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Facilely synthesized nitrogen-doped reduced graphene oxide functionalized and/or co-doped with metal ions as electrocatalyst for oxygen reduction reaction

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ABSTRACT

Due to fossil fuels depletion and environmental pollution, clean and sustainable energy technologies, e.g. fuel cells and metal-air batteries, have attracted extensive attention.

To push further the research on these electrochemical devices, low-cost, durable and efficient electrocatalysts alternative to platinum are required, to boost the oxygen reduction reaction (ORR).

A microwave-assisted method has been optimized, to obtain effective heterogeneous catalyst for ORR, starting from graphene oxide (GO), urea and a transition metal (e.g. Mn and Cu) precursor. We have proved that our synthetic method originates porphyrin-like structures containing pyrrole rings within the reduced GO (rGO) basal plane which coordinate the Mn^{2+}. In the case of copper, however, Cu^{2+} forms an ionic tetra coordinated structure anchored at the rGO surface via residual oxygen containing functional groups. In both cases, metal complex acts as an ORR highly efficient catalytic reaction center and their identification were strongly supported by several characterization techniques, such as X-ray Photoelectron Spectroscopy (XPS), X-ray absorption spectroscopies (XAS) and Transmission Electron Microscopy (TEM), together with Density Functional Theory (DFT) simulations. All synthesized materials exhibit outstanding catalytic properties toward ORR, as evidenced by electron transfer numbers larger than 3.8 and peroxide percentages lower than 7%, similar to Pt/C reference electrode.

Video to this article can be found online at https://doi.org/10.1016/j.sctalk.2022.100073.

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Figures and Tables

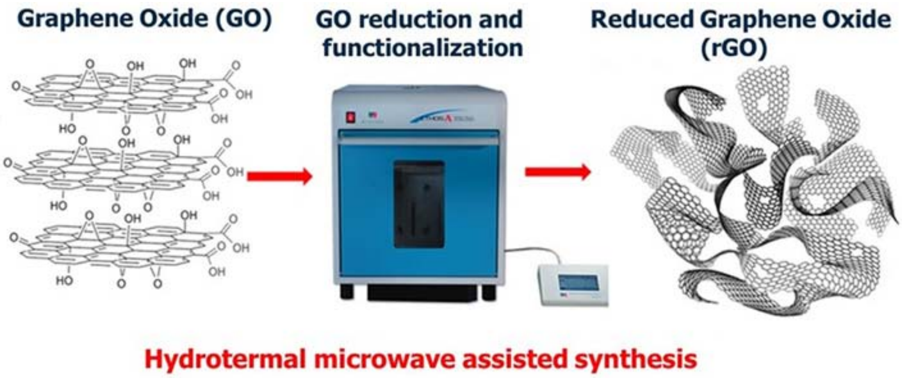

Fig. 1. Schematic illustration of the synthesis of reduced graphene oxide (rGO) starting from commercial graphene oxide (GO) by means of a hydrothermal assisted microwave setup.

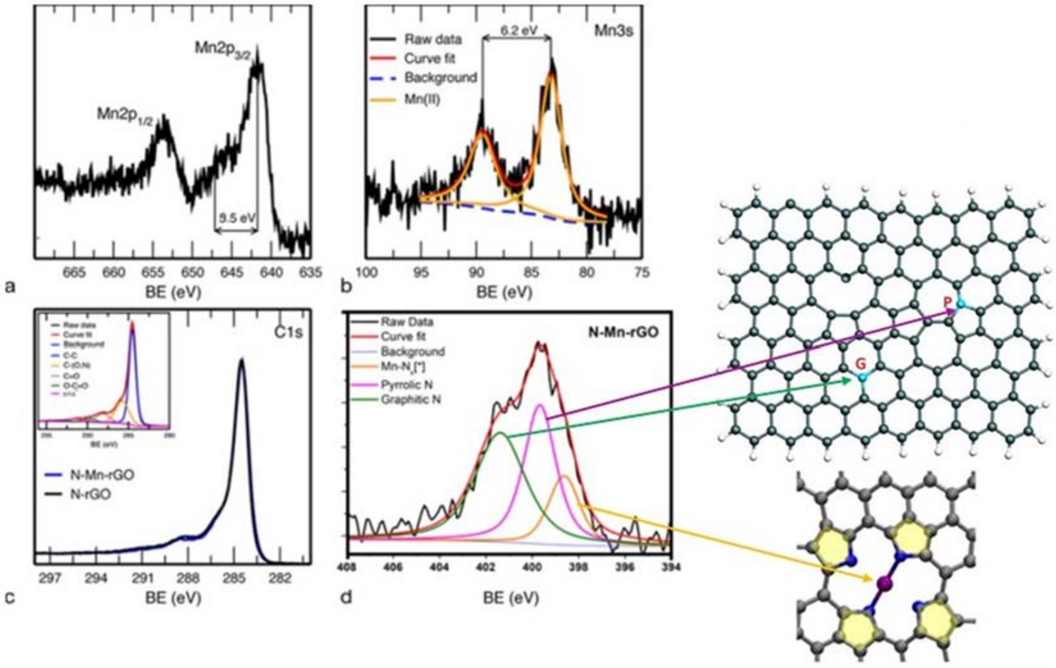

Fig. 2. XPS HR spectra of Mn2p (a) and Mn3s (b) doublets, C1s (c) and N1s (d) peaks for N-rGO and N-Mn-rGO samples. Image adapted from [1].

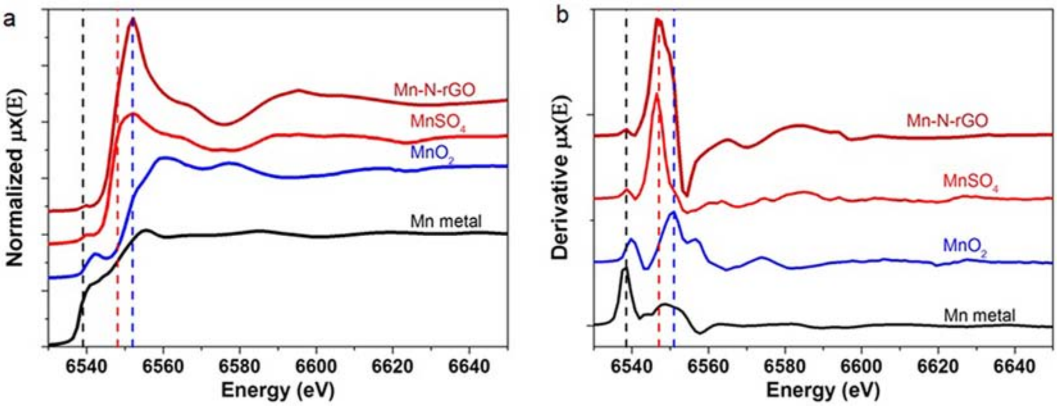

Fig. 3. XANES spectra of (a) Mn metallic foil, MnO2, MnSO4 and Mn-N-rGO powder and their derivative (b). The vertical dotted lines represent the position of the Mn absorption K-edge for the oxidation states 0, +2 and +4 (black, red and blue, respectively). Image adapted from [1].

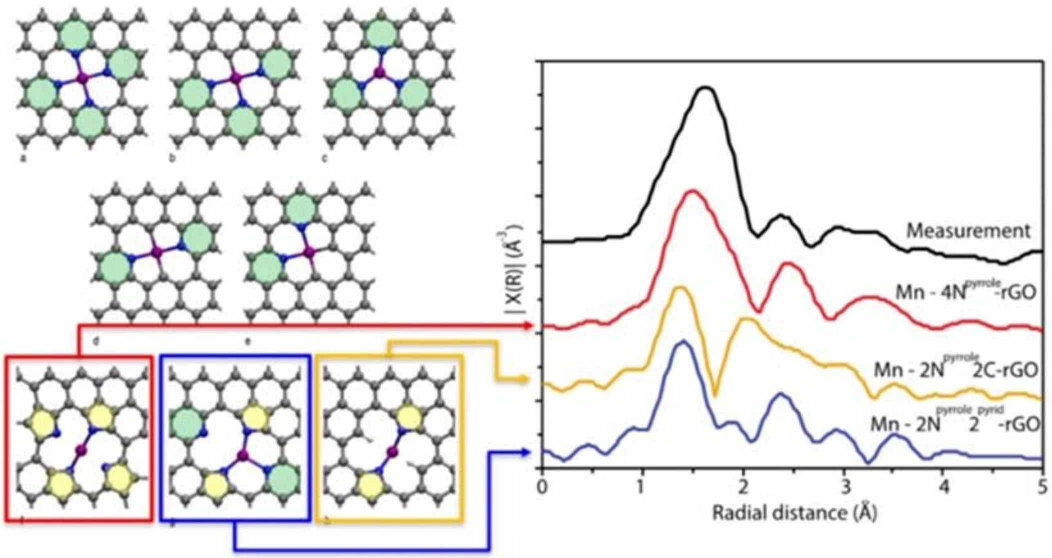

Fig. 4. Mn K edge EXAFS corresponding Fourier transform in R space of the Mn-N-rGO sample. Black line represents experimental data, while red, yellow and blue lines represent the fit procedures obtained using the structures shown in the left side of the figure. The best fit has been obtained with the red line, which represents the Mn atom in a porphyrin-like structure as shown in inset (d).

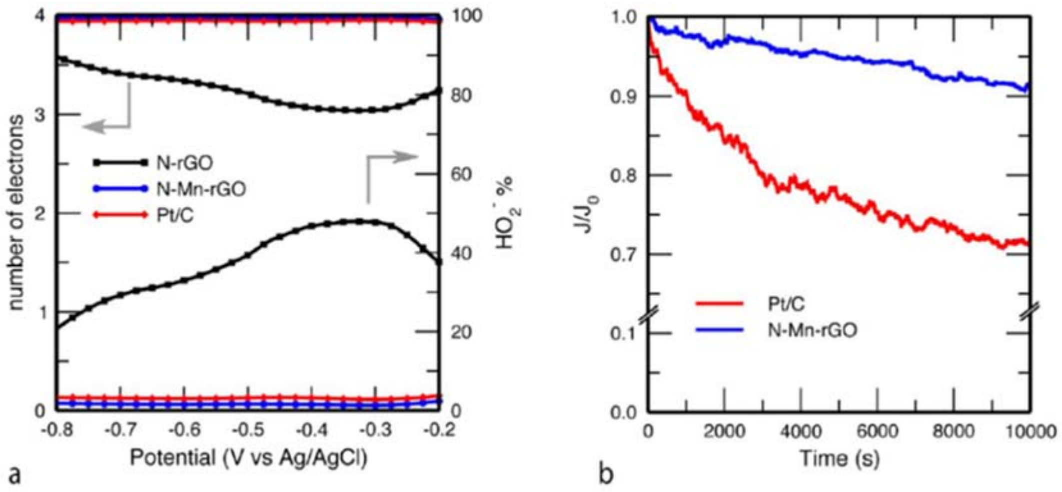

Fig. 5. (a) Comparison of electron transfer number (left axis) and peroxide percentage (right axis) evaluated from RRDE measurements. (b) Chronoamperometric curves normalized with respect to the initial current value.

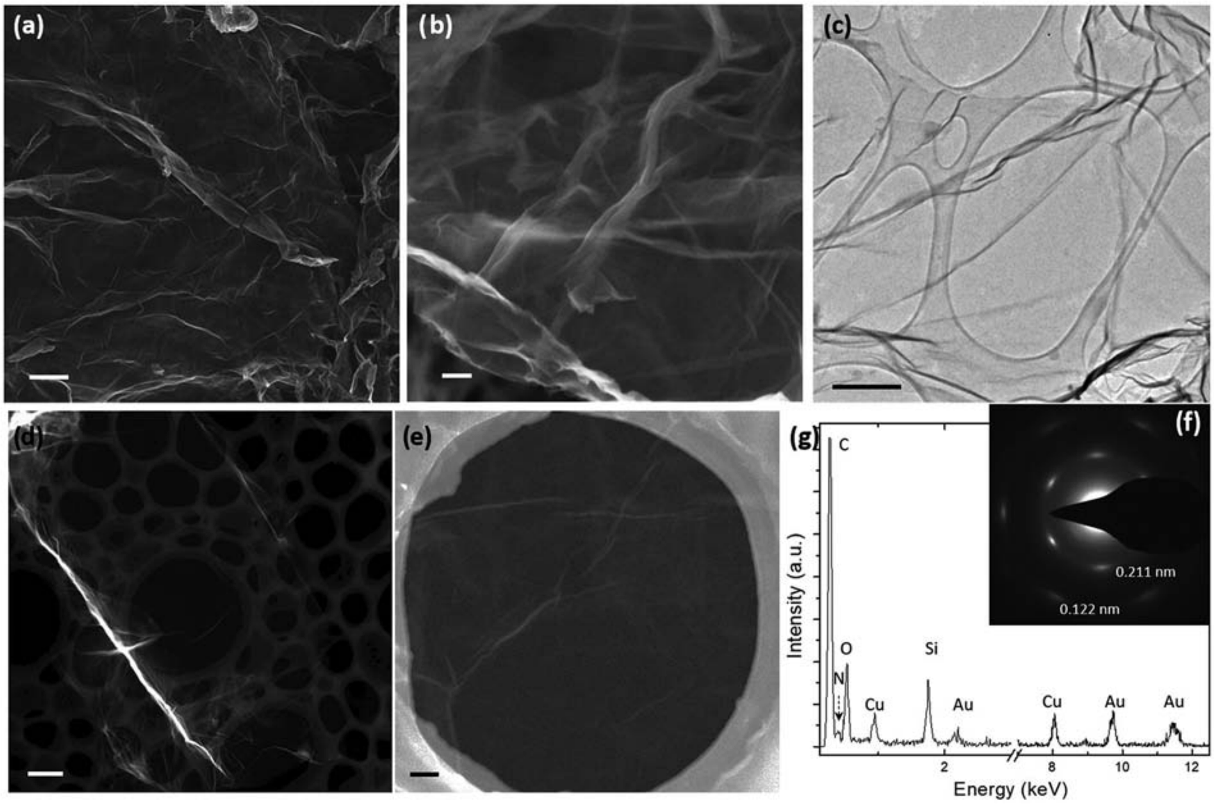

Fig. 6. Electron microscopy characterization of Cu-N-rGO sample. (a) FESEM micrograph (scale bar: 1 μm), (b) FESEM micrograph (scale bar:100 nm), (c) BFTEM image (scale bar: 500 nm), (d) STEM micrograph (scale bar: 1 μm), (e) STEM micrograph (scale bar: 100 nm), (f) selected area electron diffraction pattern and (g) EDX spectrum. Image adapted from [2].

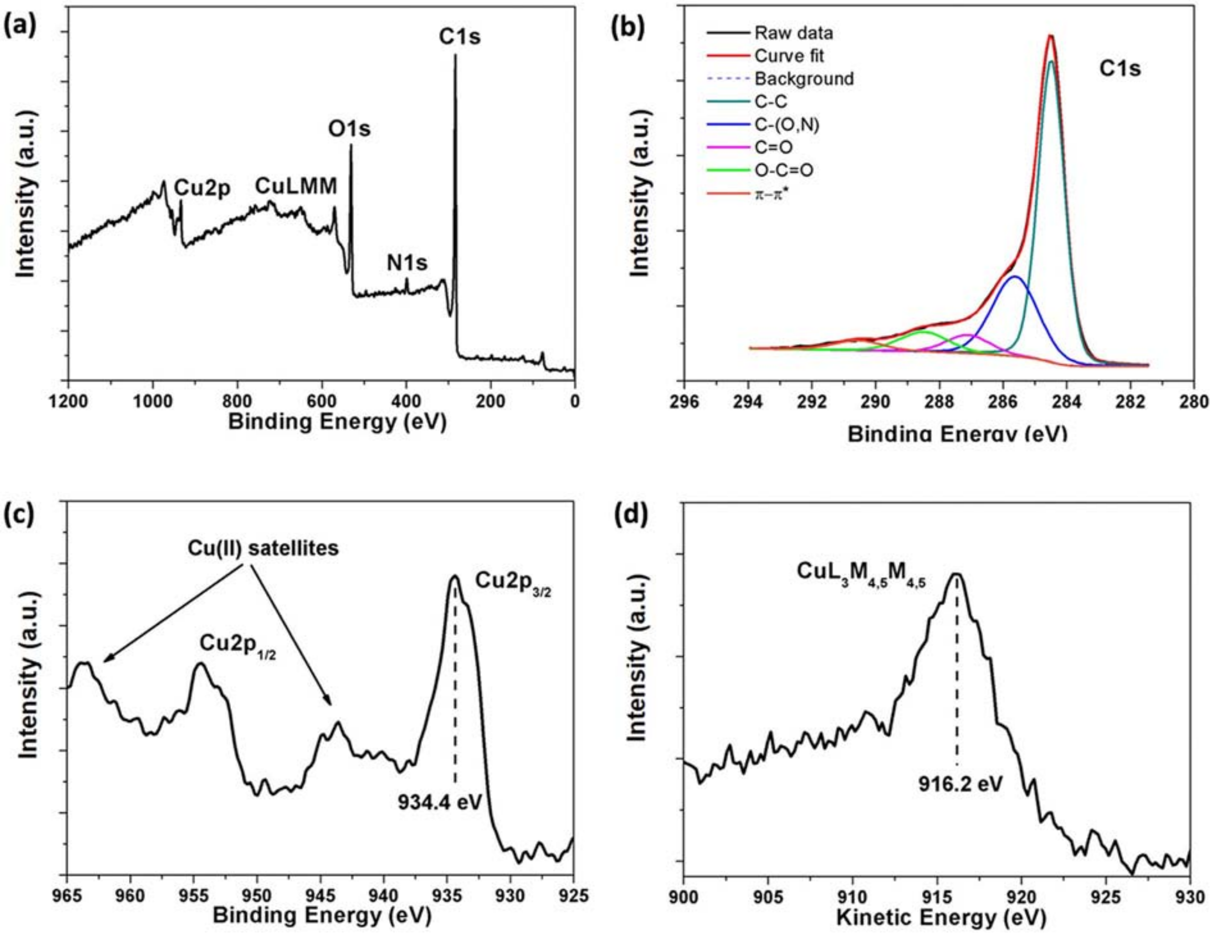

Fig. 7. XPS characterization of Cu-N-rGO sample. (a) Survey spectrum, (b) C1s HR spectrum with deconvolution procedure, (c) Cu2p HR doublet and (d) CuLMM Auger peak. Image adapted from [2].

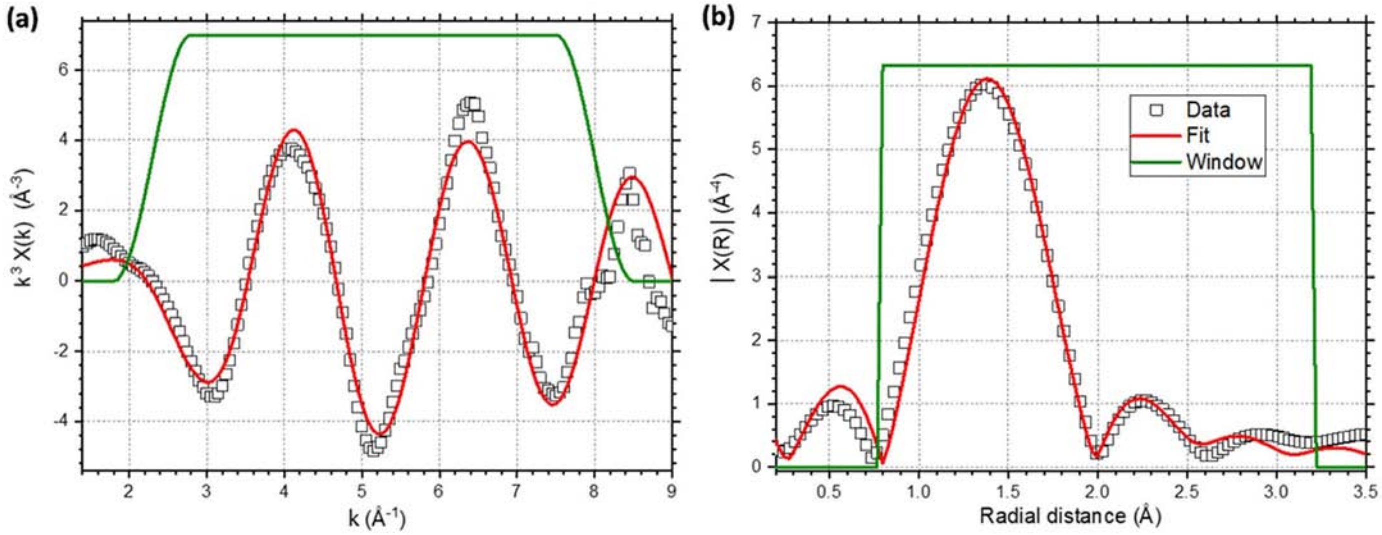

Fig. 8. EXAFS study of Cu-N-rGO sample. (a) k3-weighted Cu K edge EXAFS, (b) corresponding Fourier transform in R-space. The solid red lines represent the best fit obtained using the structure of Cu ion coordinated to two surface —O— groups and also bound to hydroxyl groups. Image adapted from [2].

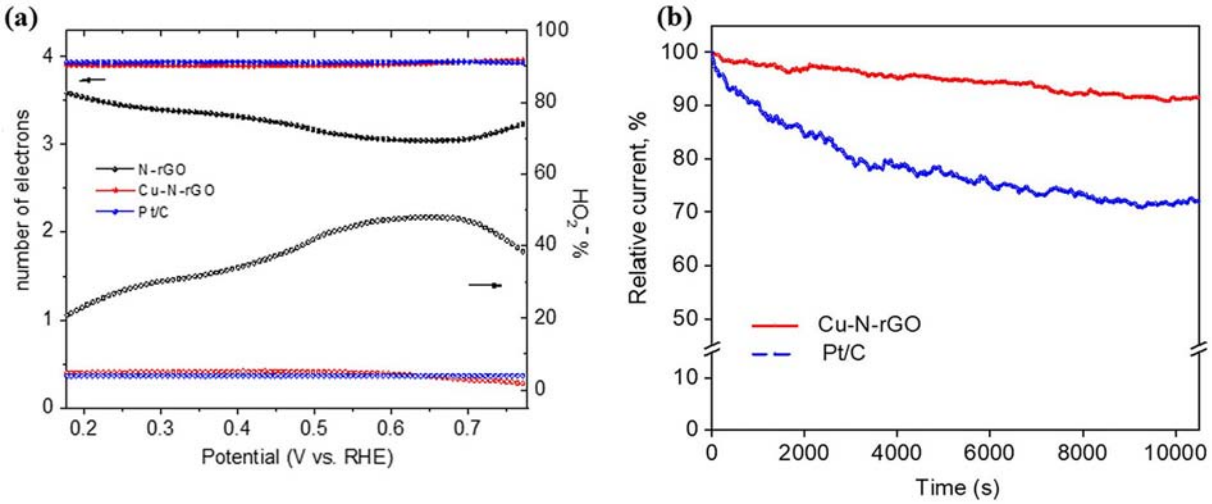

Fig. 9. (a) Rotating ring disk electrode study. Number of electrons (left axis) and peroxide percentage (right axis) on graphene-based and reference Pt/C catalysts in air-saturated 0.1 M KOH solution. (b) CA measurements on Cu-N-rGO and reference Pt/C catalysts in air-saturated 0.1 M KOH solution. Image adapted from [2].

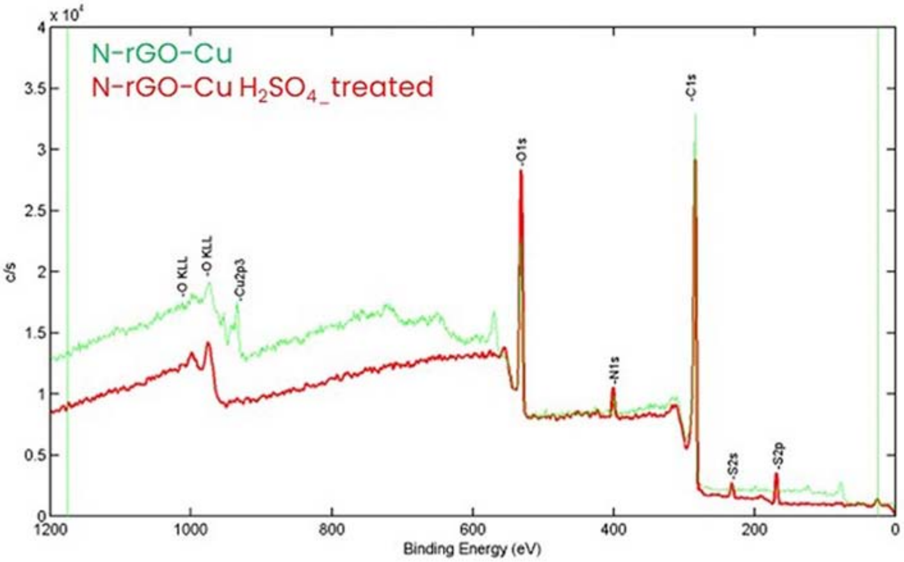

Fig. 10. XPS survey spectra of Cu-N-rGO sample before (green line) and after (red line) H_2SO_4 treatment.

CRediT author statement

J.Z., A.S., N.G., and G.C. contributed to the conceptualization. C.F.P. contributed to funding acquisition. J.Z., N.G., A.S., M.C., K.B., A.C., F.R., M.R.F., G.C., J.S.-R. contributed to formal analysis and investigation. All authors contributed to writing, review and editing original draft.

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Declaration of interests

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

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Further reading

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