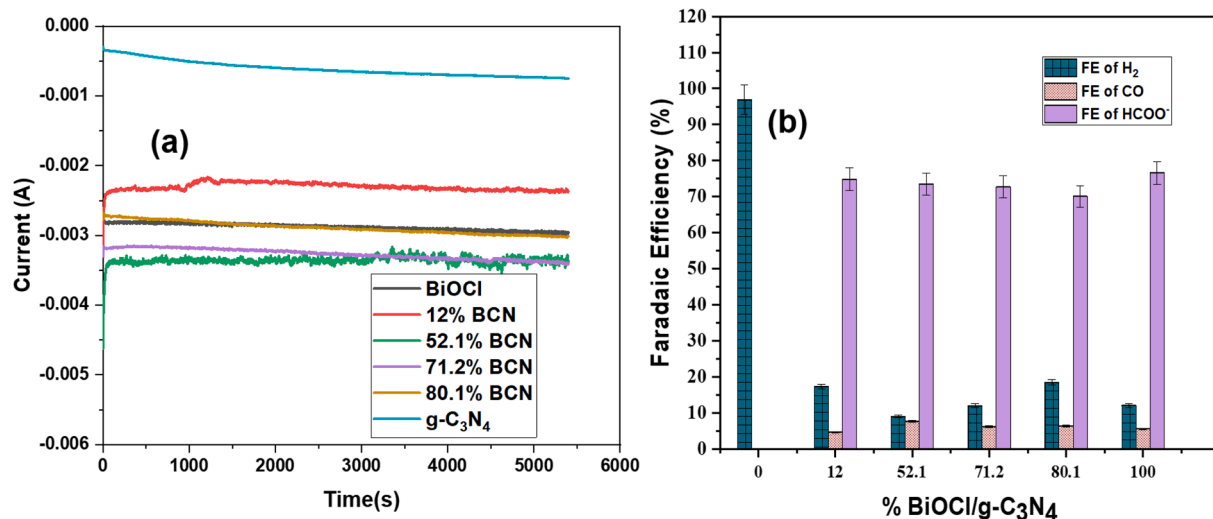


Fig. 3. Electrochemical CO₂ reduction tests at -1.06 V vs RHE for 5400 s using gas-tight cell (a) CA analyses. (b) FEs of different products H₂, CO, and HCOO⁻ of all the catalysts with CA analysis of 5400 s.

> 80 % whereas cadmium and lead catalysts equated for < 80 % [10]. Bismuth-based materials have high selectivity for formate; synthesis strategies enhancing their activity and selectivity [11–15], with control of the morphology to expose most of the active facets [16] have been described. Among the bismuth oxyhalides i.e. BiOX (X = Cl, Br, and I), BiOCl is seen to have much interest for eCO₂RR. It was studied in 2021 by Hsieh et al. that Pd-doped BiOCl nanosheets, prepared by a wet-chemical approach, had an FE of 30 % for HCOO⁻ from eCO₂RR [17]. BiOCl was transformed into its subcarbonate chloride form by electro-reduction which accounted for 97.9 % of FE for formate while pure Bi₂O₂CO₃ accounted for 81.3 % FE for formate [18]. In another study, N-doped carbon with BiOCl dispersed resulted in 84.3 % of FE for formate [19]. g-C₃N₄ is a type of carbon-nitride that has a 2D lamellar polymeric structure comprising triazine and heptazine rings. It is a widely used semiconductor in photocatalysis [20]. However, recent studies can be seen where its electrocatalytic role has also been explored [20–22]. Nazir et al. in 2020 reported the use of carbon-nitride based nanocomposites for the production of formic acid by eCO₂RR. It was found that g-C₃N₄/CuAg/Cu₂O had higher selectivity for formic acid when compared to g-C₃N₄/Cu/Cu₂O [23]. Cu-doped carbon-nitride was reported for electrocatalytic Oxygen Reduction Reaction (ORR), showing good electrocatalytic response as a cathode in an alkaline environment. It showed an onset potential of 0.92 V vs RHE with long-term durability and less than 4 % H₂O₂ formation as compared to Pt/C. Such behavior was attributed to the strong interaction between the Cu-N_x active sites and the C₃N₄ matrix [24]. The increment in the catalyst's durability was reported when using g-C₃N₄ and Pd-aided nanocomposites and was reported to have only 8 % activity loss as compared to 45 % loss demonstrated by commercial 10 wt% Pt/C in Oxygen Reduction Reaction (ORR) [25].

Despite extensive research on bismuth-based materials, nanocomposites of BiOCl with g-C₃N₄ haven't been reported yet on their electrocatalytic activity for eCO₂RR. In this work, a range of BiOCl/g-C₃N₄ composites have been synthesized, as well as morphologically, structurally and chemically characterized, and tested for their eCO₂RR activity. Uniform distribution of the oxychloride nanoplates over the g-C₃N₄ surface is desired to expose more active sites for CO₂ reduction fostering the catalytic activity.

2. Experimental

2.1. Materials used

Melamine (CAS Number 108–78-1, Sigma-Aldrich), Bi(NO₃)₃·5H₂O (CAS Number 10035–06-0, Chempur), NaCl (CAS Number 7647–14-5, Fluka), Glycine (CAS Number 56–40-6, Fluka), Nafion™ 117 (CAS Number 31175–20-9, Sigma-Aldrich) were all purchased in reagent grade and used without further purification. KHCO₃ (CAS Number 298–14-6, 99.999 %) was purchased from Sigma-Aldrich.

2.2. Synthesis procedure

BiOCl: 23.376 mg of NaCl was dissolved in 10 mL of bi-distilled water and was heated to 90 °C. To it, 194.028 mg of Bi(NO₃)₃·5H₂O in 5 wt% glycine solution was added dropwise. The reaction mixture was reacted at 90 °C at 400 rpm for 2 h. A pearl-white precipitate was obtained which was washed three times with bi-distilled water and once with ethanol. The material was then dried in a vacuum oven at 40 °C for 16 h.

g-C₃N₄: It was prepared according to a procedure reported in the literature [26] using melamine decanted in a half-covered crucible and directly heating it at 550 °C for 3 h under static air in a muffle furnace. The obtained powders were then ball-milled for 20 min at 20 Hz, sieved, and washed with bi-distilled H₂O and ethanol.

2.2.1. BiOCl/g-C₃N₄ composite

Sol A: in a round bottom flask containing 10 mL bi-distilled water, 23.376 mg of NaCl and the required amount of g-C₃N₄ were stirred and sonicated for 2 h.

Sol B: in a beaker, 194.028 mg of Bi(NO₃)₃·5H₂O was stirred in 10 mL 5 wt% glycine solution.

Sol A was heated till 90 °C and then Sol B was added dropwise to it. The reaction mixture was reacted at 90 °C for 2 h. The precipitate was washed three times with bi-distilled water and once with ethanol, and then dried under vacuum at 40 °C for 16 h. Thus, the obtained composites were 12 wt% BiOCl/g-C₃N₄ (12 % BCN), 52.1 wt% BiOCl/g-C₃N₄ (52.1 % BCN), 71.2 wt% BiOCl/g-C₃N₄ (71.2 % BCN) and 80.1 wt% BiOCl/g-C₃N₄ (80.1 % BCN).

2.3. Structural and morphological characterization

The morphology of the synthesized materials was investigated by

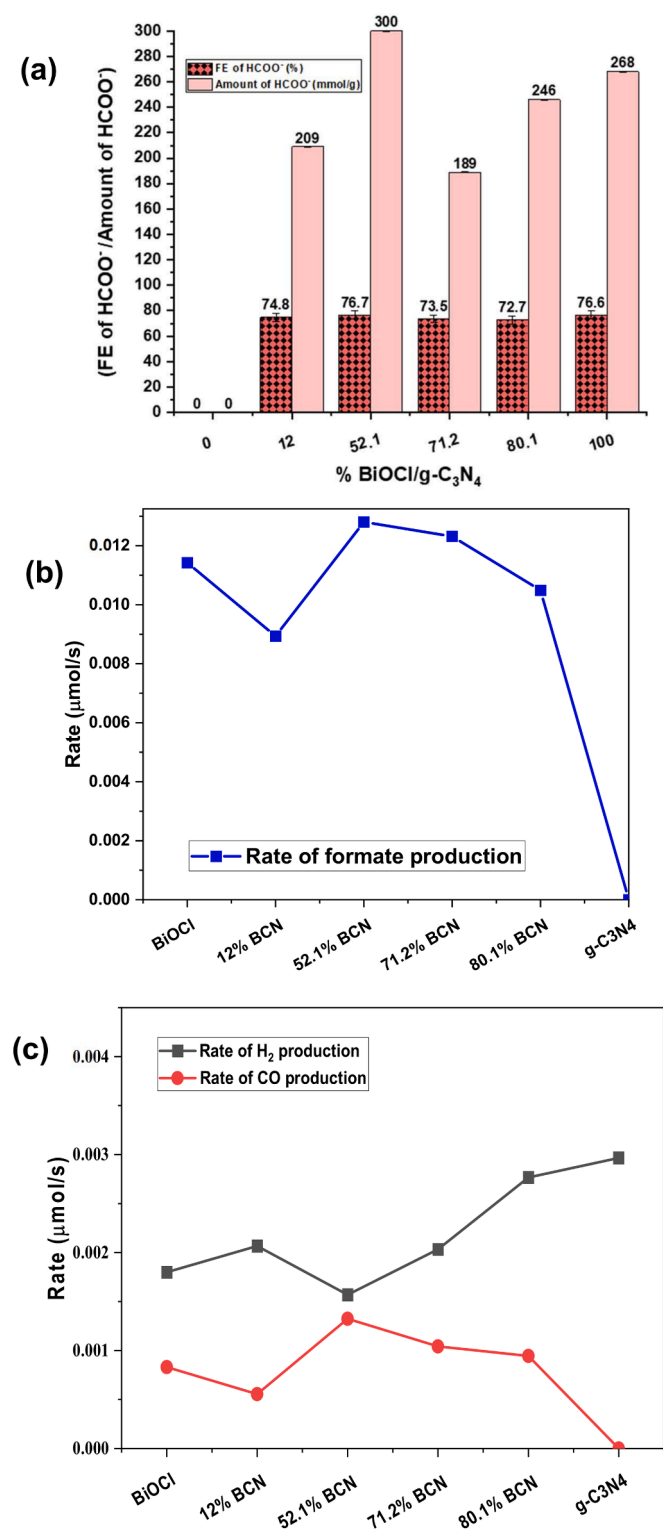


Fig. 4. Electrochemical CO₂ reduction tests at -1.06 V vs RHE for 5400 s using gas-tight cell (a) FE and amount of HCOO⁻ for all the catalysts. (b) Rate of formate production for all the different catalysts. (c) Rate of H₂ and CO production for all the different catalysts.

Scanning Electron Microscopy (SEM) using Nova NanoSEM 450 at an accelerating voltage of 5 kV. X-ray Diffraction (XRD) study was carried out to understand the crystalline nature of the catalysts on PANalytical X'Pert Pro MPD instrument with Cu K α radiation ($\lambda = 0.1541$ nm). Raman spectra were acquired using an Invia Reinshaw spectrometer

equipped with a diode laser ($\lambda = 785$ nm). N₂ physisorption was performed with a Micrometrics ASAP 2020 analyzer at liquid nitrogen temperature. All the catalysts were degassed at 120 C for 12 h before analysis. The specific surface area was calculated by applying the BET equation. Pore size distributions were determined with the desorption branch of the isotherms with the Barrett-Joyner-Halenda (BJH) method. XPS analysis was carried out employing an in-house built apparatus consisting of an analysis chamber operated in a base pressure of about 1×10^{-9} mbar for these experiments, a hemispherical analyzer (VSW-HA100) equipped with a 16-channel detector which was operated in normal incidence and was served by a differential pumping system. The employed source is a non-monochromatic Al K α (1486.7 eV, VSW-TA10). Samples were insulated to avoid differential charging using Kapton foils [27]. The analysis was carried out cooling down the system to 160 K using liquid nitrogen to minimize the thermal degradation of the samples. The Infrared (IR) spectra were recorded with an Affinity-1 S Shimadzu FT-IR, equipped with a QATR accessory, diamond crystal.

2.4. Electrochemical measurements

The electrochemical measurements were carried out in two types of cells at room temperature. For the analysis of the gaseous products, a gas-tight cell connected to an online gas chromatography unit was used. This homemade cell, designed on the model of the commercial prototype Dr. BobTM cell, has the anodic compartment separated from the cathodic compartment via a glass tube equipped with a VycorTM frit. A Pt wire (1.00 mm thick, 99.9 % purity, Sigma Aldrich) serves as the counter electrode inserted in the glass tube containing the electrolyte. Ag/AgCl (KCl_{SAT}) and a carbon paper electrode (Toray Carbon Paper, R 2.5 x 0.5 cm) serve as the reference and working electrode support respectively. 12 mL of the electrolyte contained in the single compartment of the cell was purged in with Ar or CO₂ at a flow rate of 20 mL min⁻¹ for 25 min before starting the electrochemical measurements. This was done to saturate the electrolyte with the respective gases. The same flow rate was later maintained for the electrochemical measurements as well. Another type of three-electrode cell, equipped with a Rotating Disc Electrode (RDE, Autolab, diameter = 5 mm) was used for the preliminary electrochemical characterization. This three-electrode configuration contained a saturated calomel electrode (SCE) as the reference electrode and Pt as the counter electrode. The RDE glassy-carbon electrode with fixed area (0.19 cm²) served as the working electrode support. 0.1 M KHCO₃ was used as the electrolyte for this setup as well. The electrochemical experiments were performed using a Metrohm Autolab PG302N electrochemical workstation. Moreover, the difference in performance of the catalysts in the two different cells was also investigated (Fig. S5).

The preliminary electrochemical characterization was evaluated using linear sweep voltammetry (LSV) in the potential range of 0 V to -1.1 V vs RHE using the RDE setup described in Fig. S1. Before such electrochemical measurements, cyclic voltammetry (CV) scans were carried out sweeping across a potential range of 0 V to -0.8 V vs RHE with a scan rate of 0.1 V/s. This was necessary to ensure the removal of any additional species covering the electrode surface. Then, the LSVs were recorded at a rotation speed of 1600 rpm with 5 mV/s as scan rate in Ar and CO₂ saturated electrolyte. The Ar saturated electrolyte served as a blank test to the CO₂ atmosphere.

3. Results and discussion

3.1. Characterization of catalysts

The morphological information of the prepared materials can be obtained by SEM analysis. BiOCl was formed as irregular aggregated nanoplates with an average diameter of 105 nm and a mean thickness of 17 nm (Fig. 1a) while g-C₃N₄ was present in its bulk form with aggregated sheets (Fig. 1b). SEM analysis of BiOCl/g-C₃N₄ nanocomposites

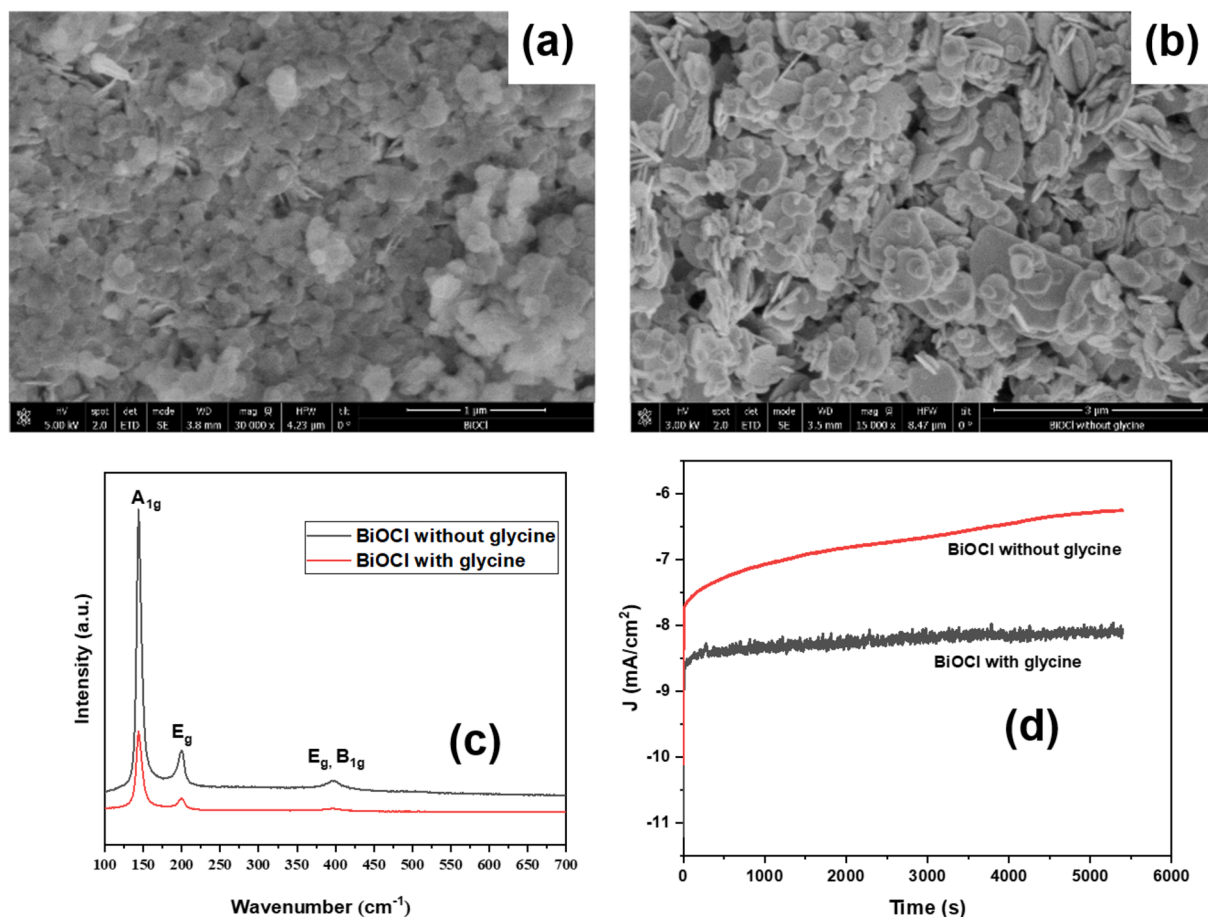


Fig. 5. (a) SEM image of BiOCl nanoplates synthesized with glycine. (b) SEM image of BiOCl microplates synthesized without glycine. (c) Raman spectra showing the correct formation of BiOCl without glycine. (d) CAs of BiOCl with and without glycine with scan interval of 1 s.

(Fig. 1c-f) showed that g-C₃N₄ particles are homogeneously covered by BiOCl nanoplates, irrespectively from the composition of the material.

The formation of the pure form of BiOCl can be confirmed by the proper indexing of XRD patterns (Fig. 2a) to the tetragonal phase of BiOCl with reflections appearing at $2\theta = 11.9^\circ$ (001), 24.09° (002), 25.9° (101), 32.5° (110), 33.4° (102), 34.7° (111), 36.5° (003), 40.9° (112), 46.6° (200), 48.4° (201), 49.7° (113) (JCPDS card no. 06-0249) [19]. The crystalline structure of g-C₃N₄ was also confirmed with the XRD spectrum. The reflections indexed at 12.95° and 27.34° corresponded to the (100) plane of characteristic packing of tri-s-triazine units and (002) facet of graphitic structure respectively [26]. As seen in Fig. 2a, the XRD patterns of both g-C₃N₄ and BiOCl are evident in the formation of composites. However, a progressive decline in the intensity of g-C₃N₄ reflections in the composite materials is justifiable due to the higher scattering properties of heavy atoms of BiOCl. It must be underlined that, in all the patterns related to BiOCl phase, the (*hkl*) reflections with $l = 0$ (directions orthogonal to *c* axis) show very sharper peaks with respect to the reflections with $l \neq 0$. This is an indication of formation of BiOCl nanoplates elongated along the *a* and *b* directions and thinned along the *c* direction. This result is consistent with the nanoplates' formation observed by SEM.

Raman spectroscopy was carried out for all the different materials under 785 nm excitation. Fig. 2b shows the Raman active modes of BiOCl as well as g-C₃N₄. BiOCl has its strong bands existing at 142 cm^{-1} and at 198 cm^{-1} which can be assigned to A_{1g} internal Bi-Cl stretching mode and E_g external Bi-Cl stretching mode, respectively. The weak signal at 396 cm^{-1} signifies E_g and B_{1g} vibration modes produced by the motorial oxygen atoms of the oxyhalide [28]. The intensity of the respective peaks appears to diminish in the composites with the decrease

in their respective loadings. Moreover, for g-C₃N₄ the characteristic peaks can be observed in all the composites. The peak at 1232.8 cm^{-1} can be ascribed to sp² carbon bending vibration and the pair of peaks at 753.7 cm^{-1} and 703.4 cm^{-1} to the layer-layer deformation vibrations of g-C₃N₄ were also evident [29]. The characteristic D band and G band of g-C₃N₄ can also be found at peaks 1480.2 cm^{-1} and 1560.7 cm^{-1} , respectively [30].

N₂ sorption analysis at the liquid nitrogen temperature of pristine g-C₃N₄, BiOCl and the composite 52.1 % BCN shows type IV isotherm with H3 hysteresis loop (Fig. 2c). BET surface areas were calculated, showing a surface area of $12\text{ m}^2\text{ g}^{-1}$ for the composite material as compared to the pristine g-C₃N₄ and BiOCl with surface areas of $8\text{ m}^2\text{ g}^{-1}$ in both cases. These values confirm the synergy between BiOCl and g-C₃N₄ is crucial to improve the properties of nanocomposites with respect to the pristine counterparts. Despite low surface areas, pore size distribution (Fig. 2d) showed a broad distribution, ranging from 2 to 200 nm, suggesting the formation of mesopores as well as macropores [31]. It can be noted that the mesoporosity is higher in the composite 52.1 % BCN than in BiOCl and in g-C₃N₄. This synergistic presence of *meso* and *macro*-pores in a proper balance could positively affect the performance of the catalysts in obtaining the aimed efficiency and product yield. Thus, in the case of the composite 52.1 % BCN, the observed bimodal pore structure in the layer of the electrocatalyst could provide a disparity of pressure. This means that the bimodal structure of the pores allows the presence of pressure difference on the electrode surface. It enables the liquid reactant to diffuse into the surface of the electrocatalyst layer, which therefore enhances the electrocatalytic activity with this characteristic. Thus, the liquid reactant i.e. CO₂ saturated 0.1 M KHCO₃ could diffuse into the electrocatalyst layer more easily reducing the

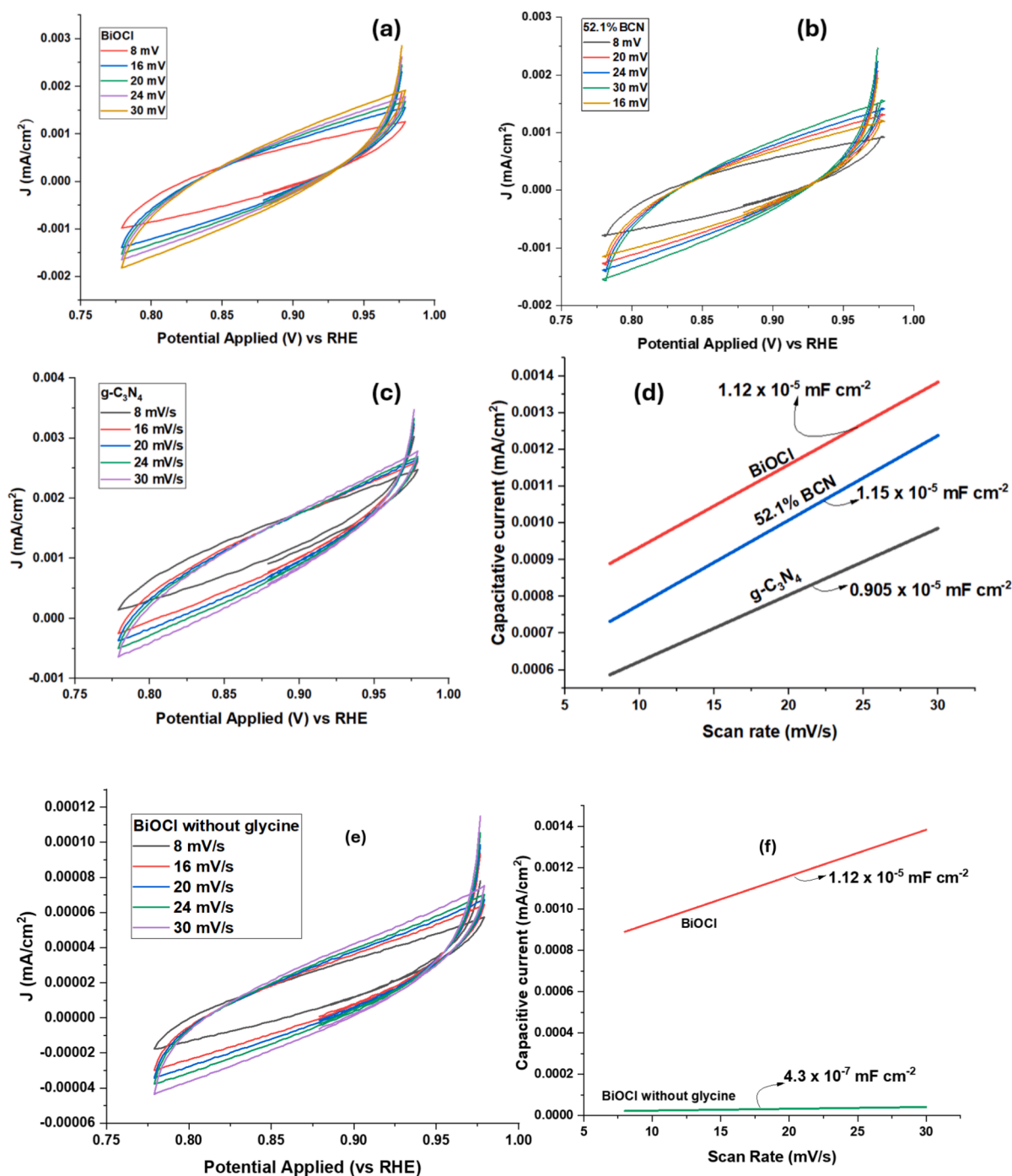


Fig. 6. CV scans across potentials 0.77 V to 0.97 V with non-faradaic process for (a) BiOCl, (b) 52.1 % BCN, (c) g-C₃N₄ (e) BiOCl without glycine (d) Capacitive current density plots at different CV scan rates; the current densities were obtained from double-layer charge/discharge curves at 0.88 V vs RHE. (f) Capacitive current density plot for BiOCl and BiOCl without glycine.

liquid sealing effect [32].

3.2. CO₂ electroreduction tests

The CO₂ electroreduction performances have been evaluated for BiOCl, g-C₃N₄, and all the other composites (12 % BCN, 52.1 % BCN, 71.2 % BCN, 80.1 % BCN). Fig. S1 provides the LSV curves for all the materials in Ar and CO₂ atmosphere conducted in the RDE set-up. We can note the increase in the current density in the CO₂-saturated 0.1 M KHCO₃ as compared to the inert atmosphere. This increment in the cathodic current densities can be attributed to the potential catalytic

activity in eCO₂RR. The onset potential, as observed from the LSVs for BiOCl (Fig. S1), was determined to be -0.81 V vs RHE whereas for 52.1 % BCN the value equaled -0.67 V vs RHE. Considering the onset potentials, CA analyses were recorded at -0.86 V and -1.06 V vs RHE to evaluate the behavior of the catalysts in eCO₂RR. Applying -0.86 V and -1.06 V vs RHE, a CA of 5400 s was recorded in the case of BiOCl and 52.1 % BCN by the RDE set-up as a preliminary investigation (Fig. S2). HCOO⁻ was detected as the liquid product analyzed by ion chromatography. At -0.86 V vs RHE, the FE_{HCOO} values of BiOCl and 52.1 % BCN were 76 % and 26 % and the amounts of HCOO⁻ produced were 39 and 19 mmol g⁻¹ h⁻¹, respectively. At -1.06 V vs RHE, the FE values of BiOCl

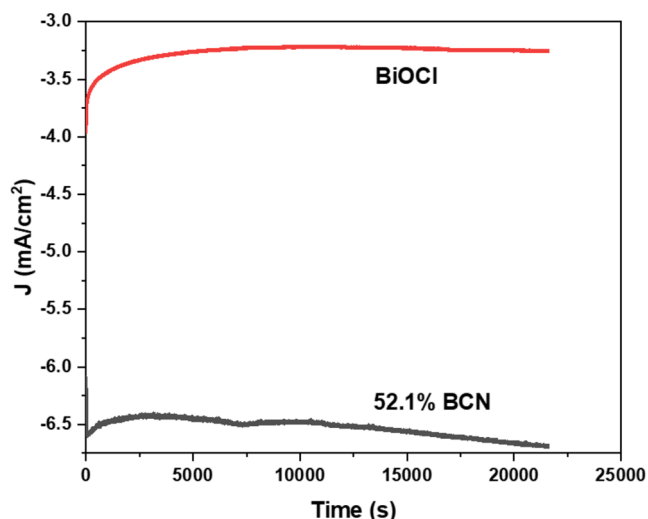


Fig. 7. Chronoamperometry curves of 52.1 % BCN composite and BiOCl for 6 h with 0.1 M KHCO₃ electrolyte with glassy carbon electrode with a scan interval of 5 s.

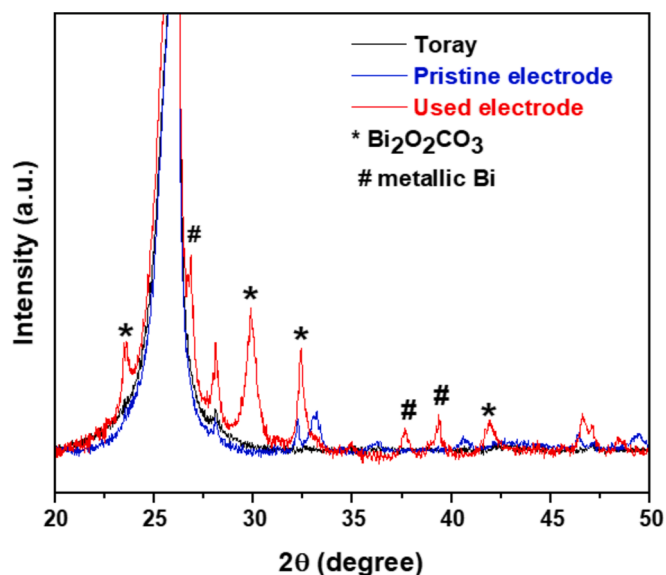


Fig. 8. XRD patterns of Toray carbon paper, BiOCl on Toray carbon paper electrodes before CA and after CA duration of 2 h. Conditions: -1.06 V vs RHE, 0.1 M KHCO₃ electrolyte, three-electrode gas-tight cell. The used electrode was secured with Kapton tape to avoid any air contact. In the spectra, the asterisk (*) represents the reflections corresponding to Bi₂O₂CO₃ and that of hash mark (#) represents the reflections corresponding to metallic Bi.

Table 1

XPS analysis with ratio determination of Bi/O and Bi/Cl [41–47].

Sample	Bi/O	Bi/Cl
BiOCl powder	1.0	1.3
52.1 % BCN powder	1.0	1.3
BiOCl before LSV	1.3	1.3
52.1 % BCN before LSV	1.3	1.1
BiOCl post LSV	1.0 (0.30 with OH/CO ₃ component)	–
52.1 % BCN post LSV	1.2 (0.90 with OH/CO ₃ component)	–
BiOCl post catalysis	1.5 (0.50 with OH/CO ₃ component)	–
52.1 % BCN post catalysis	2.0 (0.50 with OH/CO ₃ component)	–

Table 2

XPS results and binding energies (B.E.) of the fitting curves with species identification.

Sample	Bi 4f _{7/2;5/2} (eV)	Cl 2p _{3/2;1/2} (eV)	O 1s (eV)
BiOCl powder	159.5;164.8 Bi ³⁺ BiOCl [41–43] 159.0;164.3 Bi ³⁺ Bi ₂ O ₃ [41]	198.2; 199.8Cl ⁻ [43,44]	530.4 Bi-O [43,47,49] 532.1 Bi-OH/Bi-CO ₃ [43,47,49]
52.1 % BCN powder	157.6;162.9 Bi ³⁺ [41,48] 159.4;164.7 Bi ³⁺ BiOCl 158.9;164.2 Bi ³⁺ Bi ₂ O ₃	198.2; 199.8Cl ⁻	530.4 Bi-O 532.1 Bi-OH/Bi-CO ₃ 530.5 Bi-O 532.7 water 534.7 polymer [45,46]
BiOCl before LSV	159.7;165.0 Bi ³⁺ BiOCl	198.2; 199.8Cl ⁻	530.5 Bi-O 532.7 water 534.7 polymer
52.1 % BCN before LSV	159.6; 164.9 Bi ³⁺ BiOCl	198.2; 199.8Cl ⁻	530.5 Bi-O 532.8 water 534.7 polymer
BiOCl post LSV	159.7;165.0 Bi ³⁺ compound 158.5; 163.8 Bi ³⁺ Bi ₂ O ₃	–	530.5 Bi-O 531.8 Bi-OH/Bi-CO ₃ 533.8 polymer 530.5 Bi-O
52.1 % BCN post LSV	159.5;164.8 Bi ³⁺ 158.8;164.1 Bi ³⁺ Bi ₂ O ₃	198.2; 199.8Cl ⁻	531.8 Bi-OH/Bi-CO ₃ 534.7 polymer 530.5 Bi-O
BiOCl post catalysis	159.6;164.9 Bi ³⁺ compound	–	531.9 Bi-OH/Bi-CO ₃ 534.0 polymer
52.1 % BCN post catalysis	160.1;165.4 Bi ³⁺ compound	–	530.6 Bi-O 531.9 Bi-OH/Bi-CO ₃ 534.7 polymer

and 52.1 % BCN were 52 % and 82 %, and subsequently the amounts of HCOO⁻ were 609 and 670 mmol g⁻¹h⁻¹, respectively. From the values obtained with preliminary tests, it can be understood that 52.1 % BCN performs with the highest FE and HCOO⁻ production value at -1.06 V vs RHE. Fig. S3 provides the CA carried out for 3600 s and FE values of 52.1 % BCN in a gas-tight cell to confirm the evolution of products as a result of eCO₂RR by using Ar atmosphere as a blank. Along with HCOO⁻, H₂ and CO also evolved in CO₂ atmosphere while only H₂ evolved in the case of Ar. Therefore, considering -1.06 V as the optimized potential, in the following section, analysis of the products and the determination of their FE values varying with the variation in the composite composition are investigated.

To obtain a better understanding of the efficiency and selectivity properties of the prepared electrocatalysts, CA in CO₂-saturated atmosphere (Fig. 3a) at a constant potential of -1.06 V vs RHE were performed for all the different composites as well as the pristine BiOCl and g-C₃N₄ in the gas-tight cell for 5400 s. For the quantitative analyses of the products evolved, gas chromatography and ion chromatography analyses were carried out at the end of those electrochemical measurements at 5400 s. The catalysts were seen to form HCOO⁻ as the major product and H₂ and CO as minor products. The selectivity of the products' formation was particularly high for formate accounting for 70 % to 77 % (Fig. 3b) with H₂ and CO just forming minimal amounts. For H₂, the value ranges from 9–19 % for all the catalysts except g-C₃N₄ which is equal to 96 %. Similarly, the FE values for CO range from 1–2 % for all the catalysts except g-C₃N₄ for which there is no production of CO. Among all the catalysts, noting the similar FE values for HCOO⁻, the product yield was calculated. 52.1 % BCN produced the highest yield of HCOO⁻ equating to 200 mmol g⁻¹h⁻¹ as compared to all the other catalysts as shown in Fig. 4a, in addition to possessing the highest current values (Fig. 3a). Pristine BiOCl produced 179 mmol g⁻¹h⁻¹ under the same conditions. Moreover, in the case of the composite 52.1 % BCN, the uniform distribution of the oxychloride nanoplates over g-C₃N₄ allows for increased availability for the electrolyte-catalyst interaction, directly

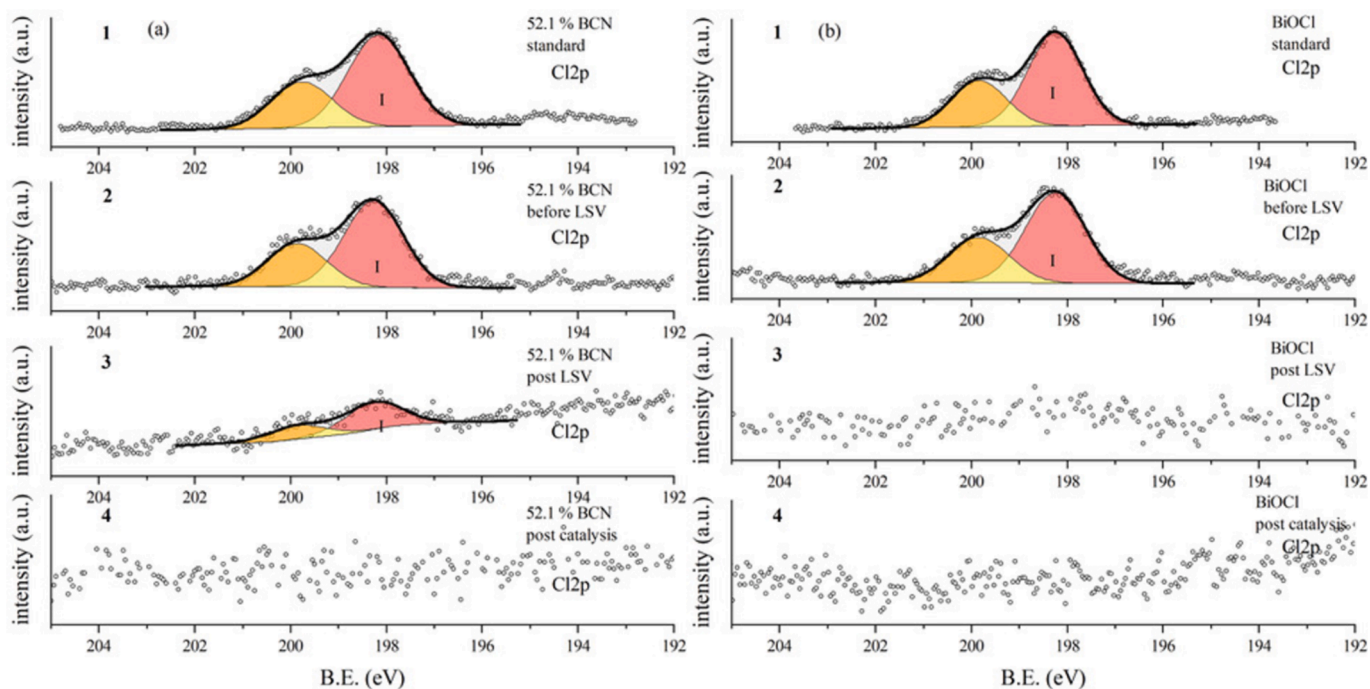


Fig. 9. XPS analysis of Cl 2p spectra of (a) 52.1% BCN and (b) BiOCl in the different stages of eCO₂RR including (1) powdered catalyst, (2) dropcast on carbon paper before LSV measurement, (3) post-LSV, and (4) post-catalysis.

affecting the production rates of the products shown in Fig. 4b and 4c. The variation in the composite percentages instigated an effective distribution allowing for sufficient exposure of the active sites of the nanoplates. This can be attributed to the availability of sufficient facets of BiOCl exposed in the catalysts. Pristine BiOCl nanoplates observed in the SEM images were seen to agglomerate which also resulted in lesser surface area as confirmed by N₂ adsorption-desorption isotherm. In addition, the composites with a higher percentage of BiOCl (71.2 %, 80.1 %) had a lower rate of reaction as well as a lower amount of produced formate. This can be attributed to the over-saturation of the nanoplates on the g-C₃N₄ surface disallowing sufficient exposure of the active facets to the CO₂-infused electrolyte.

An interesting electrocatalytic difference was noted for BiOCl which was synthesized with and without the size-controlling agent, glycine. Fig. 5a and 5b compare representative SEM images collected for BiOCl synthesized with and without glycine. It's evident that glycine is crucial to limit the growth of nanocrystal, forming microplates when glycine is not used. BET surface area of BiOCl microplates and nanoplates were very similar (8 m² g⁻¹). However, BiOCl microplates possess a lower pore volume as a result of a pore size distribution centered at larger diameter (Fig. S6). Moreover, as seen in Fig. 5c, BiOCl synthesized without glycine has a higher intensity in the Raman spectra if compared to BiOCl synthesized with glycine, which explains the higher crystallites formed in the case of the BiOCl microplates. IR spectroscopy was carried out for BiOCl synthesized with glycine, BiOCl synthesized without glycine, and pure glycine (Fig. S8). The signal at 3554 cm⁻¹ and 1630 cm⁻¹ for BiOCl synthesized without glycine and at 3559 cm⁻¹ and 1618 cm⁻¹ for BiOCl synthesized with glycine can be attributed to OH symmetrical stretching and scissoring, respectively. The signals located at 511 cm⁻¹ and 493 cm⁻¹ can be ascribed to Bi-O bonds and the signals at 1445 cm⁻¹ and 1395 cm⁻¹ can be attributed to stretching vibrations of BiOCl for BiOCl synthesized with and without glycine respectively. Again, in the case of pure glycine, the signal at 3150 cm⁻¹ can be ascribed to NH₃⁺ stretching vibrations. The signal at 1495 cm⁻¹ can be attributed to symmetric stretching of COO⁻ group. Again, 1324, 692, 493 cm⁻¹ can be attributed to CH₂ twisting, COO⁻ bending and COO⁻ rocking respectively. The signals at 1108, 1029, 891 and 606 cm⁻¹ can

be ascribed to NH₃⁺ rocking, CCN asymmetric stretching, CCN symmetric stretching and COO⁻ wagging vibrations respectively [33,34]. It has been reported in literature studies that the presence of amino acids could facilitate the adsorption of CO₂ with the presence of N sites. However, in the case of BiOCl synthesized with glycine, the NH₃⁺ stretching and rocking vibrations are absent which excludes the contribution of glycine in eCO₂RR [35].

To compare the current densities between both catalysts, a WE with a fixed geometrical area of 0.19 cm² was used. The obtained current densities with the CA analyses have been shown in Fig. 5d. A clear difference in the current densities is seen with a higher value for BiOCl synthesized with glycine if compared to the one without. The FEs were calculated for both cases as well as the amount of HCOO⁻ was calculated. This setup wasn't gas-tight due to which the evaluation of gaseous products was not possible. BiOCl synthesized with the size-controlling agent produced nanoplates forming 957 ± 2 mmol g⁻¹h⁻¹ of formate with 85 % of FE while BiOCl synthesized without it produced 39 ± 2 mmol g⁻¹h⁻¹ of HCOO⁻ with 4 % of FE after 5400 s of C.A. at -1.06 V vs RHE. This can be attributed to the nano-structuring of BiOCl and effective size tuning (Fig. 5a and 5b) which has been proven to affect the adsorption of CO₂ as studied by Liu et al. in 2021 [36]. It must be considered that productivity values in mmol g⁻¹h⁻¹ are reported for comparison with the reported literature since current values are not constant in all the chronoamperometries throughout the work.

The Electrochemical Surface Area (ECSA) for the pristine material i. e. BiOCl, BiOCl synthesized without glycine, g-C₃N₄ and 52.1 % BCN were evaluated using the glassy carbon electrode with fixed geometrical area (0.19 cm²). The CV measurements were recorded in 0.1 M KHCO₃ electrolyte which was Ar saturated with the electrode at 1200 rpm as shown in Fig. 6. The scan rates to carry out the CV response of the prepared electrodes were 8 mV/s, 16 mV/s, 20 mV/s, 24 mV/s, and 30 mV/s across a potential range from 0.77 V to 0.97 V vs RHE. This potential range was chosen to avoid the contribution of any faradaic processes. Further, the ECSA was calculated as follows:

$$ECSA = R_f * S \quad (3)$$

where R_f denotes the roughness factor. It is defined as the ratio of the

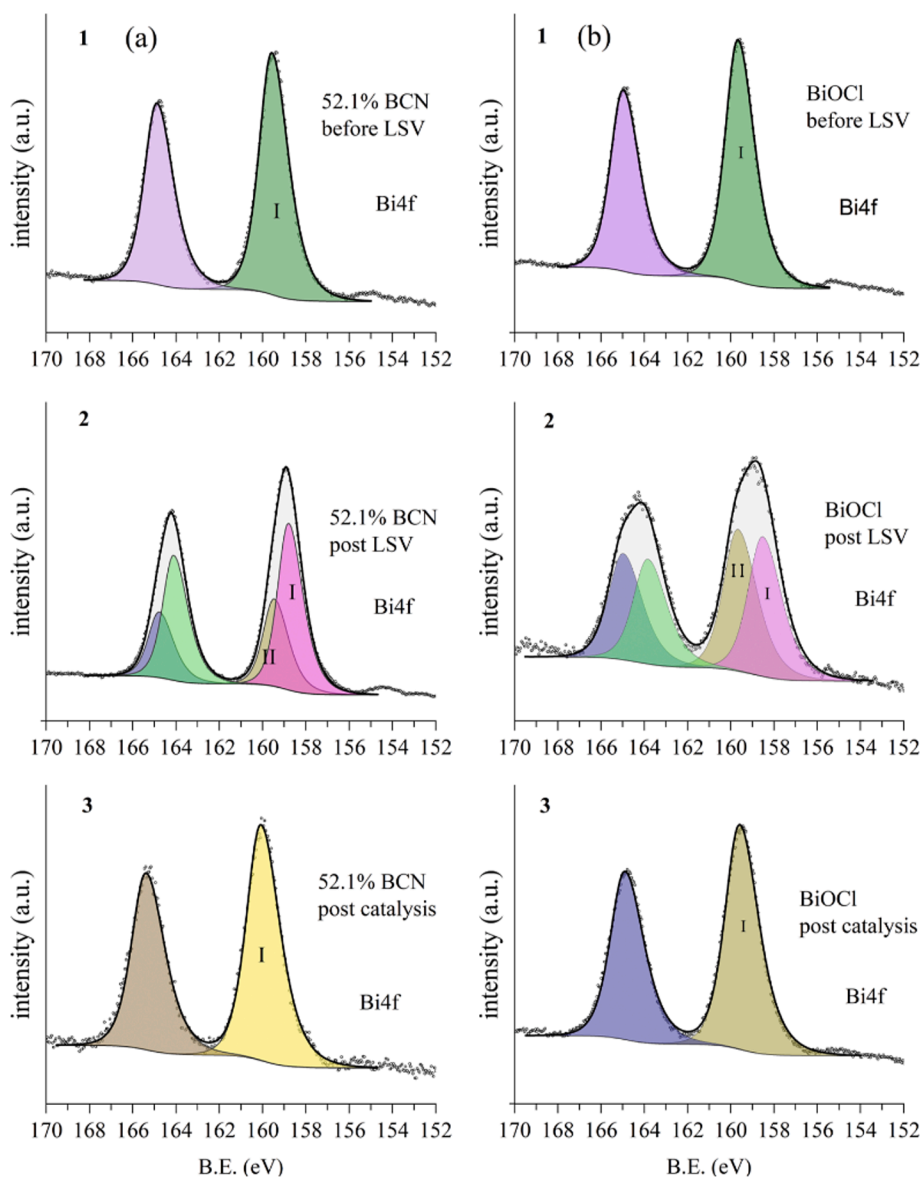


Fig. 10. XPS analysis of Bi 4f spectra of (a) 52.1% BCN and (b) BiOCl in the different stages of eCO₂RR including (1) catalyst dropcast on carbon paper before LSV measurement, (2) post-LSV, and (3) post-catalysis.

double layer capacitance C_{dl} of the working electrode to that of the corresponding smooth glassy carbon electrode. S represents the geometrical surface area of the smooth glassy carbon electrode support. The C_{dl} value can be determined by establishing a linear relationship between $\Delta j = (j_a - j_c)$, where j_a and j_c denotes the anodic and cathodic current density, respectively, considering the values at the scan rate at 0.88 V vs. RHE. The C_{dl} value of the smooth glassy carbon was determined to be $0.65 \times 10^{-5} \text{ mF cm}^{-2}$. Fig. 5a, 5b, 5c and 5e show the various CV scans carried out at the scan rates mentioned above for BiOCl, BiOCl synthesized without glycine, 52.1 % BCN, and g-C₃N₄ respectively. We determined the R_f values to be 1.73, 0.06, 1.39, and 1.77 while ECSA values to be 0.33 cm^2 , 0.01 cm^2 , 0.26 cm^2 , and 0.34 cm^2 for BiOCl, BiOCl synthesized without glycine, g-C₃N₄, and 52.1 % BCN, respectively. Moreover, CO₂ adsorption studies were carried out at 304 K and BiOCl was seen to have a higher adsorption isotherm followed by 52.1 % BCN and then g-C₃N₄ (Fig. S7). It must be taken into account that these studies involve CO₂ adsorption, where CO₂ in its gas phase is adsorbed on the solid surface of the catalyst. However, it has been reported that eCO₂RR involves the interaction of carbonic acid with the solid catalysts [37,38].

Additional electrochemical CO₂ reduction processes such as extended duration CA were recorded and the catalyst on the formation of the composite was also tested. The CA curves are shown in Fig. 7. The glassy carbon-based electrode support was used for these studies where the same electrode was used for 6 h of continuous bias application. CAs were run at -1.06 V vs RHE in CO₂-saturated 0.1 M KHCO₃ with the pristine BiOCl and the composite 52.1 % BCN. FE values of BiOCl and 52.1 % BCN equaled 77 % and 73 % with HCOO⁻ amounts equivalent to $357 \pm 1 \text{ mmol g}^{-1}\text{h}^{-1}$ and $678 \pm 1 \text{ mmol g}^{-1}\text{h}^{-1}$ with CA for 6 h, respectively.

3.3. Post-characterization of the catalysts

To gain insight into the structural and morphological information of the catalyst, post-eCO₂RR characterization was carried out. Characterization techniques such as XRD and XPS were employed for the pristine BiOCl and the composite 52.1 % BCN.

XRD patterns have been collected on the BiOCl carbon paper electrodes pre-catalysis and post-catalysis and were compared with the pristine BiOCl material (Fig. 8). It must be underlined that the post-

catalysis electrode was immediately sealed within two Kapton adhesive tapes to avoid long exposure to air. The XRD pattern of the post-catalysis electrode indicates the presence of $\text{Bi}_2\text{O}_2\text{CO}_3$ as well as metallic Bi. The reflections at 12.59, 23.64, 25.74, 30.03, 32.50, 39.10, 42.05, 46.75, 51.97, and 54.27 can be indexed to (002), (011), (004), (013), (110), (006), (114), (020), (121), and (123) of $\text{Bi}_2\text{O}_2\text{CO}_3$ [39]. Similarly, the reflections at 27.12, 38.03, and 39.67 can be attributed to (012), (104), and (110) crystallographic planes of metallic Bi (JCPDS 05–0519) [40]. Additional peaks appearing in the spectra are attributed to the non-subtracted peaks of carbon Toray paper. It must be also acknowledged that the ex-situ XRD technique limits the information on the phase evolution of the catalyst.

XPS characterization was also performed on BiOCl and 52.1 % BCN before and after eCO_2RR . The XPS analysis was carried out in the powders of the catalyst, the catalyst dropcasted on the electrodes, the electrodes after running an LSV, and the electrodes post-catalysis. It is evident from the elemental composition as well as the data analysis of the regions of interest that the ink deposition step in the electrodes did not induce any degradation of the BiOCl (Table 1 and Table 2). Post-LSV, both materials showed a marked loss of chloride (Table 1, Fig. 9a and 9b) and a formation of two different species of bismuth (Table 2, Fig. 10a and 10b), one ascribable to Bi^{3+} as Bi_2O_3 and the other to Bi^{3+} in presence of either oxygen vacancies or a formation of a different Bi^{3+} compound such as $\text{Bi}_2\text{O}_2\text{CO}_3$, following the high amount of oxygen attributable to carbonated species. The content of chlorine, in the post-catalysis series, results in the accessible area (thus within the first 5–10 nm from the surface) below the detection limit of the technique in both of the samples, bismuth has been identified as Bi^{3+} (single component) ascribable to a compound with a bismuth to oxygen ratio higher than the one of Bi_2O_3 , more resembling the one of $\text{Bi}_2\text{O}_2\text{CO}_3$ (Table 1). XPS analysis of O 1 s spectra of all the stages of BiOCl and 52.1 % BCN are presented in Fig. S4.

4. Conclusions

In a conclusive view, BiOCl when synthesized into nanoplates has higher catalytic activity as compared to microplates. It was seen how the use of the size-controlling agent glycine aided in the nanostructuring of the catalyst. Further, effective uniform deposition of BiOCl nanoplates on g-C₃N₄ allowed for sufficient exposure of the active sites of the catalyst which in the case of 52.1 % BCN allowed for uniform deposition and hence allowed for its highest catalytic performance. Minimal production of side products like H₂ and CO gives an added advantage of increased selectivity of HCOO⁻. 52.1 % BCN produced 200mmol g⁻¹h⁻¹ as compared to 179mmol g⁻¹h⁻¹ for pristine BiOCl at 5400 s applying -1.06 V vs RHE in a gas-tight cell. Extended hours of testing were carried out to understand the behavior of the catalyst with a longer duration. The behavior was noted to be stable for both 52.1 % BCN and BiOCl for 6 h with the yield of HCOO⁻ being 678mmol g⁻¹h⁻¹ and 1428mmol g⁻¹h⁻¹ for 52.1 % BCN and BiOCl, respectively. The catalysts were characterized by SEM, XRD, Raman spectroscopy, IR spectroscopy, sorption analysis, and XPS, and then for post-catalysis and in the different stages of the eCO_2RR by XRD and XPS. Post-catalytic characterization has shown the presence of $\text{Bi}_2\text{O}_2\text{CO}_3$ instead of pure metallic bismuth. The bimodal pores' distribution of 52.1 % BCN further explains the improved diffusion of the electrolyte into the catalyst surface. Low production of H₂ and CO was obtained which makes this catalyst highly suitable for scale-up use considering also the simple cost-effective synthesis method.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Tiziano Montini reports financial support and article publishing charges were provided by University of Trieste. If there are other authors, they

declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ica.2024.122395>.

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