Copper single-atoms embedded in 2D graphitic carbon nitride for the CO\textsubscript{2} reduction

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We report the study of two-dimensional graphitic carbon nitride (GCN) functionalized with copper single atoms as a catalyst for the reduction of CO\textsubscript{2} (CO\textsubscript{2}RR). The correct GCN structure, as well as the adsorption sites and the coordination of the Cu atoms, was carefully determined by combining experimental techniques, such as X-ray diffraction, transmission electron microscopy, X-ray absorption, and X-ray photoemission spectroscopy, with DFT theoretical calculations. The CO\textsubscript{2}RR products in KHCO\textsubscript{3} and phosphate buffer solutions were determined by rotating ring disk electrode measurements and confirmed by \textsuperscript{1}H-NMR and gas chromatography. Formate was the only liquid product obtained in bicarbonate solution, whereas only hydrogen was obtained in phosphate solution. Finally, we demonstrated that GCN is a promising substrate able to stabilize metal atoms, since the characterization of the Cu-GCN system after the electrochemical work did not show the aggregation of the copper atoms.

ARTICLE

INTRODUCTION

The depletion of fossil fuels and the increase of the atmospheric CO\textsubscript{2} levels encourage the continuous search for alternative energy sources and routes to transform CO\textsubscript{2} into fuels or other value-added chemicals, which would allow us to move the C-economy from a linear- to a cyclic-one\textsuperscript{1,2}. Awkwardly, CO\textsubscript{2} is an extremely stable molecule and its reduction involves a multi-electron transfer process and a diversity of intermediates and products, such as CO, methane, methanol, formic acid, etc.

In the search for highly active, selective, and durable catalysts that will make possible the commercialization of this technology, the dispersion of single metal atoms on a substrate is taking much interest in the last years\textsuperscript{3–5}. The most commonly explored single-atom catalysts (SACs) for CO\textsubscript{2}RR are transition metal elements due to their electronic configuration (vacant orbitals and d electrons) that can facilitate the M-CO\textsubscript{2} bonding as well as the desorption of the reduction products\textsuperscript{6–8}. On one hand, the use of SACs allows maximizing the atomic efficiency of the metal catalysts (the well-known atom economy concept of Green Chemistry), which often have shown unexpected activity\textsuperscript{9–11}. On the other hand, it allows controlling the nature of the active sites, which could help to improve the products selectivity, since there is no presence of different phases. Unfortunately, these materials are often unstable and tend to aggregate into clusters/nanoparticles because of their high surface free energy, which enhances their mobility on the support surface\textsuperscript{12,13}. In particular, under catalytic conditions, the interaction between the single atoms and the substrate decreases due to new interactions established between the single atoms and the reactant, favoring the migration of the single atoms on the support\textsuperscript{6,14,19}. Therefore, finding a suitable and effective method to stabilize single atoms is a crucial requirement for the use of SACs.

The most used approaches in the literature for the stabilization of SACs are: (i) the establishment of strong metal–support interactions, and/or (ii) the confinement of the single atoms into a limited space, thus decreasing their mobility\textsuperscript{16,17}. In this sense, graphitic carbon nitride (GCN) presents properties that make it an interesting support for SACs. It is a polymeric organic semiconductor that consists of 2D layered structures that can be easily synthesized from several precursors such as melamine, urea, thiourea, etc\textsuperscript{16,19} and shows a high physicochemical stability and non-toxicity. In its fully-polymerized configuration, GCN presents structural cavities (six-fold N cavities) where SACs could be confined and stabilized through strong metal-nitrogen interactions\textsuperscript{20,21}, although the formation of less regular polymorphs has to be carefully evaluated in order to investigate the correct coordination of the metal atoms. Compared with nitrogen-doped graphene-related materials, which are frequently used for the dispersion of SACs\textsuperscript{22–26}, GCN contains a higher amount and uniform type/arrangement of nitrogen species that offer abundant and more precisely defined coordination sites for single atoms\textsuperscript{27–30}. No less important it is the fact that it has a relatively small band gap (2.7 eV\textsuperscript{31}) therefore, it is able to absorb the light, reducing the external input necessary for the CO\textsubscript{2}RR\textsuperscript{32,33}. Alone, GCN shows a high electron–hole recombination rate that limits the overall photocatalytic efficiency of the single-phase GCN\textsuperscript{32,33}. However, combined with SACs, the separation of photogenerated charge carriers can be significantly enhanced since the metal atoms can act as electron traps as well as catalytic sites\textsuperscript{28,34–36}.

Among the different metals, copper is of particular interest since is the only one able to reduce CO\textsubscript{2} to relatively high-hydrocarbons (up to 6 C atoms) with a considerably high Faradaic efficiency (FE)\textsuperscript{37–43}. Therefore, in order to convert CO\textsubscript{2} into C–C hydrocarbons, copper has to be included in the catalyst formulation. A few works about the study of Cu single atoms dispersed in GCN can be found in the literature\textsuperscript{28,36,44}. For example, Quiao and coworkers reported a theoretical and experimental study on the electro-CO\textsubscript{2}RR in an aqueous medium catalyzed by Cu atoms dispersed in a GCN structure\textsuperscript{44}. They obtained H\text subscript{2} (>50%) and CO as main products, and low amounts of CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{6}, C\textsubscript{2}H\textsubscript{4}, C\textsubscript{2}H\textsubscript{5}OH, and C\textsubscript{3}H\textsubscript{8}OH. Wang et al.
have recently prepared a single-atom copper-modified GCN that has shown to be a competing photocatalyst for the photconversion of CO$_2$ into CO, CH$_3$OH, and CH$_4$ in an aqueous solution$^{36}$. Moreover, Li and coworkers have reported a study of Cu atoms supported on crystalline GCN as photocatalyst for the selective reduction of CO$_2$ into CO$^{28}$. However, the stability of this kind of materials has not been investigated.

In the study reported herein, we have modified the exfoliated GCN with copper single atoms in order to exploit the catalytic activity of the Cu-GCN hybrid system towards the electrochemical CO$_2$RR, studying the effect of the visible light on the catalytic process. Both the substrate and the catalyst have been characterized by a large variety of techniques in order to get a comprehensive understanding of their physicochemical properties. The experimental observations have been combined with density functional theory (DFT) simulations of several models of 2D GCN, accounting for different coverages of Cu atoms, and of the XPS spectra to achieve an atomistic description of the systems under investigation. Regarding the electrochemical CO$_2$RR, the dependence of the reaction products on the electrolyte has been investigated by using quantitative techniques (such as gas chromatography and $^1$H-NMR) coupled with rotating ring-disk electrode (RRDE) measurements, so evidencing an important role of the electrolyte in the products selectivity. In addition, the stability of the Cu-GCN hybrid system after the electrochemical work has been investigated by using other characterization techniques. No copper clusters or nanoparticles are observed in Fig. 1f for the Cu-GCN sample with 20 wt.% of Cu, suggesting the successful formation of copper single atoms, but we cannot exclude the presence of small clusters not detected by the TEM microscope used for the analysis.

The X-ray diffraction (XRD) patterns of 2D GCN and Cu-GCNs show two diffraction peaks at around 27.3° and 12.2°, indexed to the (002) and (100) planes of GCN, respectively (Fig. 2a)$^{47,48}$. The first peak is characteristic of the interlayer stacking of the conjugated aromatic systems; while the second one is associated with the in-plane repeated units, i.e., the distance of the adjacent heptazine units. A shift of the (100) peak toward lower 2-theta values is observed for the exfoliated material (12.2°), compared to the bulk GCN (13.1°), in Supplementary Fig. 1a. This shift indicates an increase of the distance between the adjacent heptazine units, in agreement with the hypothesis of the cleavage of the bridging −NH− between heptazine units due to the hydrolysis/oxidation during the H$_2$SO$_4$ exfoliation treatment$^{48,49}$, as schematized in Fig. 1e. In addition, GCN materials usually contain structural defects (primary or secondary amines) due to the incomplete condensation of the heptazine units that may facilitate the breakage of the GCN sheets$^{46,50}$. This hypothesis is further investigated below by using other characterization techniques. The exfoliated material shows the characteristic layered-like structure with nanosheets of some hundreds of nanometers, as seen in Fig. 1b, d. However, after the exfoliation process, a decrease in the size of the aggregates is observed. The change in the morphology can be attributed to the cleavage of the bridging −NH− between heptazine units due to the hydrolysis/oxidation during the H$_2$SO$_4$ exfoliation treatment$^{48,49}$, as schematized in Fig. 1e. The exfoliation process facilitates the breakage of the GCN sheets$^{46,50}$. This hypothesis is further investigated below by using other characterization techniques.

RESULTS

Physicochemical characterization

Two-dimensional (2D) GCN was obtained through an exfoliation treatment of the bulk material with H$_2$SO$_4$. A complete comparison of the bulk and exfoliated 2D GCN materials can be found in Supplementary Fig. 1. Subsequently, it was modified with copper atoms (20 wt.%) by using a well-established method for the introduction of single atoms (details in the “Experimental section”$^{40,45,46}$. The morphology of the GCN-based materials was investigated by scanning and transmission electron microscopies (SEM and TEM) (Fig. 1). The bulk material consists of stacked layers forming agglomerates of some micrometers, as seen in Fig. 1a, c, and in accordance with observations reported in the literature$^{47,48}$. The exfoliated material shows the characteristic layered-like structure with nanosheets of some hundreds of nanometers, as seen in Fig. 1b, d. However, after the exfoliation process, a decrease in the size of the aggregates is observed. The change in the morphology can be attributed to the cleavage of the bridging −NH− between heptazine units due to the hydrolysis/oxidation during the H$_2$SO$_4$ exfoliation treatment$^{48,49}$, as schematized in Fig. 1e. In addition, GCN materials usually contain structural defects (primary or secondary amines) due to the incomplete condensation of the heptazine units that may facilitate the breakage of the GCN sheets$^{46,50}$. This hypothesis is further investigated below by using other characterization techniques. No copper clusters or nanoparticles are observed in Fig. 1f for the Cu-GCN sample with 20 wt.% of Cu, suggesting the successful formation of copper single atoms, but we cannot exclude the presence of small clusters not detected by the TEM microscope used for the analysis.

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In order to investigate the structure and coordination of the Cu atoms, XAS measurements were performed on Cu-GCN(20). The analysis of the XANES region indicates that the Cu atoms have an average oxidation state of around $^{\pm}1.4$ (Supplementary Fig. 2), suggesting the presence of both Cu$^{+}$ and Cu$^{+}$, due to different Cu–N coordination arrangements. The presence of two different valence states has been already reported for Cu single atoms embedded in carbon nitride or N-doped graphene-related materials$^{34,53,55}$. Fig. 2b shows the Cu K edge Fourier transformed (FT) extended X-ray absorption fine structure (EXAFS) spectra for Cu-GCN (20) and the samples used as references. The absence of an intense peak at 2.23 Å (not-phase shift corrected) suggests the absence of copper clusters (Cu-Cu bonds), confirming the dispersion of single Cu atoms in the GCN matrix$^{34}$. Taking into account the characterization results for the Cu-GCN sample and the results reported in the literature for this kind of materials, the peak at 1.5 Å (not-phase shift corrected) can be related to Cu coordinated to N atoms in the first shell$^{38,52,53}$, although the presence of Cu–O interactions cannot be excluded; while the one at 2.4 Å could be attributed to Cu–C interactions$^{5}$. In order to fit the EXAFS data, we included Cu–N and Cu–C scattering paths, taking into account the most feasible structure of the Cu-GCN sample (Amino I and Amino II in Fig. 3d and Supplementary Figure 4 described below). In order to improve the fit, we also included the Cu-Cu path. Results revealed the presence of three N atoms at 1.9 Å, four Cu atoms at 2.85 Å, and one Cu atom at 2.50 Å from the Cu center (Fig. 2b and Supplementary Table 1). The value obtained for the Cu–N bond length is in agreement with those reported in the literature for this kind of materials$^{52-55}$, although different coordination numbers are reported depending on the GCN and/or Cu-GCN structures proposed. For example, Yang et al. stated that a Cu atom substitutes a C atom of the heptazine unit and gave a Cu–N coordination number of three$^{52}$. Li et al., however, proposed a fully condensed GCN structure with a Cu atom in the cavity formed by three heptazine units and obtained a Cu–N coordination number of six$^{56}$ whereas Wu et al. obtained a nitrogen coordination number of four even if they proposed the same structure than Li et al.$^{55}$. Regarding the Cu–C and Cu–Cu shells, it is difficult to establish a comparison with the literature since usually only the fit of the first Cu–N shell is reported. The addition of the Cu–Cu shell improved the $R_{f}$ factor (compared to $R_{f}=0.023$ without including the Cu–Cu shell). However, it should be noted that the coordination number for this shell is very small. It could be attributed to (i) very small Cu clusters not detected by other techniques or, most probably, to (ii) other single Cu atoms coordinated to an adjacent melem unit, which would be in agreement with the ‘high’ Cu coverage regions determined by DFT calculations, as described below.

Another approach to get insights on the position and on the coordination sphere of Cu is to combine experimental XPS measurements with DFT simulations. According to the existing DFT calculations, single metal atoms should be mainly located in the empty cavities in between fully-polymerized heptazine units, as a consequence of the in-plane coordination with the nitrogen atoms that induces a significant stabilization$^{20,21,57}$. Fig. 3a reports the Cu 2p XPS region for the Cu-GCN(20) sample. From the fit of the Cu 2p$_{3/2}$ region, it is evident that Cu is present in different oxidation states. The first component centred at 933.3 eV could be associated with both the presence of metallic Cu (933.2 eV) or Cu$^{+}$ (933.4 eV)$^{34,58,59}$. Taking into account the XANES analysis, the presence of metallic Cu could be excluded; however, in order to confirm its absence, the Cu LMM Auger peak was analyzed as well (inset of Fig. 3a). The spectrum consists of a broad band between 915 and 920 eV with a maximum centred at 915.6 eV, which is characteristic of Cu$^{+}$. On the other hand, the second component at 934.2 eV in the Cu 2p$_{3/2}$ peak, as well as the intense satellite peak at 940.7 eV, are related to the presence of Cu$^{2+}$ confirming the presence of Cu in two different oxidation states (Cu$^{+}$ and Cu$^{2+}$).
and Cu$^{2+}$), in agreement with the XANES results. We take this result as a strong indication on the actual structure of GCN in the sample: a fully-polymerized GCN, in fact, is not expected to provide two different chemical environments to the adatoms, since Cu ions preferentially interact with the pyridinic N atoms and not with tri-coordinated N atoms (from our DFT calculations). Thus, we consider a partial polymerization, where the monomers retain some amino functional groups that can also involve Cu atoms in some coordinative bonds (see the melon models below), to be more consistent with the existence of two oxidation states for Cu.

The analysis of the C 1s and N 1s regions of Cu-GCN and GCN is reported in Fig. 3b, c and in Supplementary Tables 2–4. Regarding the C 1s region, both Cu-modified and pristine 2D GCN materials show the component at around 288 eV, which is attributed to C−(N)$_3$ and is characteristic of GCN$^{61,62}$. The addition of copper atoms results in a 0.7 eV shift of this component toward higher binding energy (BE), which we can rationalize with the fact that copper atoms attract electrons from carbon atoms in Cu−N−C. The other three C 1s components observed for both Cu-modified and pristine 2D GCN systems are related to the adventitious carbon present in the sample holder. The adventitious carbon is visible due to the very thin film of the sample deposited in order to avoid charging effects.

Focusing on the N 1s region of 2D GCN, we deconvoluted the broad experimental band in four features at 398.0, 399.0, 400.7, and 401.7 eV as shown in Fig. 3c (bottom). These are in good agreement with the simulated peaks by DFT calculations reported in Fig. 3e (pristine) and also, with more details, in Supplementary Fig. 3e. We must note that the simulated spectrum is obtained by the overlap of the calculated lines for the alternated and linear models of melon (see Supplementary Fig. 3a, c). As reported in Fig. 3e, for pristine 2D GCN, we assign the four inequivalent nitrogen components to C−N−C, C−N−H$_2$, (C$_2$−N−H, and N−(C)$_3$ species, respectively, in order of growing BE$^{61}$. This theoretical assignment is in contrast with most of those present in the literature and based on chemical intuition, where graphitic and amino features are considered to be inverted$^{63,64}$. However, in contrast with the experiments, our theoretical approach is unambiguous because each calculation specifically targets a single inequivalent atomic component. Moreover, our findings are in line with other previous experimental and theoretical works$^{61,63,64}$.

We now consider what happens after the addition of copper atoms. Again, we fit the N 1s XPS region in Fig. 3c (top) with four components at 398.5, 399.3, 400.2, and 401.3 eV, respectively, thus at slightly different BE than before. Their intensities, especially for those at higher BEs, suggest the formation of a Cu-loaded melon phase. To rationalize the effect of the presence of the Cu atoms, we designed and optimized various melon models with different Cu concentration, reported in Supplementary Fig. 4. Then, we used such models to build two coverage regimes of Cu atoms, namely ‘low’ and ‘high’, corresponding to an average load of ~10 wt.% and >50 wt.%, respectively. Since the DFT adsorption energy of Cu on the amino sites (in the range between −1.6 and −2.9 eV, see Supplementary Fig. 4) is larger than that on the top sites, where Cu atoms are only physisorbed, in the low coverage regime we have only single Cu atoms at different amino sites, whereas in the high coverage regimes we saturate all the amino sites and further add Cu atoms on top sites. If we only considered the models with lower coverage, we would match the nominal...
Cu concentration in the experimental samples, but we would not satisfactorily describe the experimental XPS spectrum, because the feature at 400.2 eV would not appear. Therefore, we must consider a mixture of all models, i.e., pristine melon together with the Cu-loaded systems, at both low and high coverage regimes, in the assumption that the sample is not homogeneous.

We built the simulated N 1s XPS spectrum by considering the calculated BEs and their corresponding chemical shift, as described in the computational methods, for all the N species in the investigated models. The experimental spectrum was then fitted by using this mixture of models with non-homogeneous Cu distribution, fixing the position of the peaks and their gaussian broadening in order to extract the optimal weight of the different coverage regimes, as reported in Fig. 3e and Supplementary Table 5. The resulting fit is satisfactory and leads to an extracted average Cu concentration of 14 wt.%, which is close to the total Cu loading determined experimentally (14.8 wt.%).

The presence of Cu atoms at different adsorption sites can explain the observation of two distinct Cu oxidation states in XAS and XPS spectra. However, since our computational setup is not suited to assess this specific aspect, we cannot reach a definitive conclusion. Qualitatively, the simulated N 1s XPS components indicate that Cu atoms directly interact with both pyridinic N and primary amines, whose XPS features are observed at increased BE because of some charge transfer to the metal atoms. Secondary amines and, to an even smaller extent, graphitic N are, instead, only indirectly affected by Cu atoms, as they experience the overall charge re-arrangement through the delocalized π system.

**CO2RR activity and products analysis**

Once Cu-GCN was chemically and structurally fully characterized, the electrochemical activity towards the CO2 reduction was tested by linear scan voltammetry (LSV) in two different aqueous electrolytes, 0.5 M KHCO3 (pH = 6.8) and 0.1 M phosphate buffer solution (pH = 7). The comparison of the LSV under N2 and CO2 atmosphere in 0.5 M KHCO3 solution is reported in Fig. 4a, whereas the results in phosphate buffer solution are shown in Supplementary Fig. 5b. In both electrolytes, a catalytic behaviour for CO2RR is suggested since the onset of the reduction wave is positively shifted by 91 and 48 mV under the CO2 atmosphere, respectively. In KHCO3, a crossing between the lines in N2 and CO2 is attained at around −1.5 V, suggesting a preferential production of H2 from this applied potential. When the measurements are performed under visible irradiation, an increase of the current density and a shift of the onset potential toward less negative values are observed (Fig. 4a, and Supplementary Figs. 5b and 6), indicating a positive effect of the light attributed to the GCN substrate (Supplementary Fig. 5a).

Several catalyst loadings were tested in order to optimize the current density at different applied potentials (Fig. 4b). Higher differences in the current density with the catalyst loading were observed when the applied potential became more negative. From these results, a catalyst loading of 66 μg cm−2 was selected for the successive RRDE experiments. The RRDE studies were performed in order to qualitatively determine the CO2 reduction products in both electrolytes. With this aim, the catalyst-modified disk was held at different potentials from −0.6 to −1.7 V vs SCE, while the Pt ring potential was scanned from −0.4 to +1 V vs SCE to detect (oxidize) the reduction products. In both electrolytic solutions, only the production of hydrogen was observed in the absence of CO2 as expected (Fig. 5a and Supplementary Fig. 7a), since only the wave related to the H2 oxidation was observed at the Pt ring. The current associated with this process is higher in the phosphate buffer solution, suggesting that the production of hydrogen is favoured in this media. In presence of CO2, a completely different CV is observed at the Pt ring in 0.5 M KHCO3: an oxidation current between −0.1 and +0.4 V, with peak potential at around +0.2 V, is observed (Fig. 5b), which can be attributed to HCOO− oxidation. The attribution of this peak to the formation of HCOO− at the catalyst surface and subsequent oxidation at the Pt ring was confirmed by comparing the CVs in Fig. 5b with those performed at the Pt ring in the presence of added HCOOH (Supplementary Fig. 8). The peak position shifted towards lower potential values upon decreasing the pH, indicating a similar shift reported in the literature upon increasing the HCOOH concentration. The attribution of this peak to HCOO− is also supported by the 1H-NMR analysis of the liquid phase after controlled-potential electrolysis experiments (see below).

RRDE experiments point out the importance of the electrolyte in the product selectivity and the beneficial effect of the bicarbonate salt with respect to the phosphate buffer towards CO2RR. The analysis of Supplementary Fig. 7 shows that H2 is the main reduction product in 0.1 M phosphate buffer solution, both under N2 and CO2 atmosphere, since no evident re-oxidation peaks of carbon products were detected at the Pt ring. This observation is in strong agreement with previous reports in the literature, where the use of phosphate buffer led to a significant increase in the H2 production.

Measurements on pristine 2D GCN were carried out in both electrolytes at different rotation rates in order to confirm that the activity was due to the presence of Cu (Supplementary Figs. 9 and 10). No peaks related to the oxidation of HCOO− or other C-products were observed. Therefore, the catalytic production of HCOO− under CO2 atmosphere in KHCO3 is attributed to the presence of single Cu atoms in the carbon nitride layers. Conversely, in phosphate buffer solution, the presence of the
Cu atoms induces the promotion of the hydrogen evolution reaction, even under the CO2 atmosphere (Supplementary Fig. 11). Chronoamperometry tests were performed in 0.5 M KHCO3 at \(-1.35\) and \(-1.55\) V vs SCE under a continuous flow of CO2, in order to analyze the products by 1H-NMR and gas chromatography and compare them with the RRDE results. A 12% FE for HCOO\(^-\) production was measured at both potential values for Cu-GCN(20), while the rest of the charge was attributed to H2 evolution according to RRDE tests and chronoamperometry experiments carried out in a sealed cell under CO2. No other liquid products were detected, as shown in Supplementary Fig. 12. The same tests were also performed on pristine 2D GCN and Cu-GCN samples with 10 and 30 wt.% Cu loading. The current measured during the experiment for 2D GCN (0.04 mA/cm\(^2\)) was very low and almost negligible with respect to that obtained for Cu-GCN (3.6 mA/cm\(^2\)), as already observed in Supplementary Fig. 5, confirming that GCN does not reduce CO2. Regarding the samples with copper, we observed an increase of the current density with the amount of copper (Supplementary Fig. 13a). The current density displayed by Cu-GCN (10) sample during the electrolysis was very small and no liquid products were detected. The current density displayed by Cu-GCN(30) was higher than that obtained with Cu-GCN(20), as reported in Supplementary Fig. 13b; however, formate was obtained with a lower FE (9%, 40 µmol mg\(^{-1}\) h\(^{-1}\)) than with the sample with 20 wt% Cu (12%). This could be attributed to the presence of copper oxide nanoparticles. It should be highlighted that the results obtained with our Cu-GCN system are in line with those reported in the literature for similar systems\(^44,56\).

Jiao et al. reported a GCN substrate modified with copper atoms as electrocatalyst for the reduction of CO2\(^2\), obtaining CO (ca. 30% FE) as the main CO2 reduction product, together with a variety of different products such as CH4, CH3OH, and several C2 species with a very low FE (<4%). Even if the FE for some of the products was higher than that obtained with our system, the evolution of H2 accounted for the largest charge consumption also in this case. Regarding the current density, similar results were obtained at the same applied potential values (5–10 mA cm\(^{-2}\) at \(-1.6\) V vs SCE). However, the mixture of different liquids and gas products requires a further separation step. The catalytic activity, in terms of current density, of our Cu-GCN (14 mA/mgcat) system is also comparable with the copper-doped cyanographene (10–20 mA/mg) reported by Pieta et al.\(^56\).

**Cu-GCN stability**

The stability of Cu-GCN under CO2RR conditions was investigated by subjecting it to a cycling treatment and then characterizing it by XRD and EXAFS. Results are reported in Fig. 7. The comparison of the XRD patterns for the fresh and cycled electrodes do not show the formation of copper or copper oxides nanoparticles after the cycling treatment under CO2RR conditions (Fig. 7a, b); however, the absence of peaks associated to copper species does not exclude the formation of clusters smaller than 2 nm (XRD detection limit). For this reason, the sample was analyzed by EXAFS. After the cycling treatment, the FT EXAFS spectrum does not differ significantly from the fresh one (Fig. 7c). The absence of an intense peak at 2.2 Å after the cycling treatment indicates that copper nanoparticles are not formed under catalytic conditions, differently to what reported in the literature for other Cu single atoms structures under CO2RR.
The structural parameters obtained from the fit, reported in Supplementary Table 1, indicate that the Cu-GCN sample is stable under CO2RR conditions, which could be attributed to the confinement of the Cu atoms in the structural cavities of GCN and to the strong copper–nitrogen interaction.

**DISCUSSION**

In this work, we synthesized and carefully characterized a 2D GCN functionalized with Cu single atoms by combining experimental and theoretical techniques. In this way, we demonstrated the formation of non-homogeneous samples with Cu adatoms at different adsorption sites and at different local concentrations, which explains the presence of two oxidation states. Subsequently, we tested Cu-GCN as electrocatalyst for the CO2 reduction reaction in two different electrolytes in order to determine the effect on the products selectivity. In bicarbonate solution, formate was obtained as the only product in the liquid phase facilitating its separation; whereas, in phosphate solution, hydrogen was the only product detected. The catalytic results obtained are in line with those reported in the literature for similar systems. Even if a further improvement of the system will be necessary in order to increase the products selectivity, the results obtained suggest that GCN is a promising substrate able to stabilize metal atoms in its structural cavities thanks to the strong copper–nitrogen interaction established.

**METHODS**

**Synthesis of carbon nitride and copper-modified carbon nitride**

1 g of melamine was placed in an alumina crucible with a cover and introduced in a tubular furnace. The temperature was increased up to 100 °C and maintained for 30 min in order to remove the humidity. Then, it was further increased up to 400 °C and kept for 2 h in order to let the melamine condense and form heptazine units (melem). Finally, the temperature was increased up to 550 °C and kept for 4 h to get the final polymerized product. The thermal process was carried out in Ar atmosphere (10 sccm) and using a temperature ramp of 2 °C min−1. The powder obtained had a yellow colour, characteristic of the bulk GCN (bulk GCN)72.

In order to obtain the 2D material, an exfoliation step was carried out. 1 g of bulk GCN was added into 30 mL of H2SO4 (98 % w/w, Sigma-Aldrich) and kept under stirring overnight. Then, the suspension was cooled down in an ice/water bath and 100 mL of deionized water was added drop by drop. The diluted suspension was kept under sonication for 2 h and then under stirring for 24 h. The exfoliated GCN product was centrifuged at 9000 rpm for 10 min and washed with deionized water. The final product (GCN) was obtained by drying under vacuum. The powder showed the characteristic white colour of the 2D GCN73.

In order to modify 2D GCN with copper, 0.08 g of GCN and the necessary amount of Cu(NO3)2·2.5H2O (Sigma-Aldrich) to obtain a nominal metal loading of 10, 20, or 30 wt.% were dispersed in 100 mL of Milli-Q water and sonicated for 3 h under Ar atmosphere. Then, 20 mL of 0.5 M NaBH4 solution were slowly added and let react for 1 h. Finally, the catalyst was separated by centrifugation, washed with Milli-Q water and ethanol, and...
dried under vacuum. The materials obtained were labelled as Cu-GCN(X), with X = 10, 20, 30.

**Characterization techniques**

SEM images were acquired with a ZEISS Supra VP35 microscope, whereas the TEM images with a FEI Tecnai G2 microscope. The XRD characterization was performed with a Bruker D8 Advence, configured with a glancing angle geometry, operating with Cu Kα radiation (λ = 0.15406 nm) generated at 40 kV and 40 mA. Raman spectra were collected using a ThermoFisher DXR Raman microscope using a laser with an excitation wavelength of 532 nm (1 mW), focused on the sample with a 50× objective (Olympus). Solid-state Fourier Transform Infrared (FT-IR) KBr disk technique absorption spectra were recorded with a Jasco FT-IR-4100spectrometer. X-ray photoelectron spectroscopy (XPS) measurements were acquired in a custom-made UHV system working at a base pressure of 10⁻¹⁰ mbar, equipped with an Omicron EA125 electron analyzer and an Omicron DAR 400 X-ray source with a dual Al–Mg anode. Core-level photoemission spectra (C 1s, N 1s, O 1s, and Cu 2p) were collected at room temperature with a non-monochromatized Al Kα X-ray source (1486.3 eV). Single spectra were acquired using a 0.1 eV steps, 0.5 s collection time, and 20 eV pass energy. In order to analyze the single components of the C 1s and N 1s regions, the spectra were separated into chemically shifted components. For the C 1s region, an asymmetrical shape was used for the sp² component, whereas symmetrical Voigt functions were used for the sp³ component, the C–O functional groups, and C–(N) species. For the N 1s region, symmetrical Voigt functions were used. X-ray absorption spectrum measurements were recorded on beamline B18 of the Light Source (UK) with ring energy of 3 GeV and a current of 300 mA. The monochromator used was Si(311) crystals operating in Quick EXAFS (QEXAFS) mode. Pellets of Cu-GCN and the oxides used as references were measured in transmission mode at the Cu K (7709 eV) absorption edge at 298 K with a 36-element Ge detector. The Cu foil was measured simultaneously. In addition, a button electrode was prepared by painting a carbon paper electrode (1 x 1 cm) with the Cu-GCN sample, and subjected to an accelerated ageing treatment (1000 cycles between −0.6 and −1.5 V vs CuSO₄ at 50 mV s⁻¹ in 0.5 M HClO₄). The cyclic voltammetry was also measured by ex situ XAS in fluorescence mode. Calibration of the monochromator was carried out using the Cu foil previously to the measurements. The acquired data were processed and analyzed using the Athena programme. Solid-state absorption spectra were recorded using a Cary 5000 UV–Vis-Spectrometer equipped with a Diffuse Reflectance Accessory. The spectra were acquired and plotted as Kubelka–Munk function F(R) = A°C/ S (A = absorbance, C = Concentration, S = scattering coefficients).

**Electrochemical methods**

Electrochemical measurements were conducted in a three-electrode cell using a saturated calomel electrode (SCE in KCl sat.) as a reference electrode and a graphite rod or a Pt wire as a counter electrode. All the experiments were performed at room temperature. The currents reported are normalized by the electrode geometric area and the potential values are referred to SCE. The working electrode consisted of a thin-film catalyst layer deposited on a glassy carbon (GC) electrode (3 mm diameter for the rotating-disk experiments, 1 or 2 cm² GC plate for the electrolysis measurements). Before the catalyst modification, the GC electrode was polished with 0.25 μm diamond paste and sonicated in isopropyl alcohol. The catalyst ink was prepared by mixing 2 mg of catalyst, 10 μL Nafion® (5 wt.%, Sigma-Aldrich), 500 μL of Milli-Q water, and 500 μL of dimethylformamide. The ink was sonicated for 20 min in order to facilitate the formation of the catalyst. After ink deposition, the electrodes were dried in the air. Measurements were carried out in N₂-saturated 0.5 M KHCO₃/0.1 M phosphate buffer, prepared from high purity reagents (Sigma-Aldrich). The RDE measurements were recorded in the absence and presence of light, using a white LED lamp (OSRAM—9 LED Star Oslon 150 white 1170 lm cm⁻²@350 mA) as a light source, to investigate any activity enhancement by light. The ohmic drop compensation was performed during the data treatment, by using a value for the solution resistance measured by electrochemical impedance spectroscopy (generally 40 Ω for the KHCO₃ solution).

A RRDE with a GC disk (5 mm diameter) and the platinum ring was used for the characterization of the products obtained during the CO₂RR. The ring was cycled between −0.4 and −1.0 V vs SCE at 0.2 Vs⁻¹ (3500 or 500 ppm as rotating speed), while the disk was held at different potential values between −0.6 and −1.7 V vs SCE. A H-type cell was used for the chronocoulometry tests. Both the graphite counter electrode (or Pt wire) and the SCE were separated from the cathodic compartment by a ceramic frit. Two kinds of experiments were carried out: on one hand, the cell was completely sealed after 1-h purging with CO₂ and the solution was kept under magnetic stirring during the test. The gas and liquid products were analyzed by headspace gas chromatography and ¹H-NMR, respectively. Preliminary experiments showed that only H₂ and HCOO⁻ were produced. On the other hand, the solution was continuously purged by CO₂ during the whole experiment and the liquid phase was analyzed by ¹H-NMR.

**Analysis of the products**

The liquid products were determined by ¹H-NMR analysis using a Bruker Avance (300 MHz) with the water pre-saturation method. Samples were prepared by mixing 400 μl of the electrolytic solution with deuterated water (D₂O, 50 μl) and 50 μl of DMSO solution (prepared by dissolving 43.1 mg DMSO in 50 ml of Milli-Q water) as an internal standard (the DMSO peak was fixed at 2.71 ppm). The gaseous products (H₂, CO, and CH₄) were analyzed by gas chromatography (Agilent Technologies 7890 A) equipped with a Molsieve 5 Å column, using a thermal conductivity detector and Ar as a carrier gas. The calibration curves for the different volatile products were obtained by injecting exact amounts of the pure gases. The measurements were carried out by sampling the headspace with a 500 μl gas-tight syringe.

The amount of HCOO⁻ produced by a 0.26 mg cm⁻² modified GC disc (1.1 cm²) in a 4-h experiment under a continuous flow of CO₂ at −1.55 V vs SCE was 35 μmol. In more detail, the concentration of the product in the NMR tube was calculated by using Eq.

\[
\text{HCOO}^- = \frac{\text{Area HCOO}^- \text{ peak}}{\text{Area DMSO peak}} \times \frac{H}{\text{HDMSO peak}} \times \text{HDMSO} \times \frac{100}{\text{Charge (f)}}
\]

with F (Faraday constant) = 96485 C mol⁻¹.

**Computational methods**

The calculations were carried out within the DFT framework, using the plane-waves code QuantumESPRESSO75–77, through the Perdew–Burke–Ernzerhof exchange-correlation functional78, accounting for the Van der Waals dispersion forces in the form of the Grimme-D3 correction term79. Ultrasoft pseudopotentials80 were employed from the most recent versions of the code, and the chemical monomers, in order to allow the proper number of degrees of freedom for the structural optimization; for these structures, a converged grid of shifted Monkhorst–Pack82 mesh of k-points was used.

The N 1s XPS spectra were calculated through the ΔSCF scheme83, with the use of pseudopotentials modified as to contain a core-hole. In this way, given a chosen model, by running a separate calculation for each inequivalent core-excited atom it is possible to reconstruct the shift of its binding energy (BE) from an artificial reference, called core level shift (CLS). In our setup, the reference BE was chosen as the average, different for each structure, of the total energies of the core-excited systems. The chemical shift between the XPS spectra of different models was calculated through the inclusion of an N₂ molecule far from the surfaces, acting as a common reference, which has already proven useful in the past84. In order to get a better comparison with experimental results, a Gaussian line shape was superimposed to each calculated CLS, with a half-width-half-maximum of 0.7 eV.

We constructed the pristine structure (2D GCN) as a 2D sheet of melon, whose calculated properties, namely XRD and XPS spectra, show a good agreement with the ones observed experimentally: the models and their results are shown in Supplementary Figs. 3 and 4. To fit experimental data, we take into account the formation of different melon structures, which we label ‘alternated’ or ‘linear’, differing by the relative arrangement of the monomers.
The Cu-SCN models were built by placing single Cu adatoms at three N sites in the monomer fragment, as shown in Fig. 3d or in Supplementary Fig. 4, which are labelled ‘Amino I’, ‘Amino II’ and ‘Top’, respectively. Two coverage regimes are considered, namely ‘low’ and ‘high’, as defined in Supplementary Fig. 4 and detailed in the Supplementary Discussion.

DATA AVAILABILITY

All the data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Data related to this paper may be requested from the authors.

CODE AVAILABILITY

The code used in this work is available at www.quantum-espresso.org.

REFERENCES

1. Aresta, M., Dibenedetto, A. & Angelini, A. The changing paradigm in CO2 utili-
2. Aresta, M. & Dibenedetto, A. Utilisation of CO2 as a chemical feedstock: oppor-
3. Lu, F. et al. Electrochemical CO2 reduction: from nanoclusters to single atom
4. Li, J. et al. Highly active and stable metal single-atom catalysts achieved by strong
5. Zhang, X. et al. Catalytically active single-atom niobium in graphitic layers.
6. Sun, S. et al. Single-atom catalysis using Pt/graphene achieved through atomic
7. Jiang, K. et al. Isolated Ni single atoms in graphene nanosheets for high-
8. Choi, C. H. et al. Tuning selectivity of electrochemical reactions by atomically
9. Davis, K., Li, R. & Sun, X. Recent advances and strategies in
10. Tong, J. et al. Rapid and high-yield production of g-C3N4 nanosheets via che-
11. Chen, Z. et al. Single-atom heterogeneous catalysts based on distinct carbon
12. Fei, H. et al. Single atom electrocatalysts supported on graphene or graphene-like carbons. Chem. Sci. 48, 5207–5241 (2019).
13. Kwak, J. H. et al. Coordinatively unsaturated Al3
14. Vilé, G. et al. A stable single-site palladium catalyst for hydrogenations. Angew. Chem. Int. Ed. 54, 11265–11269 (2015).
15. Chen, Z. et al. Single-atom heterogeneous catalysts based on distinct carbon
16. Fei, H. et al. Single atom electrocatalysts supported on graphene or graphene-like carbons. Chem. Sci. 48, 5207–5241 (2019).
17. Li, J. et al. Highly active and stable metal single-atom catalysts achieved by strong
18. Wang, X. et al. Confined Fe–Cu clusters as sub-nanometer reactors for efficiently
19. Wang, X. et al. Confined Fe–Cu clusters as sub-nanometer reactors for efficiently
20. Vilé, G. et al. A stable single-site palladium catalyst for hydrogenations. Angew. Chem. Int. Ed. 54, 11265–11269 (2015).
21. Chen, Z. et al. Single-atom heterogeneous catalysts based on distinct carbon
22. Fei, H. et al. Single atom electrocatalysts supported on graphene or graphene-like carbons. Chem. Sci. 48, 5207–5241 (2019).
23. Deng, D. et al. A single iron site confined in a graphene matrix for the catalytic
24. Zhuo, H.-Y. et al. Theoretical understandings of graphene-based metal single-
25. Baby, A., Trovato, L. & Di Valentin, C. Single atom catalysts (SAC) trapped in
defective and nitrogen-doped graphene supported on metal substrates. Carbon 174, 772–788 (2021).
26. Cai, Y. et al. Insights on forming N,O-coordinated Cu single-atom catalysts for
electrochemical reduction CO2 to methane. Nat. Commun. 12, 586 (2021).
27. Wang, X. et al. Confined Fe–Cu clusters as sub-nanometer reactors for efficiently
28. Wang, X. et al. Confined Fe–Cu clusters as sub-nanometer reactors for efficiently
29. Li, Y., Li, B., Zhang, D., Cheng, L. & Xiang, Q. Crystalline carbon nitride supported copper single atoms for photocatalytic CO2 reduction with nearly 100% CO selectivity. ACS Nano 14, 10552–10561 (2020).
30. Feng, J. et al. A Mn-N3 single-atom catalyst embedded in graphitic carbon nitride
31. Ong, W.-J., Tan, L.-L., Ng, Y. H., Yong, S.-T. & Chai, S.-P. Graphitic carbon nitride
32. Wang, H. et al. Insights into the excitonic processes in polymeric photocatalysts.
33. Tahir, M., Tahir, B., Nawawi, M. G. M., Hussain, M. & Muhammad, A. Cu-NPs
34. Shi, G. et al. Photocatalytic reduction of CO2 to CO over copper decorated g-
35. Karapinar, D. et al. Electroreduction of CO2 on single-site copper-nitrogen-
doped carbon material: selective formation of ethanol and reversible restructuration of the metal sites. Angew. Chem. Int. Ed. 58, 15098–15103 (2019).
36. Jiang, K. et al. Isolated Ni single atoms in graphene nanosheets for high-
37. Hou, P., Song, W., Wang, X., Hu, Z. & Kang, P. Well-defined single-atom cobalt
38. Choi, C. H. et al. Tuning selectivity of electrochemical reactions by atomically
39. Sun, S. et al. Single-atom catalysis using Pt/graphene achieved through atomic
40. Zhang, X. et al. Catalytically active single-atom niobium in graphitic layers. Nat.
41. Wang, Y. et al. Single atom electrocatalysts supported on graphene or graphene-like carbons. Chem. Sci. 48, 5207–5241 (2019).
42. Kas, R. et al. Electrochemical CO2 reduction on Cu2O-doped carbon nanotubes: controlling the catalytic selectivity of hydrocarbons. Phys. Chem. Chem. Phys. 16, 12194–12201 (2014).
43. Nitopi, S. et al. Progress and perspectives of electrochemical CO2 reduction on copper in aqueous electrolyte. Chem. Rev. 119, 7610–7672 (2019).
44. Jiao, Y., Zheng, Y., Chen, P., Jaroniec, M. & Qiao, S.-Z. Molecular scaffolding
45. Chen, Z. et al. Stabilization of single metal atoms on graphitic carbon nitride. Adv. Funct. Mater. 27, 1605785 (2017).
46. Chen, Z. et al. Merging single-atom-dispersed silver and carbon nitride to a joint
electronic system via copolymerization with silver tricyanomethanide. ACS Nano 10, 3166–3175 (2016).
47. Tahir, B., Tahir, M. & Amin, N. A. S. Ag-La loaded protonated carbon nitride nanotubes (pC3N4) with improved charge separation in a monolithic honeycomb photocatalyst for enhanced birefringence of methane (BRM) to fuels. Appl. Catal. B: Environ. 248, 167–183 (2019).
48. Tong, J. et al. Rapid and high-field production of g-C3N4 nanosheets via che-
49. Wang, W., Yu, J. C., Shen, Z., Chan, D. K. L. & Gu, T. g-C3N4 quantum dots: direct
50. Wang, W., Yu, J. C., Shen, Z., Chan, D. K. L. & Gu, T. g-C3N4 quantum dots: direct
51. Wang, W., Yu, J. C., Shen, Z., Chan, D. K. L. & Gu, T. g-C3N4 quantum dots: direct
52. Wang, W., Yu, J. C., Shen, Z., Chan, D. K. L. & Gu, T. g-C3N4 quantum dots: direct
50. Zhang, J., Zhang, M., Lin, L. & Wang, X. Sol processing of conjugated carbon nitride powders for thin-film fabrication. Angew. Chem. Int. Ed. 54, 6297–6301 (2015).

51. Fina, F., Callier, S. K., Carins, G. M. & Irvine, J. T. S. Structural investigation of graphitic carbon nitride via XRD and neutron diffraction. Chem. Mater. 27, 2612–2618 (2015).

52. Yang, P. et al. Carbon nitride-based single-atom Cu catalysts for highly efficient photocatalytic alkynes with atmospheric CO2. Ind. Eng. Chem. Res. 59, 7327–7335 (2020).

53. Wu, B. et al. Cu single-atoms embedded in porous carbon nitride for selective oxidation of methane to oxygenates. Chem. Commun. 56, 14677–14680 (2020).

54. Zhang, T. et al. Single atomic Cu–N2 catalytic sites for highly active and selective hydroxylation of benzene to phenol. Science 322, 97–108 (2019).

55. Wang, G. et al. Modulating location of single copper atoms in polymeric carbon nitride for enhanced photoredox catalysis. ACS Catal. 10, 5715–5722 (2020).

56. Pieta, I. S. et al. The hallmarks of copper single atom catalysts in direct alcohol fuel cells and electrochemical CO2 fixation. Adv. Mater. Interfaces 8, 2001822 (2021).

57. Sun, S. et al. Boosting oxygen evolution kinetics by Mn–N–C motifs with tunable spin state for highly efficient solar-driven water splitting. Adv. Energy Mater. 9, 1901505 (2019).

58. Biesinger, M. C. Advanced analysis of copper X-ray photoelectron spectra: advanced analysis of copper X-ray photoelectron spectra. Surf. Interface Anal. 49, 1325–1334 (2017).

59. Yano, T., Ebizuka, M., Shibata, S. & Yamane, M. Anomalous chemical shifts of Cu 2p and Cu LMM Auger spectra of silicate glasses. J. Electron Spectrosc. Relat. Phenom. 131–132, 133–144 (2003).

60. Kim, J. et al. Branched copper oxide nanoparticles induce highly selective ethylene production by electrochemical carbon dioxide reduction. J. Am. Chem. Soc. 141, 6968–6994 (2019).

61. Akaike, K., Aoyama, K., Dekubo, S., Onishi, A. & Kanai, K. Characterizing electronic structure near the energy gap of graphitic carbon nitride based on rational interpretation of chemical analysis. Chem. Mater. 30, 2341–2352 (2018).

62. Liang, Q., Li, Z., Huang, Z.-H., Kang, F. & Yang, Q.-H. Holey graphitic carbon nitride nanosheets with carbon vacancies for highly improved photocatalytic hydrogen production. Adv. Funct. Mater. 25, 6885–6892 (2015).

63. Thomas, A. et al. Graphitic carbon nitride materials: variation of structure and morphology and their use as metal-free catalysts. J. Mater. Chem. 18, 4893–4900 (2008).

64. Yu, S. et al. Local spatial charge separation and proton activation induced by surface hydroxylation promoting photocatalytic hydrogen evolution of polymeric carbon nitride. Nano Energy 50, 383–392 (2018).

65. Zhang, X., Jia, C., Xue, Y. & Yang, P. Fabrication of rGO/g-C3 N4 composites via electrostatic assembly towards charge separation control. RSC Adv. 7, 43888–43893 (2017).

66. Liu, J. et al. Graphitic carbon nitride (g-C3 N4)-derived N-rich graphene with tuneable interlayer distance as a high-rate anode for sodium-ion batteries. Adv. Mater. https://doi.org/10.1002/adma.201901261 (2019).

67. Zhang, F. & Co, A. C. Rapid product analysis for the electroreduction of CO2 on Cu single-atoms embedded in nitrogen-doped graphene. ACS Catal. Acta 283, 1037–1048 (2014).

68. Briega-Martos, V., Ferre-Vilaplana, A., Herrero, E. & Feliu, J. M. Why the activity of the hydrogen oxidation reaction on platinum decreases as pH increases. Electrochim. Acta 354, 136620 (2020).

69. Hori, Y., Murata, A. & Takahashi, F. Formation of hydrocarbons in the electrochemical reduction of carbon dioxide at a copper electrode in aqueous solution. J. Chem. Soc., Faraday Trans. 1, 2309 (1994).

70. Costentin, C., Robert, M., Savéant, J.-M. & Tatin, A. Efficient and selective molecular catalyst for the CO2-to-CO electrochemical conversion in water. Proc. Natl Acad. Sci. USA 112, 6882–6886 (2015).

71. Wang, X. et al. A 133-atom free polymeric photocatalyst for hydrogen production from water under visible light. Nat. Mater. 8, 76–80 (2009).

72. Han, Q. et al. Facile production of ultrathin graphitic carbon nitride nanoplatelets for efficient visible-light water splitting. Nano Res. 8, 1718–1728 (2015).

73. Chatterjee, T., Boutilier, E. & Robert, M. Manifesto for the routine use of NMR for the liquid product analysis of aqueous CO2 reduction: from comprehensive chemical shift data to Kormalský quantification in water. Dalton Trans. 49, 4257–4265 (2020).

74. Giannozzi, P. et al. Quantum ESPRESSO: a modular and open-source software project for quantum simulations of materials. J. Phys.: Condens. Matter 21, 395502 (2009).

75. Giannozzi, P. et al. Advanced capabilities for materials modelling with Quantum ESPRESSO. J. Phys.: Condens. Matter 29, 465901 (2017).

76. Giannozzi, P. et al. Quantum ESPRESSO toward the exascale. J. Chem. Phys. 152, 154105 (2020).

77. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. Phys. Rev. Lett. 77, 3865–3868 (1996).

78. Grimme, S., Antony, J., Ehrlich, S. & Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. J. Chem. Phys. 132, 154104 (2010).

79. Vanderbilt, D. Soft self-consistent pseudopotentials in a generalized eigenvalue formalism. Phys. Rev. B 41, 7892–7895 (1990).

80. Dal Corsa, A. Pseudopotentials periodic table: from H to Pu. Comput. Mater. Sci. 95, 337–350 (2014).

81. Monkhorst, H. J. & Pack, D. Special points for Brillouin-zone integrations. Phys. Rev. B 13, 5188–5192 (1976).

82. García-Gil, S., García, A. & Ordejón, P. Calculation of core level shifts within DFT using pseudopotentials and localized basis sets. Eur. Phys. J. B 85, 239 (2012).

83. Fiori, S. et al. ‘Inside out’ growth method for high-quality nitrogen-doped graphene. Carbon 171, 704–710 (2021).

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AUTHOR CONTRIBUTIONS

L.C. and G.G. conceived and supervised the project. E.G. and C.C. synthesized the materials and performed the Raman spectroscopy, XPS, TEM characterization. G.B. and L.A. carried out the UV–Vis measurements. AM contributed to the synthesis of the materials and the FTIR characterization. C.C. conducted the electrochemical characterization and the CO2 reduction part. L.C. carried out the analysis of the results. A.U. and C.D.V. performed the theoretical study. C.C., A.U., C.D.V., and L.C. wrote the paper. All the authors took part in the results discussion and assisted during the paper preparation. C.C. and A.U. contributed equally to this work.

COMPETING INTERESTS

The authors declare no competing interests.

ADDITIONAL INFORMATION

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