

Supporting Information

Driving up the electrocatalytic performance for carbon dioxide conversion through interface tuning in graphene oxide-bismuth oxide nanocomposites

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TEM analysis

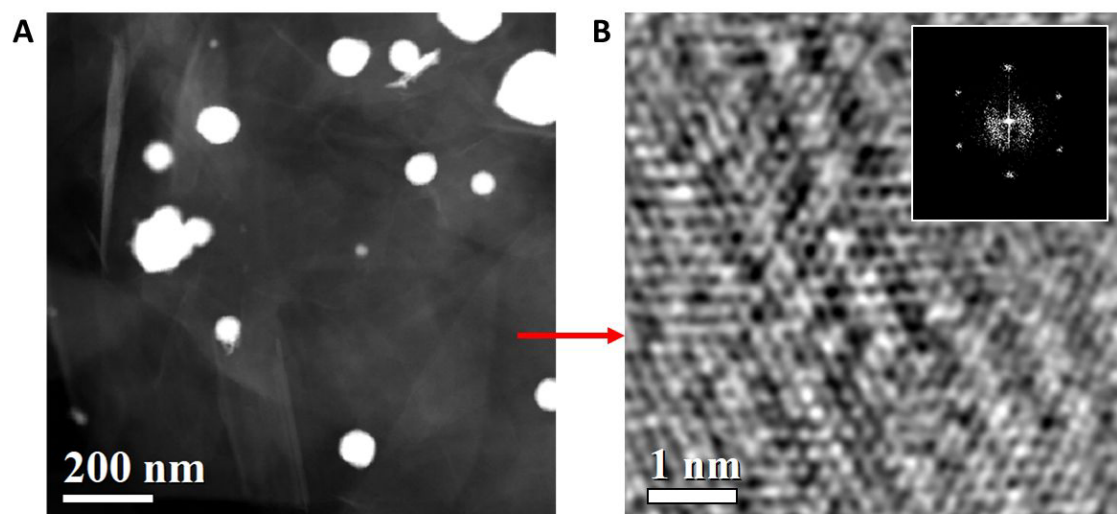


Figure S1. A) HAADF-STEM image of the Bi@BiO_x NP dispersed on the GO, B) Filtered HRTEM image of a selected area in (red arrow) with the corresponding FFT in the inset, showing the typical 6-fold symmetry of a monolayer GO.

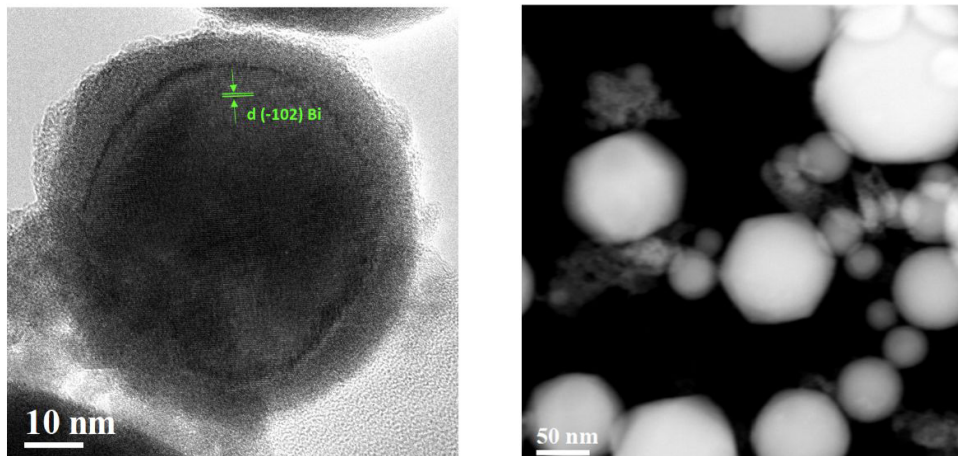


Figure S2. HRTEM of as prepared Bi@BiO_x NP showing the core-shell configuration, with the d-spacing of the rhombohedral Bi(0) core (left) and representative HAADF-STEM image (right)

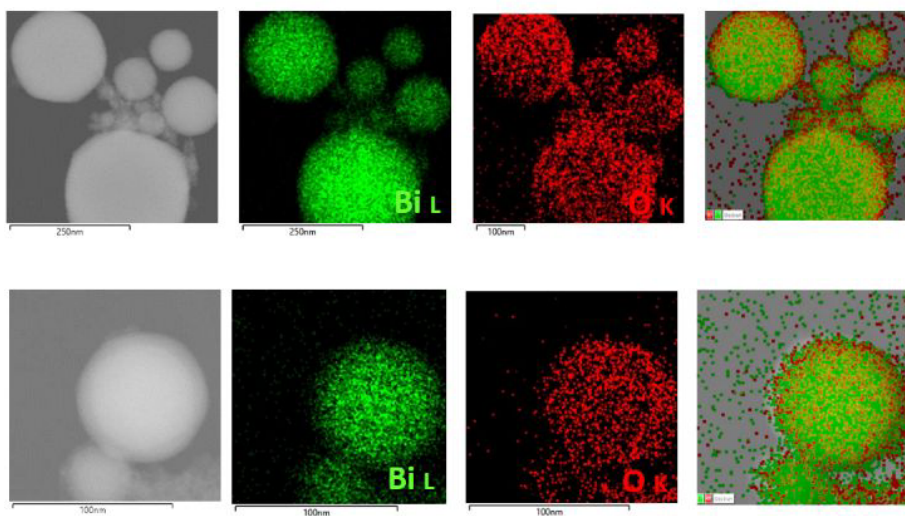


Figure S3. HAADF-STEM images of Bi@BiO_x NP with the corresponding Bi, O EDX maps (green and red) and the overlay showing that the BiO_x is distributed around the shell.

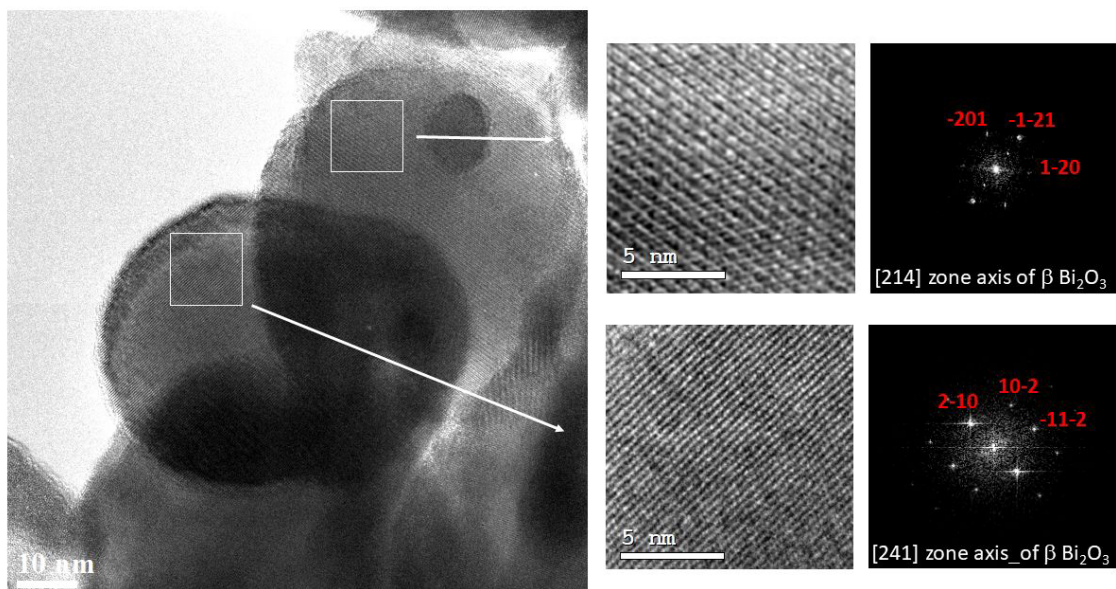


Figure S4. HRTEM of some Bi_2O_3 NP prepared by calcination of the $\text{Bi}@\text{BiOx}$ (left). Enlarged HRTEM images of the two NPs with the corresponding FFTs showing the $\beta\text{-Bi}_2\text{O}_3$ phase in two different zone axes, confirming that the whole core has been oxidized

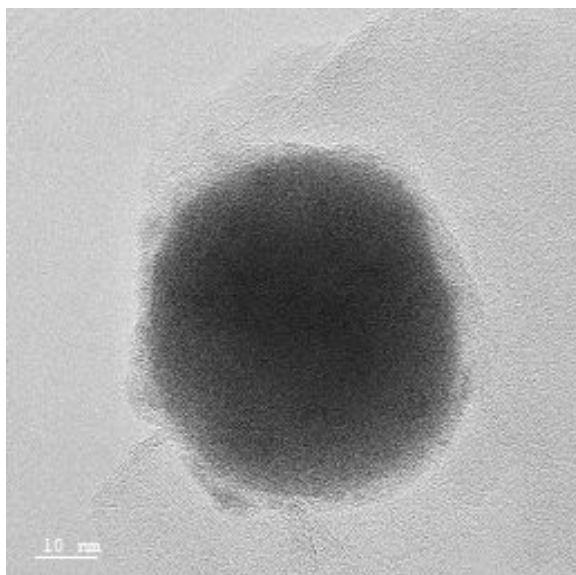


Figure S5. HRTEM of GO/Bi₂O₃ where it can be appreciated the coverage of the Bi₂O₃ NP with thin and small GO fragments.
some Bi₂O₃

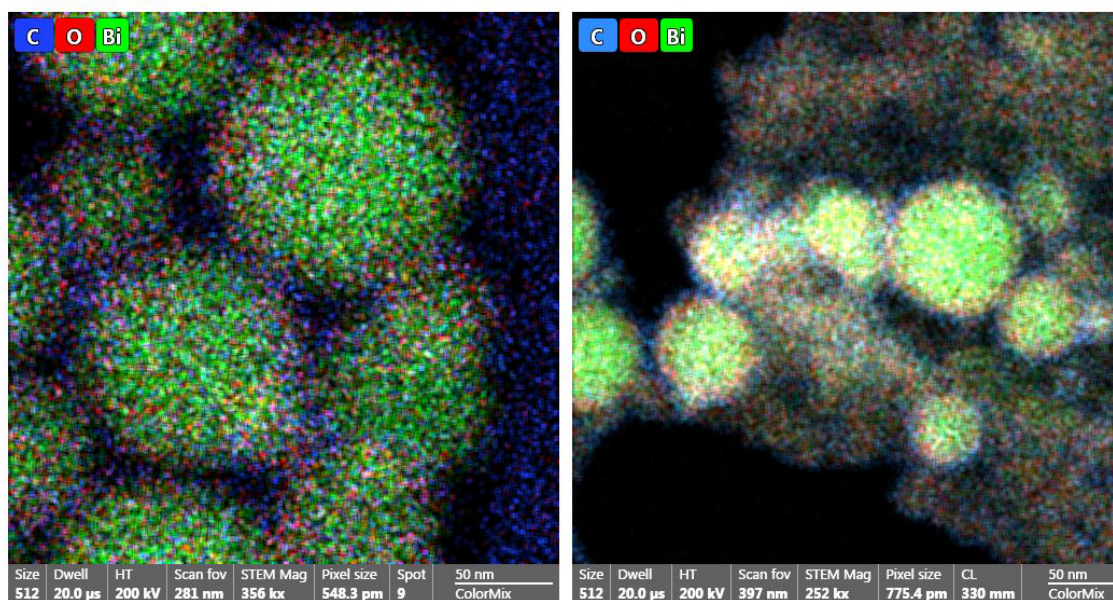


Figure S6. EDX mapping of the C, O and Bi atoms of GO/Bi₂O₃, showing that carbon (in the form of GO fragments) is spread around the whole Bi₂O₃ NP.

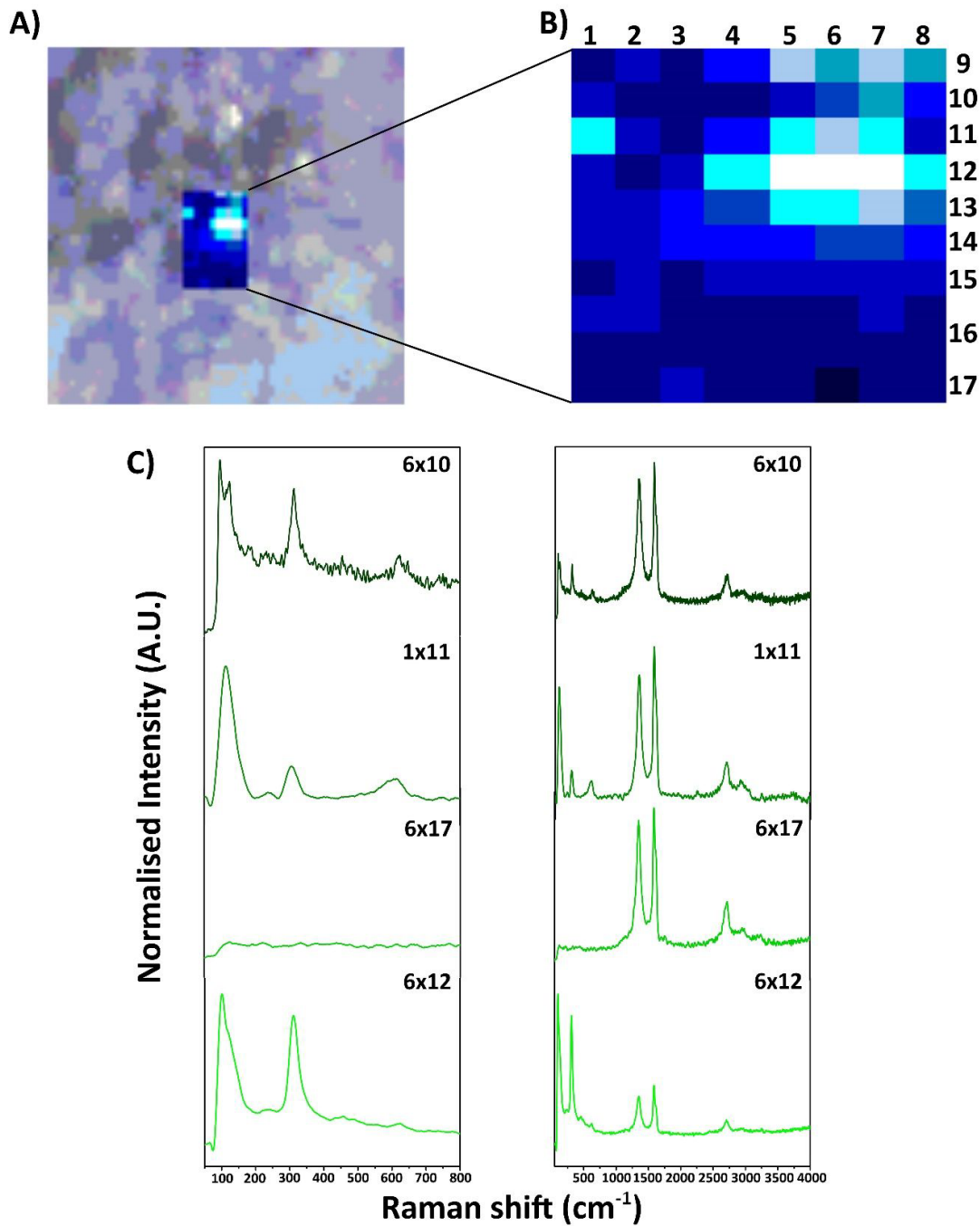


Figure S7. 80-point MicroRaman mapping of a selected area of the sample (top right: camera image; top left: expansion of the selected area) with corresponding Raman of 4 selected points of focus (bottom left: expansion in the Bi oxide Raman shift range; bottom right: full spectra)

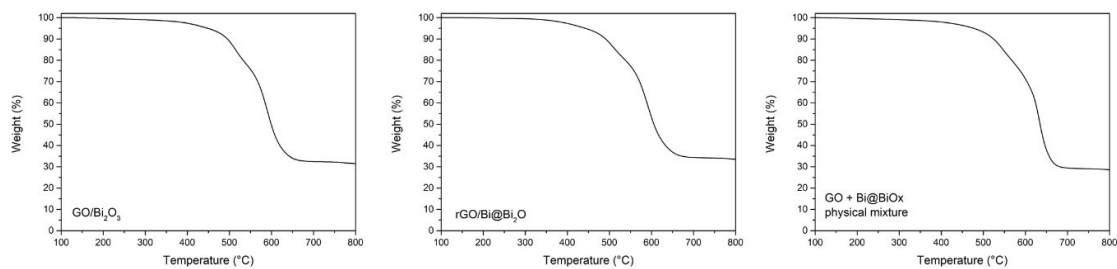


Figure S8. TGA of $\text{GO}/\text{Bi}_2\text{O}_3$, $\text{rGO}/\text{Bi}@\text{Bi}_2\text{O}_3$ and physical mixture of $\text{GO} + \text{Bi}@\text{BiO}_x$ which confirms the closeness of the Bi oxide wt % with respect to nominal composition.

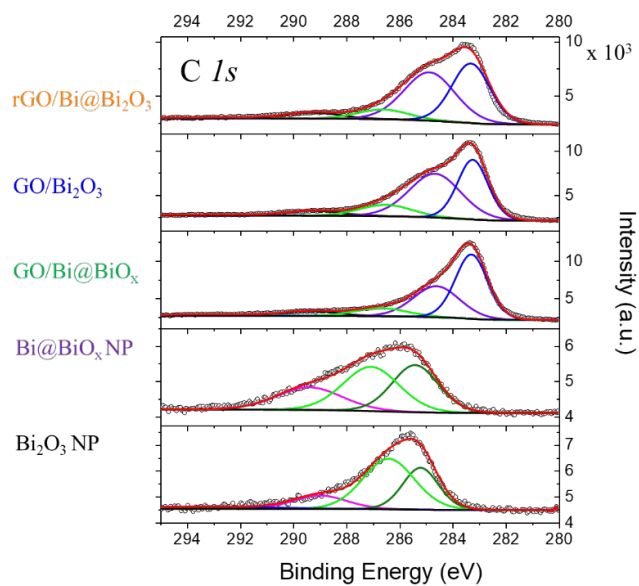


Figure S9. High-resolution XPS spectra in the C 1s region. Colours of the captions are associated to the materials as follows: black ($\text{Bi}@\text{BiO}_x$), green ($\text{GO}/\text{Bi}@\text{BiO}_x$), blue ($\text{GO}/\text{Bi}_2\text{O}_3$), orange ($\text{rGO}/\text{Bi}@\text{Bi}_2\text{O}_3$), purple (Bi_2O_3 NP).

CO₂RR catalytic performance differences between GO vs GO/Bi₂O₃

To be sure that the production formic acid is due to the catalytic activity of Bi₂O₃, the pristine GO was analysed in same condition of other samples. The FE for GO and GO/Bi₂O₃ are in figure S10.

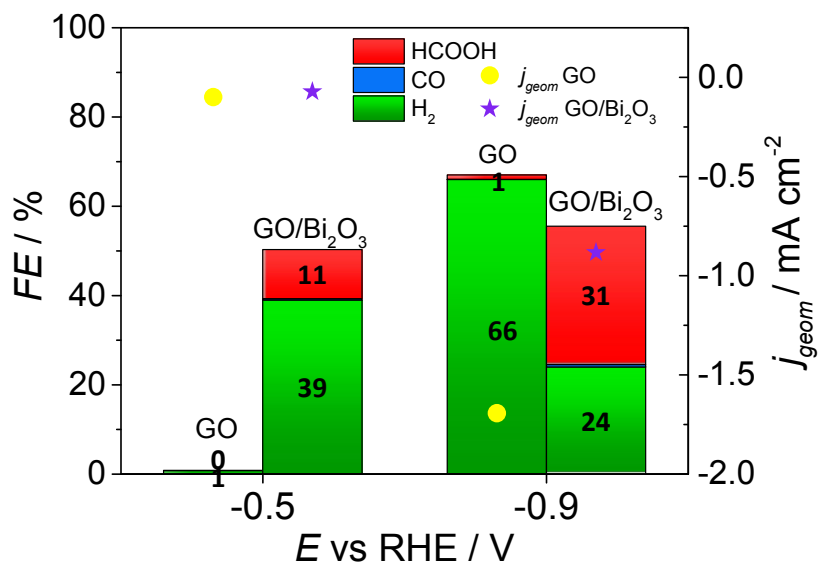


Figure S10. Faradaic Efficiency (FE) values are shown on left axis of detectable CO₂RR products: H₂ (green), CO (light blue) and HCOOH (red) for GO and GO/Bi₂O₃ at -0.5 V and -0.9 V vs RHE in CO₂-saturated KHCO₃ 0.5 M. The yellow

From the graphic is possible to notice how the GO is not able to produce the formic acid. The current density at -0.5 V vs RHE is the same for both samples, as evidence that the high current in the Bi-nanocomposites is mainly due to presence of GO, while the catalytic activity is attributed to bismuth oxide. This is evidence that GO is not active for CO₂RR, where the cathodic potential leads to the sole formation of hydrogen.

Effect of GO-MO interface on CO₂RR performance: GO/Bi₂O₃ (nanocomposite) vs GO + Bi₂O₃ (physical mixture)

Figure S11 reports the comparison between GO/Bi₂O₃, where the Bi₂O₃ nanoparticles were grown directly on GO, and physical mixture of GO and BiO_x, where the components were synthesized separately.

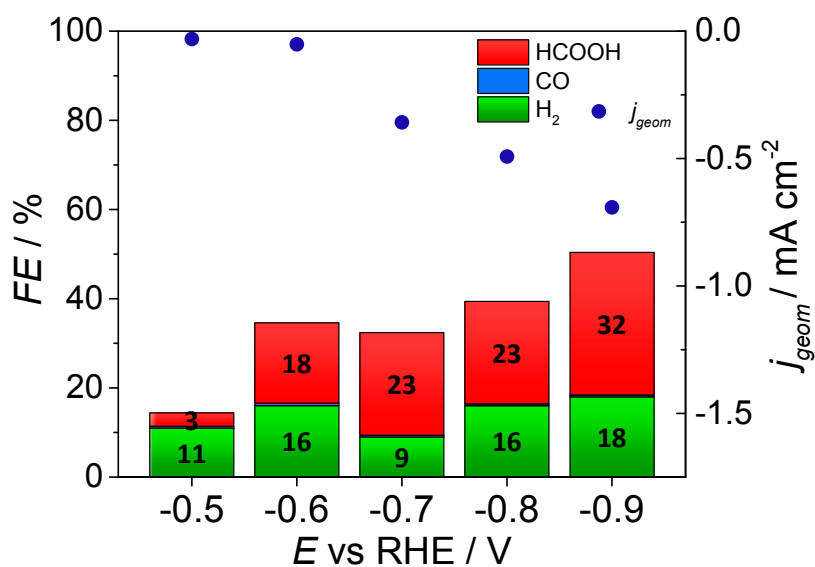


Figure S11. Faradaic Efficiency (FE) values are shown on left axis of detectable CO₂RR products: H₂ (green), CO (light blue) and HCOOH (red) for GO+BiO_x, in CO₂-saturated KHCO₃ 0.5 M. The blue points indicate the mean current density of sample

The current density the physical mixture sample is slightly lower than GO/Bi₂O₃, and also the formic acid production is lower. This is a proof that the good catalytic activity for CO₂RR derived by combination and interaction between GO and Bi₂O₃, and it is possible to obtain a good interaction only when the Bi₂O₃ is grown directly on GO.

Stability

The stability in the time of best sample was verified. The Chronoamperometry (CA) at -0.8 V vs RHE was applied for 2, 6, 12 and 18 hours at GO/Bi₂O₃ 4:1 sample. The values of FE are in the figure S12.

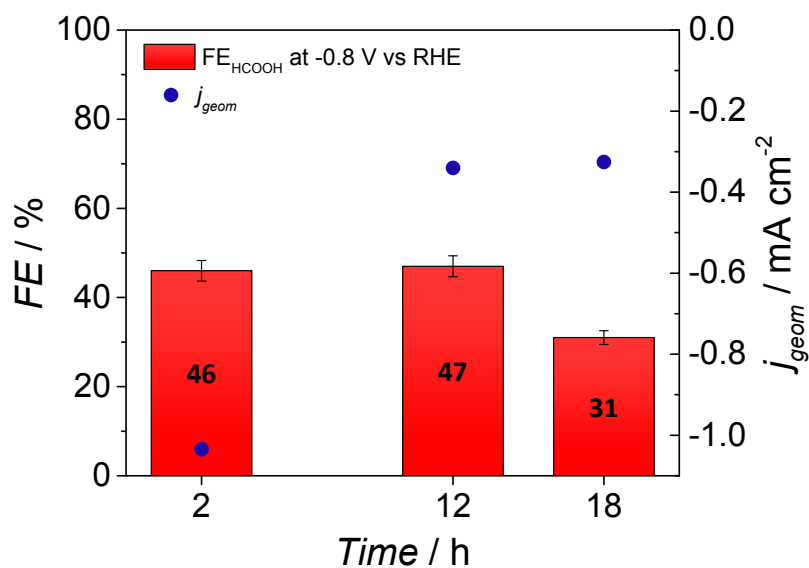


Figure S12. HCOOH Faradaic Efficiency and mean current density of GO@Bi₂O₃ 4:1 at -0.8 V vs RHE in CO₂-saturated KHCO₃ 0.5 M at different time (2, 6, 12 and 18 h). The blue points indicate the mean current density of sample at that potential; the values are shown on right axis.

The FE_{HCOOH} does not change until at 12 h, then at 18 h there is decrease, (from 47 % to 31 %). This change in terms of FE might be associate to a partial aggregation or dissolution of Bi₂O₃ nanoparticles.

Capacitance of double layer of Bi_2O_3 and $\text{rGO}/\text{Bi@Bi}_2\text{O}_3$

The figure S13 shows the CVs of double layer for the samples Bi_2O_3 and $\text{RGO}/\text{Bi}_2\text{O}_3$. From the current density values as a function of the scan rate, it was possible to extract the double layer capacitance (C_{DL}) of two sample. With add of rGO on the sample, the capacitance increases of 100 times.

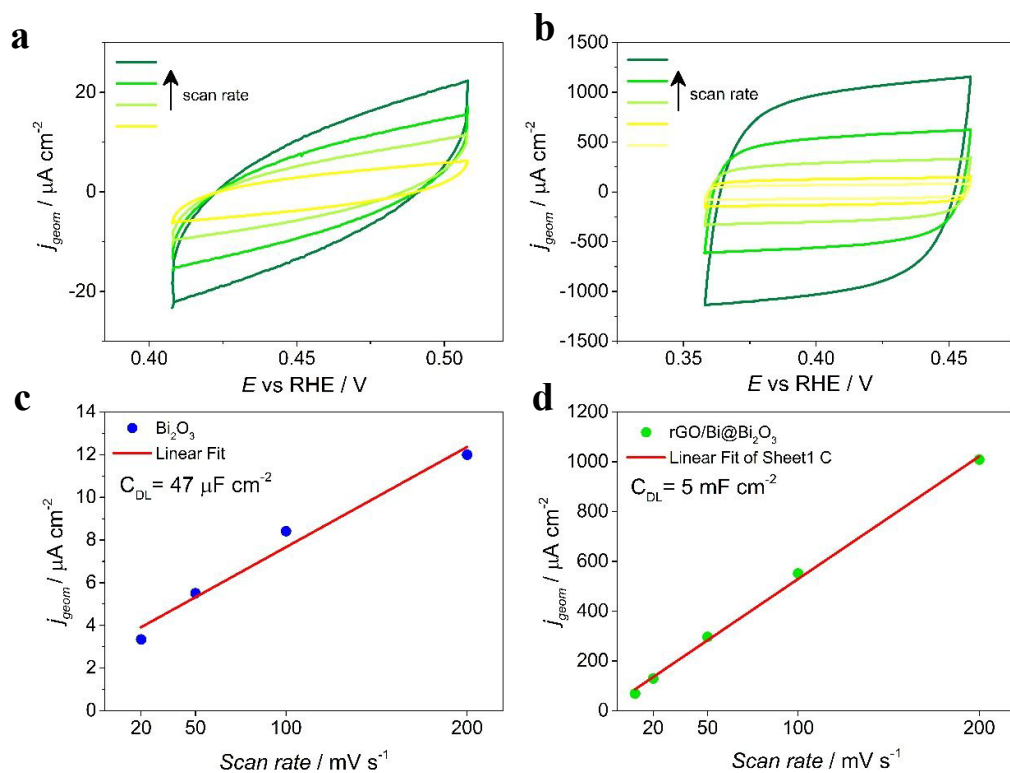


Figure S13. Measured CVs for **a** Bi_2O_3 , **b** $\text{rGO}/\text{Bi@Bi}_2\text{O}_3$ in Ar-saturated KOH 0.1 M. The current densities vs scan rate were plotted to extract the value of double layer capacitance (C_{DL}) of **c** Bi_2O_3 and **d** $\text{rGO}/\text{Bi@Bi}_2\text{O}_3$. The current densities were obtained from the double layer charge/discharge curves at -0.45 V for Bi_2O_3 and -0.40 V for $\text{rGO}/\text{Bi@Bi}_2\text{O}_3$.

Effect of Bi₂O₃ loading on CO₂RR

The figure S14 shows the FE_{HCOOH} and the average current density at -0.5 V vs RHE and -0.9 V vs RHE for the samples with different loading of Bi₂O₃: GO/Bi₂O₃ 3:1, GO/Bi₂O₃ 4:1 and GO/Bi₂O₃ 5:1.

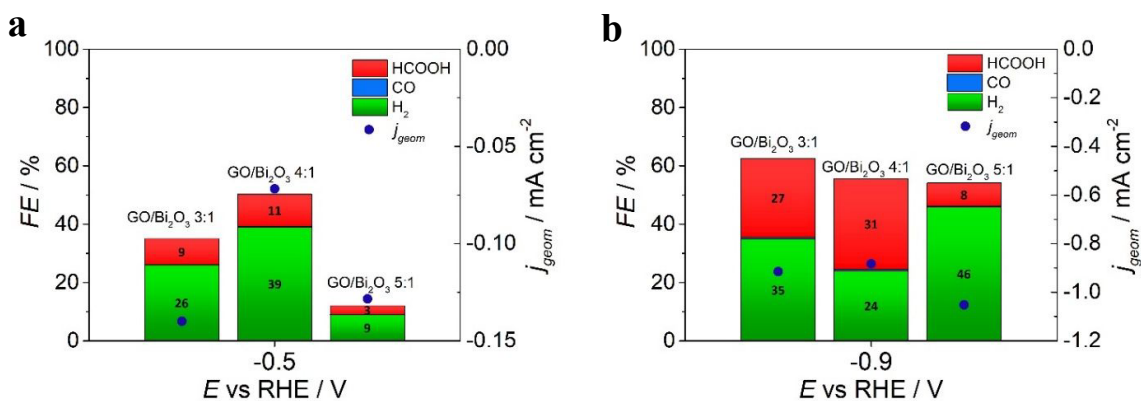


Figure S14 Faradaic Efficiency (FE) values are shown on left axis of detectable CO₂RR products: H₂ (green), CO (light blue) and HCOOH (red) for GO/Bi₂O₃ 3:1, GO/Bi₂O₃ 4:1 and GO/Bi₂O₃ 5:1 a) at -0.5 V vs RHE and b) -0.9 V vs RHE in CO₂-saturated KHCO₃ 0.5 M. The blue points indicate the mean current density of sample at that potential; the values are shown on right axis.

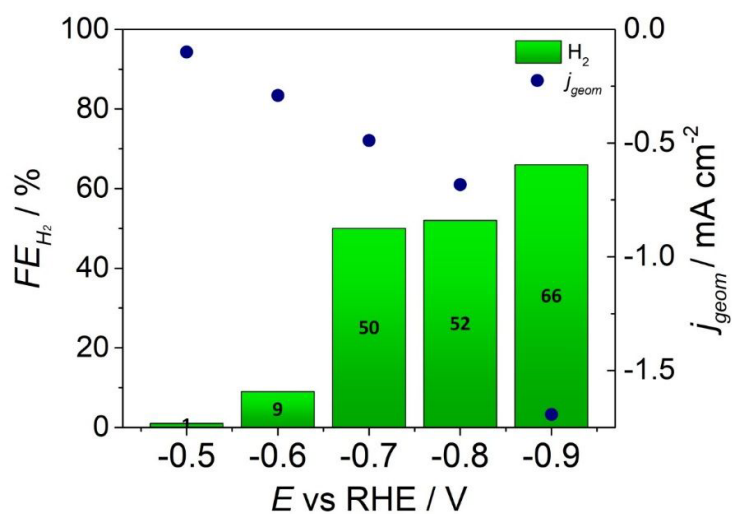


Figure S15. Faraday Efficiencies measured using only rGO as the electrocatalysts at different applied potentials. The blue points indicate the mean current density of sample at that potential; the values are shown on right axis.

Table S1. Comparison between the electrochemical performances of the nanohybrids with other recently reported Bi based materials active for the CO₂RR conversion towards HCOOC.

Catalyst	Potential (V vs RHE)	FE (%)	Reference
rGO/Bi@Bi₂O₃	-0.5	38	This work
GO/Bi₂O₃	-0.8	46	This work
Bi NP@MWCNT	-0.84	95	ACS Sustainable Chem. Eng. 2020, 8, 4871–4876
Bi@Bi₂O₃ core-shell NPs in chloroplast porous carbon	-1.0	94	Sci. Bull., 2020, 65(19), 1635–1642
Bi₂O₃ NTs	-0.74	89	Nat. Commun., 2019, 10, 2807
Cu foam@BiNW	-0.69	93	Energy Environ. Sci., 2019, 12, 1334–1340.
Bi₂O₃@ carbon nanorods	-1.1	93	Angew. Chem., Int. Ed., 2020, 59, 10807–10813
Bi nanoparticles–PVP/ CC600	-1.0	81	Applied Catalysis B: Environmental 284, 2021, 119723
Bi-based MOF material	-0.97	80	Adv. Funct. Mater. 2020, 30, 1910408
Bi/Bi₂O₃/NrGO-700 hybrid	-0.9	85	Chinese Chemical Letters 31 (2020) 1415–1421
Bi₂O₃ Nanosheets	-1.4	94	Angew. Chem. Int. Ed. 2019, 58, 13828–13833
Dendrite Bi foil	-0.74	89	ACS Catal. 2017, 7, 5071–5077
Bi₂O₃ nanoparticles	-1.2	91	ChemElectroChem 2018, 5, 3741–3747

References

1. Verlato, E. *et al.* CO₂ reduction to formic acid at low overpotential on BDD electrodes modified with nanostructured CeO₂. *J. Mater. Chem. A* **7**, 17896–17905 (2019).
2. Hori, Y. *et al.* ‘deactivation of copper electrode’ in electrochemical reduction of CO₂. *Electrochim. Acta* **50**, 5354–5369 (2005).
3. Kas, R. *et al.* Electrochemical CO₂ reduction on Cu₂O-derived copper nanoparticles: Controlling the catalytic selectivity of hydrocarbons. *Phys. Chem. Chem. Phys.* **16**, 12194–12201 (2014).