Driving up the Electrocatalytic Performance for Carbon Dioxide Conversion through Interface Tuning in Graphene Oxide–Bismuth Oxide Nanocomposites

Michele Melchionna,* Miriam Moro, Simone Adorinni, Lucia Nasi, Sara Colussi, Lorenzo Poggini, Silvia Marchesan, Giovanni Valenti,* Francesco Paolucci, Maurizio Prato, and Paolo Fornasiero*

Cite This: ACS Appl. Energy Mater. 2022, 5, 13356−13366

ABSTRACT: The integration of graphene oxide (GO) into nanostructured Bi$_2$O$_3$ electrocatalysts for CO$_2$ reduction (CO$_2$RR) brings up remarkable improvements in terms of performance toward formic acid (HCOOH) production. The GO scaffold is able to facilitate electron transfers toward the active Bi$_2$O$_3$ phase, amending for the high metal oxide (MO) intrinsic electric resistance, resulting in activation of the CO$_2$ with smaller overpotential. Herein, the structure of the GO-MO nanocomposite is tailored according to two synthetic protocols, giving rise to two different nanostructures, one featuring reduced GO (rGO) supporting Bi@Bi$_2$O$_3$ core−shell nanoparticles (NP) and the other GO supporting fully oxidized Bi$_2$O$_3$ NP. The two structures differentiate in terms of electrocatalytic behavior, suggesting the importance of constructing a suitable interface between the nanocarbon and the MO, as well as between MO and metal.

KEYWORDS: graphene oxide, bismuth oxide, carbon dioxide reduction, electrocatalysis, interfaces

INTRODUCTION

A switch to sustainable energy and chemical production is in urgent demand, triggering a vast amount of research toward the implementation of new schemes with low environmental impacts. In this context, the electrochemical reduction of carbon dioxide (CO$_2$RR) into value-added products is a highly desirable strategy to create a closed carbon cycle for fuels and chemicals.$^{1,2}$ The CO$_2$RR can proceed with a variety of possible products, including the thermodynamically more favored H$_2$ evolution (HER) when the reaction is carried out in aqueous electrolytes.$^{3−5}$ This aspect is the main driving force for the continuous development of new selective and active CO$_2$RR electrocatalysts able to operate in aqueous environment. Bismuth-based heterogeneous catalysts have flourished in recent years as attractive CO$_2$RR electrocatalysts, leading mainly to the formation of formic acid (HCOOH), a very useful feedstock for the chemical and fuel cell industry.$^{6,7}$ Most studies focused on metallic Bi(0), whose typical selectivity toward HCOOH$^{8−12}$ arises from the favorable adsorption of the $^*$OCHO intermediate onto the Bi surface in comparison with $^*$COOH and $^*$H.$^{10,12}$ Nevertheless, downsides are identified with the usually large required overpotentials and modest current densities,$^{9,13−15}$ as well as short operation time stability.$^{16,17}$ These shortcomings inspired the search for engineered Bi-based catalyst structures, in order to achieve CO$_2$RR at small overpotential with competitive intrinsic activity and selectivity. During our exploration of electrocatalytic CO$_2$RR, we have provided evidence on how the integration of carbon nanostructures (CNS) into carbon/metal oxide (MO) nanocomposite can harness a cascade of events that enables the catalytically active site to be active at earlier onset potentials with increased selectivity toward HCOOH.$^{18,19}$ This synergistic effect arises from the formation of suitable carbon-inorganic interfaces, whereby the CNS is able to (1) improve charge transfers at the interface with the metal/metal oxide, (2) add up to the catalyst’s stability, and (3) facilitate reactant diffusion to the active site, typically by increasing the available surface area and favoring the adsorption capacity of CO$_2$.$^{20,21}$ Herein, we chose to explore graphene oxide (GO) as the nanocarbon phase because of its large two-dimensional (2D) morphology, which allows optimum deposition of the MO nanoparticles with no size limitations, and also to focus on the electronic effects, ruling

Received: June 28, 2022
Accepted: October 11, 2022
Published: October 20, 2022

13356

https://doi.org/10.1021/acsaem.2c02013
ACS Appl. Energy Mater. 2022, 5, 13356–13366
out contributions from the high surface area that could arise with higher surface area CNS such as carbon nanohorns (CNH) or carbon nanotubes (CNT). The use of conductive carbon matrices has been proven to be a proficient strategy to improve current densities of Bi$_2$O$_3$, although selectivity towards HCOOH remained limited to large applied overpotentials, so that additional complexity must be considered in Bi$_2$O$_3$-based hybrid catalyst design. Recent reported studies illustrated the role of oxidation of Bi to Bi$_2$O$_3$, and how this causes a more pronounced CO$_2$ adsorption and a quicker first electron transfer step to form the initial CO$_3^{-2}$ radical intermediate, leading to enhanced catalytic performance. Hence, we explore the synergistic combination of GO and Bi$_2$O$_3$ toward improved CO$_2$RR with activity boosted by the competent electron mediating role of the CNS, which allows faster kinetics.

The GO/Bi$_2$O$_3$ nanocomposite, assembled by exploiting the GO oxygenated functional groups for better binding of the MO phase, exhibits different CO$_2$RR catalytic behavior depending on the specific structural evolution during the synthetic protocol. The observed electrocatalytic behavior in relation to the nanocomposite structure allows one to uncover many of the subtle shades that strongly affect the complex dynamics of CO$_2$RR driven by carbon−MO interfaces. In particular, we analyzed the correlation of the CO$_2$RR performance when the inorganic nanoparticles (NP) evolve from a Bi@BiO$_x$ core−shell configuration featuring an amorphous BiO$_x$ shell to (i) a fully oxidized and partially crystalline β-Bi$_2$O$_3$ NPs interfaced with GO or (ii) a truly Bi@β-Bi$_2$O$_3$ core−shell NP interfaced with reduced GO (rGO) obtained via a reductive thermal treatment. The obtained CO$_2$RR correlation indicates significant differences, and will help to establish a platform for the rational design of future and advanced multiphase CO$_2$RR electrocatalysts integrating CNS.

■ EXPERIMENTAL SECTION

Synthesis of GO−Bismuth Oxide Nanocomposites. The GO was prepared following a procedure we previously adopted. First, 200 mg of pristine graphene was added into a 100 mL round-bottomed flask containing K$_2$SO$_4$ (200 mg, 0.37 mmol), P$_2$O$_5$ (100 mg, 0.35 mmol), and H$_2$SO$_4$ (10 mL). The reaction was sonicated for 30 min and stirred at 80 °C for 4 h. The crude was cooled down, diluted with deionized water (50 mL), filtered through a Millipore membrane (JHWP, 0.45 μm), and washed with deionized water until neutralization of the washings. The black powder collected from the Millipore membrane was transferred into a round-bottom flask and dispersed in 20 mL of H$_2$SO$_4$ at 0 °C. Then, 100 mg of KMnO$_4$ (0.63 mmol) were added into the dispersion under stirring. The final mixture was cooled down, subjected to a Teflon-lined stainless autoclave, and it was heated to 120 °C for 12 h. The black solid was recovered by centrifugation and washed successively with H$_2$O and ethanol.

Bi@BiO$_x$. The pristine core−shell nanoparticles were prepared via a solvothermal method adapting a reported procedure. $^{25}$ Bi(NO$_3$)$_3$.5H$_2$O and glucose in molar ratio (1:1.5) were dissolved in ethylene glycol so to have a concentration of 0.067 and 0.1 M, respectively. The solution was stirred for 30 min and then transferred to a Teflon-lined stainless autoclave, and it was heated to 120 °C for 12 h. The black solid was recovered by centrifugation and washed successively with H$_2$O and ethanol.

Bi@Bi$_2$O$_3$. The as prepared Bi@BiO$_x$ NP samples were subjected to calcination at 250 °C under static air atmosphere, with a ramp of 3 °C min$^{-1}$. GO/Bi@BiO$_x$. GO and Bi@BiO$_x$ NP were prepared in different weight ratios (3:1, 4:1, 5:1). The procedure involved the dispersion under sonication of the two solids in ethanol so to have approximately a 2:1 mg mL$^{-1}$ dispersion of GO. After the sonication, the mixture was stirred at room temperature for 24 h. The solid was recovered by centrifugation.

GO/Bi@Bi$_2$O$_3$. The as prepared GO/Bi@Bi$_2$O$_3$ samples were subjected to calcination at 250 °C under static air atmosphere, with a ramp of 3 °C min$^{-1}$.
cannot react with CE. An Ag/AgCl was used as a reference electrode (LowProfile 3.5 mm OD of PINE research). The peculiarity of this electrode is the use of a gel instead of a KCl solution. The gel and the ceramic porous frit guarantee a low mobility of the chloride ions, preventing them from escaping from the electrode with consequent poisoning of the catalyst.

The electrolyses were performed in a near-neutral bicarbonate buffer, KHCO₃ 0.5 M. This electrolyte was pre-electrolyzed before use to guarantee high purity, as it is known that even small amounts of metal impurities can lead to surface interference with electrochemical reactions. Pre-electrolysis was carried out in a cell with a two-electrodes configuration, with Pt wire as a counter electrode and a Pt mesh as a working electrode; electrolysis of the electrolyte was performed for at least 24 h at a current of 0.1 mA while stirring the solution, which was Ar-saturated.

As for electrochemical characterization, the same inks and loading of materials were used for the CO₂RR study, but in this case, a bigger electrode area was used (GCE, geometric surface area 1 cm²). The electrode area is important because the larger the electrode area, the higher the concentration of the reaction products. In this way the detection limit of the instrument (GC) is exceeded, guaranteeing the reliability and reproducibility of the measurements.

The CO₂RR activity was evaluated by chromoanometry (CA) of 1 h and 51 min in CO₂-saturated electrolytes. The gaseous products were analyzed during measurements by online gas chromatography (GC) directly connecting the headspace of the electrochemical cell to the sample loop of a GC, while formic acid was detected by analysis of the liquid phase by ionic chromatography (IC) at the end of electrolysis. The gas phase quantification was carried out during the electrolysis with sampling every 15 min. The Faradaic efficiency (FE) for the gas products of CO₂RR was quantified following the procedure previously described by Baltrusaitis et al. (eq 1)

\[
\text{FE}(\%) = \frac{n_{\text{products}} \times F_m}{I} \times 100
\]

where \( n \) is the number of electrons needed for CO₂RR; \( F \) is the Faraday constant; \( \phi \) is the volume fraction of the gas; \( I \) is the current, and \( F_m \) is the molar CO₂ gas flow rate.

While the analyses of the liquid products were performed by means of a Metrohm model 850 Professional IC Ion Chromatograph equipped with a Metrosep A Supp 4-250/4.0 anion column and a conductivity detector. The eluent used was 0.5 mM H₂SO₄, with 15% acetone. The Faradaic efficiency (FE) for the formic acid products was quantified in the following way (eq 2):

\[
\text{FE} = \frac{Q(\text{HCOO}^-)}{Q_{\text{TOT}}} \times 100
\]

\[Q_{\text{TOT}}\]

■ RESULTS AND DISCUSSION

Synthesis and Characterization of GO–Bismuth (4) Oxide Nanocomposites. The Bi₂O₃ NP samples were synthesized via a facile solvothermal method in the presence of glucose as the additional reducing and stabilizing agent. The as-obtained Bi₂O₃ NP samples were then dispersed onto GO in an ethanol dispersion, whereby the presence of Bi₂O₃ adsorbed glucose favors the coupling with the GO surface. The formation of the nanocomposite (GO/Bi₂O₃) is confirmed by transmission electron microscopy (TEM) investigation, which shows that the Bi₂O₃ NP samples are well dispersed onto the GO (Figure S1). After separation, the solid was divided into two fractions, which were independently subjected to two different thermal treatments to cause Bi₂O₃ crystallization and removal of organic groups. One treatment consisted in a calcination under static air at 250 °C (GO/Bi₂O₃), while in the other, the GO/Bi₂O₃ fresh sample, the thermal treatment was performed under a dynamic atmosphere of H₂/Ar (rGO/Bi@Bi₂O₃). Figure 1 shows a sketch of the synthesis to the two final nanocomposites.

The evolution of the nanocomposite structures was inspected by high resolution TEM (HRTEM), revealing the core–shell configuration of the inorganic component prior and after combination with GO. In particular, in both Bi@Bi₂O₃ and GO/Bi@Bi₂O₃ the inorganic core consists of rhombohedral metallic Bi, identified by the interplanar d-spacing of 0.32 nm, typical of the Bi(012) plane (Figure 2a). While the shell is made of amorphous BiOₓ (Figure 2 and Figure S2). Interestingly, both the core and shell present a hexagonal geometry (Figure 2a, Figure 3d, and Figure S2). Energy dispersive X-ray analysis (EDX) provides the element mapping of C, O and Bi, and also confirms the core–shell nature of the nanoparticles, deductible from the EDX line profile spectra (Figure 2a, Figure 2b and Figure S3). The calcination treatment causes a full oxidation of the Bi(0) core to bismuth oxide, with partial formation of the metastable β-Bi₂O₃ as indicated by the fast Fourier transform (FFT) analysis, as well as by EDX mapping and line profile (Figure 3b). This is also noted by analyzing the HRTEM of a sample made of self-standing Bi₂O₃ NP prepared by calcination of the as-prepared Bi@Bi₂O₃, without supporting them on GO (Figure S4). It is noteworthy that, despite the fact that the entire Bi is oxidized to Bi₂O₃, the morphology as observed with the TEM retains the memory of the core–shell motif, although in this case both the core and the shell are made of Bi oxide. In contrast, when the treatment is performed in H₂/Ar, the metallic Bi character of the core is preserved, while the shell becomes oxidized to β-Bi₂O₃; thus, a truly Bi@β-Bi₂O₃ core–shell structure is established, as also confirmed by the FFT analysis of the core and the shell (Figure 2c). Annular dark-field scanning transmission electron microscopy (HAADF-STEM) analysis provides near evidence of the core–shell configuration (Figure 2c). It must be noted that in all samples the Bi oxide nanospheres are also surrounded by smaller and thinner fragments of GO, difficult to see with TEM. Nevertheless, accurate HRTEM could reveal such a structural figure, as shown in Figure S5. Moreover, different EDX color contrast on...
the GO/Bi$_2$O$_3$ nanocomposite shows that carbon surrounds the whole Bi$_2$O$_3$ NPs (Figure S6).

Importantly, the reference sample (Bi$_2$O$_3$ NP) prepared by calcination of the self-standing Bi@Bi$_2$O$_3$ NP results in the formation of several large aggregates of the nanoparticles, confirming the stabilizing role of GO, which prevents coalescence of the NP. Figure 3 shows the comparison between the HAADF-STEM images of the self-standing Bi@Bi$_2$O$_3$ NP as prepared and postcalcination (Figure 3, parts a and b, respectively) with the ones stabilized by supporting them on GO, namely GO/Bi@Bi$_2$O$_3$ and GO/Bi$_2$O$_3$ (Figure 3, parts c and d, respectively).

The nanoscale transmission electron microscopy results are in excellent agreement with large-scale X-ray diffraction (XRD) and Raman analysis. In the XRD (Figure 4), the metallic Bi phase is the only one observed for Bi@Bi$_2$O$_3$ and GO/Bi@Bi$_2$O$_3$, indexed to the rombohedral Bi (JCPDS No. 05-0519), while no relevant Bi$_2$O$_3$ could be detected, corroborating the amorphous nature of the Bi$_2$O$_3$ shell. After the calcination treatment, the Bi(0) core mostly crystallizes forming the $\beta$ phase of Bi$_2$O$_3$ (tetragonal) readily indexed to the P4$_2$$_1$$_2$$_1$ space group (ICDD crystallographic card number 01-077-5341), while the reflections of Bi(0) have considerably decreased following such an oxidation. It is worth noting that calcination also causes a broadening of the reflection at $\sim$27°, typical of graphitic carbon, suggesting that a reduction in the number of stacked layers of the multilayer GO has occurred.

In contrast, the thermal treatment under reducing conditions (rGO/Bi@Bi$_2$O$_3$) serves to crystallize the Bi$_2$O$_3$ shell, while the core preserves its metallic nature, as observed by the coexistence of the reflections assigned to rombohedral Bi and $\beta$-Bi$_2$O$_3$ in the XRD. Additionally, micro-Raman analysis confirms the XRD results. The spectrum of the as-prepared Bi@Bi$_2$O$_3$ nanoparticles confirms the presence of the two peaks (respectively at 85 and 105 cm$^{-1}$) which can be assigned to the $E_g$ and $A_{1g}$ vibrational modes of Bi–Bi in metallic bismuth, with the frequencies having been slightly blue-shifted with respect to bulk Bi due to the decrease of particle size to the nanoscale. A less intense peak at 605 cm$^{-1}$ is also observed, attributed to the amorphous Bi$_2$O$_3$ phase, perhaps being carbonated following glucose binding, and confirming that the Bi$_2$O$_3$ shell in the noncalcined samples is not crystalline. The origin of a third well-defined peak at 293 cm$^{-1}$ is not clearly assigned based on literature studies; we hypothesize it is due to some specific Bi–O Raman mode of the amorphous oxide shell still covered by carbonaceous species deriving from glucose. Accordingly, a first remarkable difference after combination with GO is that such a peak is broader and significantly blue-shifted (308 cm$^{-1}$), and the same occurs to the Bi$_2$O$_3$ peak that is blue-shifted to 627 cm$^{-1}$. No signal pattern assignable to specific Bi$_2$O$_3$ phases is observed, indicating the amorphous nature of the Bi oxide. We interpret this result as an effect of the electronic interaction between GO and the amorphous Bi$_2$O$_3$ shell, in agreement with the X-ray photoelectron spectroscopy (XPS) discussed later on. As anticipated on the basis of XRD, the crystallization of the Bi oxide in GO/Bi$_2$O$_3$ is verified by the appearance of three new peaks at ca. 123, 315, and 465 cm$^{-1}$ attributed to Bi–O stretching modes in $\beta$-Bi$_2$O$_3$. Meanwhile, the signature of GO in both GO/Bi@Bi$_2$O$_3$ and GO/Bi$_2$O$_3$ is clearly visible, with the D and G bands appearing at 1350 and 1570 cm$^{-1}$, respectively, the former related to the $A_{1g}$ breathing mode and the latter, together with another band (2D band) at 2700 cm$^{-1}$, associated with the first- and second-order allowed Raman modes $E_{2g}$. It is worth noting that both the low D/G bands intensity ratio and the sharpness and intensity of the 2D band indicate that the starting GO has a low level of oxidation and a small disorder, while the calcination treatment induces creation of defects, presumably by insertion of additional oxygen functionalities. In order to avoid any artifact in the interpretation of the signal shift, we also ran a 80-point micro-Raman mapping of a selected area of the GO/Bi@Bi$_2$O$_3$ sample. In such a specific region, the vast majority of the
material is the composite (GO/Bi@BiO\(_x\)), but there is also a small fraction of stand-alone Bi@BiO\(_x\). The analysis of the spectra confirms that the Raman patterns are different depending on whether the laser is focusing on the nanocomposite or on the isolated Bi@BiO\(_x\) NPs, in particular with the peak at 306 cm\(^{-1}\) being shifted when coupled with GO (315 cm\(^{-1}\)). Moreover, the peak due to amorphous BiO\(_x\) is barely visible in the stand-alone Bi@BiO\(_x\) and centered at 607 cm\(^{-1}\), while is better defined and centered at 627 cm\(^{-1}\) in the nanocomposite (Figure S7). Analysis of rGO/Bi@Bi\(_2\)O\(_3\) indicates that the reduction treatment has a beneficial effects in partially restoring a smaller level of defects, as expected for reduced GO and indicated by the decrease of the D band intensity in relation to the G band.\(^{38}\) Moreover, the \(\beta\) phase pattern is also found, together with a peak 103 cm\(^{-1}\) characteristic of metallic Bi.

X-ray photoelectron spectroscopy (XPS) provides the superficial electronic states of the elements so that it gives a detailed understanding on the interface GO/Bi oxide. XPS confirmed the presence of C and Bi elements in the analyzed samples (Figure 5). The high-resolution XPS of the Bi 4f core level of all the five samples shows the signature doublet of Bi with binding energies (BE) at 159.2 and 164.5 eV associated with the Bi\(^{3+}\) 4f\(_{7/2}\) and Bi\(^{3+}\) 4f\(_{5/2}\), although interesting
differences are observed among the samples. In the as-prepared Bi@BiOx NP and in the calcined Bi2O3 NP, the BE of the two main peaks is located at 161.3 eV (orange components of Figure 5) plus its spin–orbit coupling peak at 166.6 eV, in agreement with an oxidation number of the metal of 5+.40 The additional presence of two small contributions with BE of 155.5 and 158.4 eV are associated with metallic Bi (Figure 5A, green line)41,42 and Bi3+.43–45 The overall Bi 4f picture is consistent with the small penetration range of XPS, which makes difficult to detect the internal Bi core, while the oxidized shell is readily observed. The fact that the outer shell of the Bi oxide is overoxidized suggests a tendency of the NPs to react with atmosphere. However, once the Bi@BiOx NP are combined with GO (GO/Bi@BiOx), the doublet is shifted toward lower BE (158.3 and 163.65 eV) confirming, as hypothesized after Raman analysis, that there is an electronic interaction between the GO and Bi@BiOx (Figure 5, green line). Calcination of the composite (GO/Bi2O3) does not alter such a BE shift, implying that even in the crystallized form, the Bi2O3 is still electronically interacting with GO. The metallic Bi components is still quite visible in the rGO/Bi@BiOx sample, confirming that the thermal treatment under reductive conditions preserves the metallic Bi, while in the calcined sample, this contribution is very low, in agreement with XRD where the contribution of the Bi(0) is very low. This suggests that GO may contribute to the donation of electron density on the outer Bi atoms constituting the core, favoring their reduction. It is worth stressing that the Bi(0) components change as a function of the different treatment of the samples: the trend of this variation is reported in Table 1. In the Bi 4f region is possible to see a small component at 168.5 eV arising from sulfur impurity. C 1s peaks of GO/Bi2O3 were deconvoluted into four components at 284.0, 285.3, 287.2, and 290.0 eV, plus a shakeup component centered at 293.9 eV, which are ascribed to the sp2/sp3 carbons, C–OH/C–O–C, C=O bond, and O–C=O respectively, arising from the functional groups of GO (Figure 59).46–48 Consistently, in the nanocomposites prior to and after the thermal treatments, the relative intensities of such peaks are changed, as the treatments remove most of the GO oxygenated functional groups. The overall picture indicates that the electronic states of the Bi oxide phase are altered by the presence of GO,49 which does not act as a mere inert support for the nanoparticles.

**CO2RR Electrocatatlytic Performance.** The CO2RR catalytic activity was evaluated as a function of applied potential, carried out by performing chronoamperometry (CA) experiments in CO2-saturated KHCO3 for 1 h and 50 min (ranging from −0.4 to −0.9 V vs RHE). Both gas-phase and liquid phase were quantified (the former via gas chromatography, GC, and the latter by ion chromatography, IC, see the Supporting Information) after the CA in order to determine the product selectivity, reported as the Faraday efficiency (FE).

Figure 6 shows, in addition to the FE values, the average values of the involved current density (i) during the CA. All the nanocomposites (GO/Bi@Bi2O3 GO/Bi2O3 and rGO/Bi@Bi2O3) exhibit good catalytic activity for CO2RR with HCOOH as the dominant product, with the formation of HCOOH attained at potentials very near the thermodynamic potential.40 In all cases, also hydrogen evolution reaction (HER) occurs to different extents depending on the catalyst and the applied potential. The nanocomposites are also compared with the CO2RR electrocatalytic performance by GO-free Bi2O3. Control experiments show that HCOOH production is completely suppressed in the absence of CO2, while any possible contribution in the HCOOH production from the nanomaterial is excluded on the basis of the comparison of the CO2RR activity with the GO (Figure S10). For all the nanocomposites the presence of GO significantly increases the current density for CO2RR and the FEHCOOH (Figure 6) while, importantly, the onset potential is set at earlier values (Figure 9). As we previously reported in the case of HER by oxidized carbon nanotubes/titanium oxide nanocomposites, the carbon–metal oxide turns out less electrocatalytically active in the as prepared nanocomposites. In fact, in the fresh materials, the metal oxide is still in an amorphous state and the CNS presents too many COOH functional groups, leading to a less efficient electronic communication.44 This is also observed here in the case of the as prepared GO/Bi@Bi2O3 nanocomposite as compared to the two thermally treated catalysts.

In addition, the difference in the hierarchical structures is reflected in significantly different catalytic behavior. The FEHCOOH for rGO/Bi@Bi2O3 reaches a maximum value of 38% at −0.5 V vs RHE (corresponding to a HCOOH production rate of 3 ppm h−1), with a very small overpotential (100 mV), and declines with decreasing the applied potential, while H2 is always formed in relatively high FE throughout the explored potential range (part A). In contrast, GO/Bi2O3 is able to form HCOOH with a higher absolute FE in the more negative range (−0.7 to −0.9 V) peaking at −0.8 V (46%), with an HCOOH production rate of 73 ppm h−1, while the FE for the HER process is relatively small. Nevertheless, the FEHCOOH at −0.5 V is much lower (11%) in comparison with that of rGO/Bi@Bi2O3. From these results, we can conclude that the metallic Bi core plays a critical role in anticipating the potential for HCOOH formation, albeit the fact that Bi2O3 is only present in the shell of the NP may be the cause for the modest current density, whereas in GO/Bi2O3 the amount of the Bi oxide is comparatively larger (NPs are fully oxidized).

| Table 1. Semi-Quantitative XPS Relative to the % of Bi(0), Bi(III), and Bi(IV) All over the Total Amount of Bismuth |
|-----------------|--------|--------|--------|
| sample          | Bi(0)  | Bi(III)| Bi(IV) |
| rGO/Bi@Bi2O3    | 12.0   | 81.0   | 7.0    |
| GO/Bi2O3        | 8.0    | 86.0   | 6.0    |
| GO/Bi@BiOx     | 20.0   | 78.0   | 2.0    |
| Bi@BiOx-F       | 4.0    | 19.0   | 77.0   |
| Bi@BiOx-C       | 3.0    | 19.0   | 78.0   |
This is in line with previous observations during CO\textsubscript{2}RR by Bi\textsubscript{2}O\textsubscript{3} catalysts that upon reduction to metallic Bi could generate higher HCOOH current densities.\textsuperscript{51} As we previously reported in the case of HER catalyzed by oxidized carbon nanotubes/titanium oxide nanocomposites, the carbon–metal oxide turns out to be less electrocatalytically active in the as prepared nanocomposites. In fact, in the fresh materials, the metal oxide is still in an amorphous state and the CNS presents too many COOH functional groups, leading to a less efficient electronic communication.\textsuperscript{51} This is also observed here in the case of the as prepared GO/Bi@BiO\textsubscript{x} nanocomposite as compared to the two thermally treated catalysts, which show in general lower FE\textsubscript{HCOOH} at any potential. The criticality of the CNS-MO intimate contact is also demonstrated by measuring the performances of the electrocatalyst made by physically mixing GO with Bi\textsubscript{2}O\textsubscript{3} (Figure S11), which gave similar current density to those of GO/Bi\textsubscript{2}O\textsubscript{3} but much worse electrocatalytic activities and lower stability than GO/Bi\textsubscript{2}O\textsubscript{3}.

This result demonstrated not only that GO is instrumental to simply enhance the total current density by an overall improved conductivity (capacitive current) but also it contributes to an improved electron mobility toward the active Bi oxide sites, thus boosting the electrocatalytic performance.

The formic acid production rate plot (Figure 7) notes the difference in the potential range for CO\textsubscript{2}RR selectivity: the HCOOH production is higher for rGO/Bi@Bi\textsubscript{2}O\textsubscript{3} until −0.6 V, while GO/Bi\textsubscript{2}O\textsubscript{3} becomes more active in the range −0.7 to −0.9 V. However, it is worth noting that, in terms of productivity, GO/Bi\textsubscript{2}O\textsubscript{3} reaches a peak at −0.8 V and then there is a decline, whereas for rGO/Bi@Bi\textsubscript{2}O\textsubscript{3} the HCOOH productivity increases linearly with moving toward more negative potential, despite the drop in selectivity. This is a result of the much higher current density achieved when using the rGO, and we presume that also the Bi metal core contributes to a better electron transfer toward the Bi\textsubscript{2}O\textsubscript{3} active phase (see below). A comparison of HCOOH productivity with the free-standing bulk Bi\textsubscript{2}O\textsubscript{3} indicates that the thermally treated nanocomposites are considerably more efficient at any explored potential, with maximum productivity by GO/Bi\textsubscript{2}O\textsubscript{3} at −0.8 V being 4 times higher than bulk Bi\textsubscript{2}O\textsubscript{3}.

Importantly, nanocomposites also displayed great chemical and mechanical stability with a constant FE\% in prolonged electrosynthesis (>18 h, at −0.8 V; see Figure S12).
electrode electrochemical cell. The electrochemical features of bulk Bi$_2$O$_3$ prepared by conventional synthesis was first studied. Figure 8 reports the CV of bulk Bi$_2$O$_3$ at 20 mV s$^{-1}$ in Ar-saturated KOH 0.1 M.

**Figure 8.** Cyclic voltammetry investigation. CV at 20 mV s$^{-1}$ in Ar-saturated KOH 0.1 M of Bi$_2$O$_3$. Two peaks are distinct for the oxidation reaction: $A_1$ is the oxidation of Bi metal sites presents in the porosity of nanoparticles, while the $A_2$ peak is due to oxidation of Bi metal sites on nanoparticles surface. The potentials were corrected post measurement for the ohmic drop, considering the resistance of system.

Under an open circuit potential condition, the material is completely oxidized ($E_{\text{acc}} = 0.89$ V vs RHE). The bismuth oxide in contact with the alkaline solution undergoes a partial dissolution into the ionic species BiO$_2$$^-$. The cathodic peak is due in the main to reduction of dissolved species BiO$_2$$^-$, according to these reactions:

\[
\begin{align*}
\text{BiO}_2^- + e^- & \rightarrow \text{BiO}_2^2^- \\
2\text{H}_2\text{O} + 3\text{BiO}_2^- & \leftrightarrow 2\text{BiO}_2^- + 4\text{OH}^- + \text{Bi}^0 \\
\text{Bi}^0 & \rightarrow \text{Bi}_{(\text{metal})} \text{ metal deposition}
\end{align*}
\]

The oxidation peak $A_2$ and the subsequent plateau are due to the oxidation of Bi metal to Bi(III). While the peak $A_1$ is explained by Vivier et al. as the oxidation of small fraction of Bi metal sites to Bi(III) in the microporous cavities, where the amount of reactant is limited, the oxidation happens until exhaustion of OH$^-$ species. In both cases, the electrochemical reactions follow these reaction mechanisms:

\[
\begin{align*}
\text{Bi}_{(\text{metal})} & \rightarrow \text{Bi}^{+} + e^- \\
3\text{Bi}^+ & \leftrightarrow \text{Bi}^{++} + 2\text{Bi}_{(\text{metal})} \\
3\text{OH}^- + \text{Bi}^{++} & \rightarrow \text{Bi(OH)}_3 \\
\text{Bi(OH)}_3 & \rightarrow \text{BiOOH} + \text{H}_2\text{O}
\end{align*}
\]

When no potential is applied, the Bi(OH)$_3$ and BiOOH evolve spontaneously to form Bi$_2$O$_3$. The CV of both composite GO/Bi$_2$O$_3$ and rGO/Bi@Bi$_2$O$_3$ were then compared with that of bulk Bi$_2$O$_3$ to gain insights into the role of the CNS as well as of the metallic Bi. As a first important observation, the Bi$_2$O$_3$ has a lower current than samples with carbon support, and as expected, the capacitance of the double layer is 100 times higher for both composites (Figure 9 and Figure S13). Interestingly, the Faradaic current for GO/Bi$_2$O$_3$ and rGO/Bi@Bi$_2$O$_3$ is approximately three times higher as compared with that of Bi$_2$O$_3$. Based on our previous endeavors on CO$_2$RR catalyzed by CNS—metal oxide nanohybrids, we are confident in relating this effect to higher electrical conductivity of the GO, which reduces the internal system resistance and supplies electrons to the metal oxide, activating the Bi$_2$O$_3$ nanoparticles on support. In contrast, the resistance and aggregation of pure Bi$_2$O$_3$ can decrease the electrochemical active surface area.

The CNS support also increases the stability of the Bi$_2$O$_3$ nanoparticles. In fact, for a sample with pure Bi$_2$O$_3$, the faradaic current decreases with the increase in the number of cycles. It is possible to notice the different CV patterns between GO/Bi$_2$O$_3$ and rGO/Bi@Bi$_2$O$_3$ where in the first case the $A_1$ peak is larger than $A_2$, while for the sample with rGO, the $A_2$ peak decreases in favor of the $A_1$ peak. This observation well fits with the different structures of the two nanocomposites, whereby the metallic Bi core in the rGO/Bi@Bi$_2$O$_3$ and this particular core—shell motif plays a role in determining the electrochemical behavior. To this end, it is worth reporting previous findings with other core—shell electrocatalysts, such as Cu@SnO$_2$, which exhibited variable selectivity depending on the thickness of the oxide layer, with theoretical calculations indicating that possible alloying of the SnO$_2$ with Cu and resulting synergy, causing a compression of the oxide shell to trigger CO or HCOOH depending on the shell thickness.

We finally performed a compositional optimization study of the GO/Bi$_2$O$_3$ to further boost HCOOH production rates. For this purpose, two additional samples were investigated, with a higher (GO/Bi$_2$O$_3$ 3:1) or lower Bi$_2$O$_3$ loadings (GO/Bi$_2$O$_3$ 5:1), respectively. Interestingly, although the current densities do not change among the three catalysts, the FE is not directly proportional to the amount of Bi$_2$O$_3$ present in the sample. In fact, the GO/Bi$_2$O$_3$ 4:1 catalyst shows the best performance for CO$_2$RR, with $\text{FE}_{\text{HCOOH}}$ as high as 46% at $-0.8$ V, where the normalized formic acid production rate is 484 ppm/$\text{HCOOH}$ h$^{-1}$ g$_{\text{Bi}_{2}O_{3}}^{-1}$. Instead, with GO@Bi$_2$O$_3$ 3:1, bearing a higher amount of Bi$_2$O$_3$, $\text{FE}_{\text{HCOOH}}$ never exceed 10% until $-0.8$ V, with an increment at $-0.9$ V (Figure S14). It can therefore be deduced that nonoptimized GO/Bi$_2$O$_3$ may favor the reduction of CO$_2$ to formic acid upon a fine balancing between the number of active sites and the material resistance (higher, e.g., in GO@Bi$_2$O$_3$ 3:1 because of the relative lower amount of conductive GO). In line with it, GO@Bi$_2$O$_3$ 5:1 shows significantly poorer CO$_2$RR performances, where the top $\text{FE}_{\text{HCOOH}}$ is a mere 8% (at $-0.9$ V) and a greater selectivity for the HER process is instead observed, evidently deriving from the overriding HER activity of the GO, therein present in much larger relative amounts (Figure S14). It must be noted that, in all catalytic experiments, the intrinsic FE(HCOOH) of the Bi oxide active phase may be underestimated as at potentials more negative
than ~0.7 V, and there is also a contribution to HER by the graphene support, which cannot be avoided, as evaluated by screening the HER activity in CO₂ by rGO at various potentials (Figure S15). Table S1 presents a comparison with other Bi-base electrocatalysts derived however from more complex synthetic procedures and under different electrochemical cell conditions.

**CONCLUSIONS**

In conclusion, we carried out an in depth analysis on the role of GO when integrated with Bi₂O₃ nanoparticles in the electrocatalytic reduction of CO₂, revealing remarkable differences depending on the structures. The presence of GO in intimate contact with the active phase (Bi₂O₃) causes a remarkable increase in the CO₂RR performance toward the synthesis of formic acid. The results herein reinforce the concept that interfaces of MO with CNS promotes the activity and selectivity of the MO catalysts, offering an avenue to increase the electron trafficking nearby the MO, and contributing in a significant fashion to the long-term stability of the nanostructured catalysts. Differences were noted depending on the degree of oxidation of the carbon scaffold, with the rGO being more effective in favoring electron mobility as compared with the GO, thus facilitating electron transfers. Moreover, we prove that the adjustment of the hierarchy of the nanocomposite, by maintaining the metallic Bi(0) native core, gives rise to the formation of a double interfacial effect by the rGO and Bi(0) on the active Bi₂O₃ shell, resulting in a dramatic change of the catalytic behavior, such as an anticipation in the onset potential for CO₂RR performance toward the synthesis of formic acid. The results herein reinforce the concept that interfaces of MO with CNS promotes the activity and selectivity of the MO catalysts, offering an avenue to increase the electron trafficking nearby the MO, and contributing in a significant fashion to the long-term stability of the nanostructured catalysts. Differences were noted depending on the degree of oxidation of the carbon scaffold, with the rGO being more effective in favoring electron mobility as compared with the GO, thus facilitating electron transfers. Moreover, we prove that the adjustment of the hierarchy of the nanocomposite, by maintaining the metallic Bi(0) native core, gives rise to the formation of a double interfacial effect by the rGO and Bi(0) on the active Bi₂O₃ shell, resulting in a dramatic change of the catalytic behavior, such as an anticipation in the onset potential for CO₂RR performance toward the synthesis of formic acid.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsaem.2c02013.

TEM analysis, CO₂RR catalytic performance differences between GO vs GO/Bi₂O₃, effect of the GO–MO interface on CO₂RR performance, stability, capacitance of double layer of Bi₂O₃ and rGO/Bi@Bi₂O₃ effect of Bi₂O₃ loading on CO₂RR and rGO CO₂RR performances (PDF)

**AUTHOR INFORMATION**

Corresponding Authors

Michele Melchionna – Department of Chemical and Pharmaceutical Sciences, University of Trieste and Consortium INSTM, 34127 Trieste, Italy; orcid.org/0000-0001-9813-9753; Email: melchionnam@units.it

Giovanni Valenti – Department of Chemistry "Giacomo Ciancian", University of Bologna and Consortium INSTM, 40126 Bologna, Italy; orcid.org/0000-0002-6223-2072; Email: g.valenti@unibo.it

Paolo Fornasiero – Department of Chemical and Pharmaceutical Sciences, University of Trieste and Consortium INSTM, 34127 Trieste, Italy; ICCOM-CNR, University of Trieste, 34127 Trieste, Italy; orcid.org/0000-0003-1082-9157; Email: pfornasiero@units.it

**Authors**

Miriam Moro – Department of Chemistry “Giacomo Ciancian”, University of Bologna and Consortium INSTM, 40126 Bologna, Italy

Simone Adorinni – Department of Chemical and Pharmaceutical Sciences, University of Trieste and Consortium INSTM, 34127 Trieste, Italy

Lucia Nasi – CNR-IMEM Institute, 43124 Parma, Italy

Sara Colussi – Department Politecnico, University of Udine, Unità di Ricerca INSTM Udine, 33100 Udine, Italy; orcid.org/0000-0001-5316-1746

Lorenzo Poggi – Institute of Chemistry of Organometallic Compounds, National Research Council of Italy (ICCOM-CNR), 50019 Sesto Fiorentino, Florence, Italy

Silvia Marchesan – Department of Chemical and Pharmaceutical Sciences, University of Trieste and Consortium INSTM, 34127 Trieste, Italy

Francesco Paolucci – Department of Chemistry “Giacomo Ciancian”, University of Bologna and Consortium INSTM, 40126 Bologna, Italy; orcid.org/0000-0003-4614-8740

Maurizio Prato – Department of Chemical and Pharmaceutical Sciences, University of Trieste and Consortium INSTM, 34127 Trieste, Italy; Carbon Nanobiotechnology Laboratory, CIC biomaGUNE, 20009 Donostia-San Sebastian, Spain; Ikerbasque, Basque Foundation for Science, 48013 Bilbao, Spain; orcid.org/0000-0002-8869-8612

**ACKNOWLEDGMENTS**

This work was supported by the University of Trieste, INSTM, the European Commission (H2020 - RIA-CE-NMBP-2S Program, Grant No. 862030). M.Me. kindly acknowledges the FRA2022, funded by the University of Trieste. G.V. and M.P. acknowledge the Italian Ministry of Education MIUR (cifin Prot. 2017PBNXPN4). The authors thank Dr. Enrico Verlato from CNR of Padua for the IC analysis. We also thank B. Cortigiani for his assistance in using the CeTeCS platform and acknowledge “progetto Dipartimenti di Eccellenza 2018-2022 (ref. no. B96C1700020008)” and Fondazione Ente Cassa di Risparmio di Firenze for financial support.

**REFERENCES**

(1) Garg, S.; Li, M.; Weber, A. Z.; Ge, L.; Li, L.; Rudolph, V.; Wang, G.; Rufford, T. E. Advances and challenges in electrochemical CO₂ reduction processes: an engineering and design perspective looking
Electrochemical Exfoliation for Enhanced CO2 Reduction Performance. Angew. Chem., Int. Ed. 2018, 57 (40), 13283−13287.

(17) Lu, P.; Gao, D.; He, H.; Wang, Q.; Liu, Z.; Dipazir, S.; Yuan, M.; Zu, W.; Zhang, G. Facile synthesis of a bismuth nanostructure with enhanced selectivity for electrochemical conversion of CO2 to formate. Nanoscale 2019, 11 (16), 7805−7812.

(18) Melchionna, M.; Bracamonte, M. V.; Giuliani, A.; Nasi, L.; Montini, T.; Tavagnacco, C.; Bonchio, M.; Fornasiero, P.; Prato, M. Pd/TiO2/carbon nanohorn electrocatalysts: reversible CO2 hydrogenation to formic acid. Energy Environ. Sci. 2018, 11 (6), 1571−1580.

(19) Valenti, G.; Melchionna, M.; Montini, T.; Boni, A.; Nasi, L.; Fonda, E.;Criado, A.; Zitolo, A.; Voci, S.; Bertoni, G.; Bonchio, M.; Fornasiero, P.; Paolucci, F.; Prato, M. Water-Mediated Electro-Hydrogenation of CO2 at Near-Equilibrium Potential by Carbon Nanotubes/Cerium Dioxide Nanohydrs. ACS Appl. Energy Mater. 2020, 3 (9), 8509−8518.

(20) Melchionna, M.; Fornasiero, P.; Prato, M.; Bonchio, M. Electrocatalytic CO2 reduction: role of the cross-talk at nano-carbon interfaces. Energy Environ. Sci. 2021, 14 (11), 5816−5833.

(21) Melchionna, M.; Bonchio, M.; Paolucci, F.; Prato, M.; Fornasiero, P.; Catalysis-Material Crosstalk at Tailored Nano-Carbon Interfaces. In Making and Exploiting Fuller enes, Graphene, and Carbon Nanotubes; Marcaccio, M., Paolucci, F., Eds.; Springer Berlin Heidelberg: Berlin and Heidelberg, Germany, 2014; pp 139−180.

(22) Liu, S.; Lu, X. F.; Xiao, J.; Wang, X.; Lou, X. W. Bi2O3 Nanosheets Grown on Multi-Channel Carbon Matrix to Catalyze Efficient CO2 Electroreduction to HCOOH. Angew. Chem., Int. Ed. 2019, 58 (39), 13828−13833.

(23) Deng, P.; Wang, H.; Qi, R.; Zhu, J.; Chen, S.; Yang, F.; Zhou, L.; Qi, K.; Liu, H.; Xia, B. Y. Bismuth OXides with Enhanced Bismuth-Oxygen Structure for Efficient Electrochemical Reduction of Carbon Dioxide to Formate. ACS Catal. 2020, 10 (1), 743−750.

(24) Ileges, D.; Melle-Franco, M.; Kurbasic, M.; Melchionna, M.; Abrami, M.; Grassi, M.; Prato, M.; Marchesan, S. Oxidized Nanocarbons-Tri peptide Supramolecular Hydrogels: Shape Matters! ACS Nano 2018, 12 (6), 5530−5538.

(25) Chen, M.; Li, Y.; Wang, Z.; Gao, Y.; Huang, Y.; Cao, J.; Ho, W.; Lee, S. Controllable Synthesis of Core-Shell Bi@Amorphous Bi2O3 Nanospheres with Tunable Optical and Photocatalytic Activity for NO Removal. Ind. Eng. Chem. Res. 2017, 56 (37), 10251−10258.

(26) Lamagni, P.; Miola, M.; Catalano, J.; Hvid, M. S.; Mamakhet, M. A. H.; Christensen, M.; Madsen, M. R.; Jeppesen, H. S.; Hu, X.-M.; Daaberg, K.; Skrydstrup, T.; Lock, N. Restructuring Metal-Organic Frameworks to Nanoscale Bismuth Electrocatalysts for Highly Active and Selective CO2 Reduction to Formate. Adv. Funct. Mater. 2020, 30 (16), 1910408.

(27) Wang, Z.; Jiang, C.; Huang, R.; Peng, H.; Tang, X. Investigation of Optical and Photocatalytic Properties of Bismuth Nanoparticles Prepared by a Facile Thermolysis Method. J. Phys. Chem. C 2014, 118 (2), 1155−1160.

(28) Dias, L. P.; Correia, F. C.; Ribeiro, J. M.; Tavares, C. J. Photocatalytic Bi2O3/TiO2 Nanotubes for Enhanced Surface Area and Visible Light Activity. Catal. 2020, 10 (5), 445.

(29) Onari, S.; Miura, M.; Matsuishi, K. Raman spectroscopic investigation of the structural effects of catalytic oxidation on ultrathin Bi nanosheets: Uncovering the origins of enhanced electrocatalytic CO2 reduction on two-dimensional metal nanostructure. Nano Energy 2018, 53, 808−816.

(30) Gong, Q.; Ding, P.; Xu, M.; Zhu, X.; Wang, M.; Deng, J.; Ma, Q.; Han, N.; Zhu, Y.; Lu, J.; Feng, Z.; Li, Y.; Zhou, W.; Li, Y. Structural defects on coated bismuth oxide nanotubes enable highly active electrocatalysis of carbon dioxide reduction. Nano Energy 2019, 10 (1), 2807.

(31) Yang, F.; Elbawawy, A. O.; Scimminetti, R.; Song, P.; Wang, J.; Peng, Z.; Yao, S.; Deng, R.; Song, S.; Lin, Y.; Mavrikakis, M.; Xu, W. Bismuthene for highly efficient carbon dioxide electroreduction reaction. Nano Commun. 2020, 10 (1), 1088.

(32) Zhan, Y.; Li, F.; Zhang, X.; Williams, T.; Easton, C. D. Bond, A. M.; Zhang, J. Electrochemical reduction of CO2 on defect-rich Bi derived from Bi2S3 with enhanced formate selectivity. Journa l of Materials Chemistry A 2018, 6 (11), 4714−4720.

(33) Zhang, Y.; Zhang, X.; Ling, Y.; Li, F.; Bond, A. M.; Zhang, J. Controllable Synthesis of Few-Layer Bismuth Subcarbonate by
(33) Kim, S.; Dong, W. J.; Gim, S.; Sohn, W.; Park, J. Y.; Yoo, C. J.; Jang, H. W.; Lee, J.-L. Shape-controlled bismuth nanoflakes as highly selective catalysts for electrochemical carbon dioxide reduction to formate. *Nano Energy* 2017, 39, 44−52.

(34) Pereira, A. L. J.; Sans, J. A.; Vilaplana, R.; Gomis, O.; Manjón, F. J.; Rodríguez-Hernández, P.; Muñoz, A.; Popescu, C.; Beltrán, A. Isotropical Second-Order Phase Transition of $\beta$-Bi2O3 at High Pressures: An Experimental and Theoretical Study. *J. Phys. Chem. C* 2014, 118 (40), 23189−23201.

(35) Díaz-Guerra, C.; Almodóvar, P.; Camacho-López, M.; Camacho-López, S.; Piqueras, J. Formation of $\beta$-Bi2O3 and $\delta$-Bi2O3 during laser irradiation of Bi films studied in-situ by spatially resolved Raman spectroscopy. *J. Alloys Compd.* 2017, 723, 520−526.

(36) Clarament, S.; Varea, A.; López-Díaz, D.; Velázquez, M. M.; Cornet, A.; Cirera, A. The Importance of Interbands on the Interpretation of the Raman Spectrum of Graphene Oxide. *J. Phys. Chem. C* 2015, 119 (18), 10123−10129.

(37) Martins Ferreira, E. H.; Moutinho, M. V. O.; Stavale, F.; Lucchese, M. M.; Capaz, R. B.; Achete, C. A.; Jorio, A. Evolution of the Raman spectra from single-, few-, and many-layer graphene with increasing disorder. *Phys. Rev. B* 2010, 82 (12), 125429.

(38) Criado, A.; Melchionna, M.; Marchesan, S.; Prato, M. The Covalent Functionalization of Graphene on Substrates. *Angew. Chem., Int. Ed.* 2015, 54 (37), 10734−10750.

(39) Wang, J.; Zhang, H.; Hunt, M. R. C.; Charles, A.; Tang, J.; Bretcanu, O.; Walker, D.; Hassan, K. T.; Sun, Y.; Siller, L. Synthesis and Characterization of Reduced Graphene Oxide/Bismuth Composite for Electrodes in Electrochemical Energy Storage Devices. *ChemSusChem* 2017, 10 (2), 363−371.

(40) Sales, M. G.; Herweyer, L.; Opila, E.; McDonnell, S. MoS2 impurities: Chemical identification and spatial resolution of bismuth impurities in geological material. *Appl. Surf. Sci.* 2020, 508, 145256.

(41) Sun, J.; Zheng, W.; Lyu, S.; He, F.; Yang, B.; Li, Z.; Lei, L.; Hou, Y. Bi/Bi2O3 nanoparticles supported on N-doped reduced graphene oxide for highly efficient CO2 electroreduction to formate. *Chin. Chem. Lett.* 2020, 31 (6), 1415−1421.

(42) Hu, J.; Li, H.; Huang, C.; Liu, M.; Qiu, X. Enhanced photocatalytic activity of Bi2O3 under visible light irradiation by Cu(II) clusters modification. *Appl. Catal., B* 2013, 142−143, 598−603.

(43) Zhao, S.-g.; Chen, F.-y.; Hao, C.-c.; Tang, Y.-b.; Shi, W.-l. Bi2O3 decorated with SnO2 nanoparticles as direct Z-scheme heterojunction for enhanced degradation of tetracycline under visible light irradiation. *J. Chem. Technol. Biotechnol.* 2022, 97 (9), 2466−2476.

(44) Jiang, T.; Wang, K.; Guo, T.; Wu, X.; Zhang, G. Fabrication of Z-scheme MoO3/Bi2O3 heterojunction photocatalyst with enhanced photocatalytic performance under visible light irradiation. *Chin. J. Catal.* 2020, 41 (1), 161−169.

(45) Hasan, N.; Dalayoan, D. J. C.; Lee, J.-L.; Kim, J.; Bae, J.-S.; Liu, C. Ag0/Au0 nanocluster loaded Bi2O4 photocatalyst for methyl orange dye photodegradation. *RSC Adv.* 2021, 11 (43), 26607−26619.

(46) Johra, F. T.; Lee, J.; Jung, W.-G. Facile and safe graphene preparation on solution based platform. *J. Ind. Eng. Chem.* 2014, 20 (5), 2883−2887.

(47) Biesinger, M. C. Accessing the robustness of adventitious carbon for charge referencing (correction) purposes in XPS analysis: Insights from a multi-user facility data review. *Appl. Surf. Sci.* 2022, 597, 153681.

(48) Morgan, D. J. Comments on the XPS Analysis of Carbon Materials. *C* 2021, 7 (3), 51.

(49) Huang, L.-W.; Jeng, H.-T.; Su, W.-B.; Chang, C.-S. Indirect interactions of metal nanoparticles through graphene. *Carbon* 2021, 174, 132−137.

(50) Kortlever, R.; Shen, J.; Schouten, K. J. P.; Calle-Vallejo, F.; Koper, M. T. M. Catalysts and Reaction Pathways for the Electrochemical Reduction of Carbon Dioxide. *J. Phys. Chem. Lett.* 2015, 6 (20), 4073−4082.