

Supporting Information

Controlled electrochemical and electroless deposition of noble metal nanoparticles on graphene

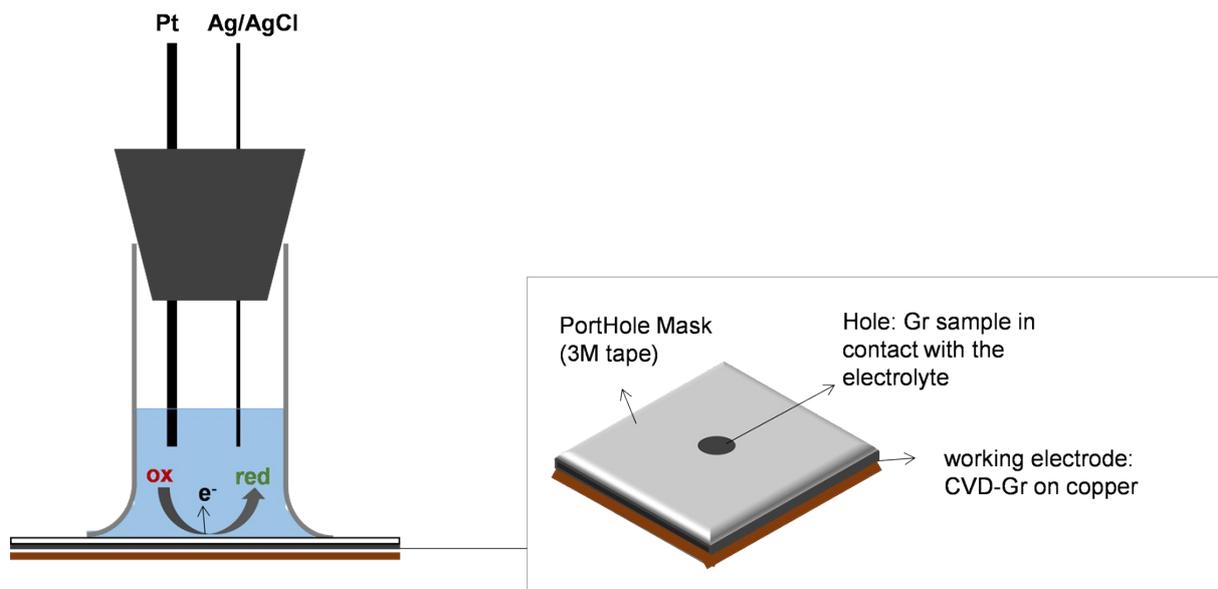
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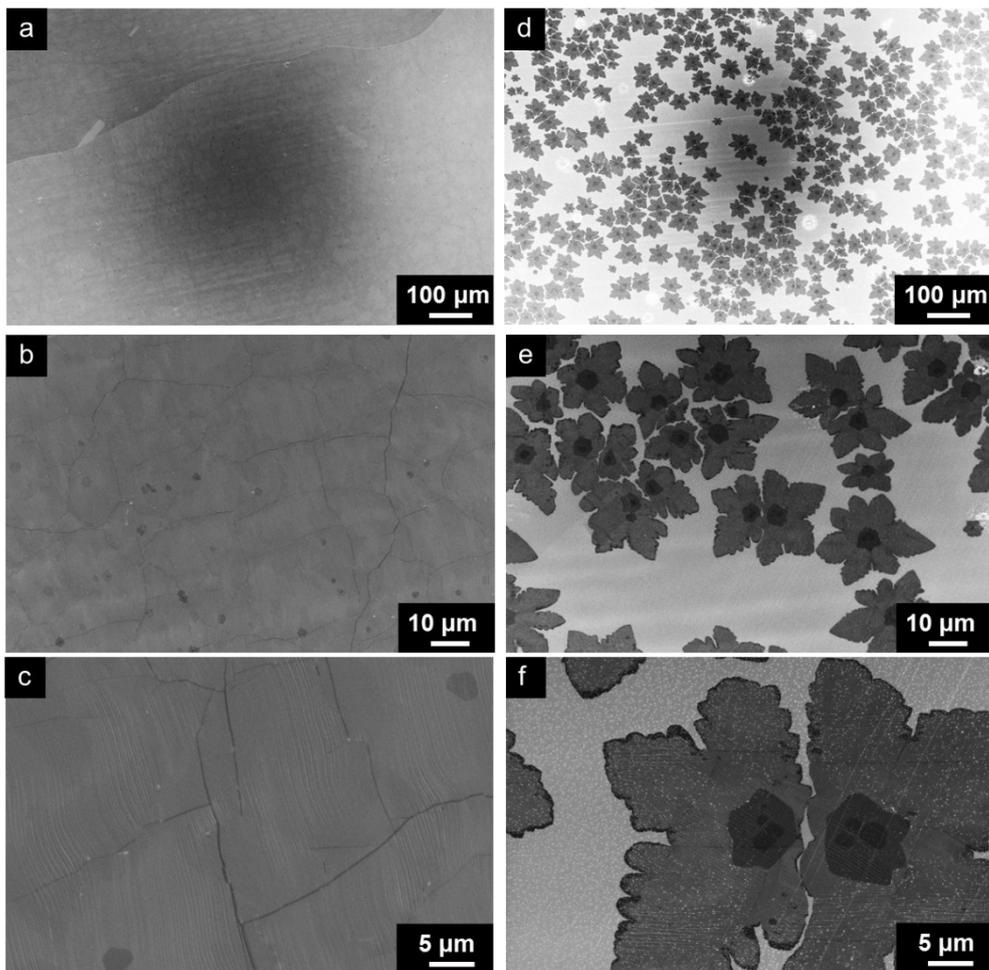
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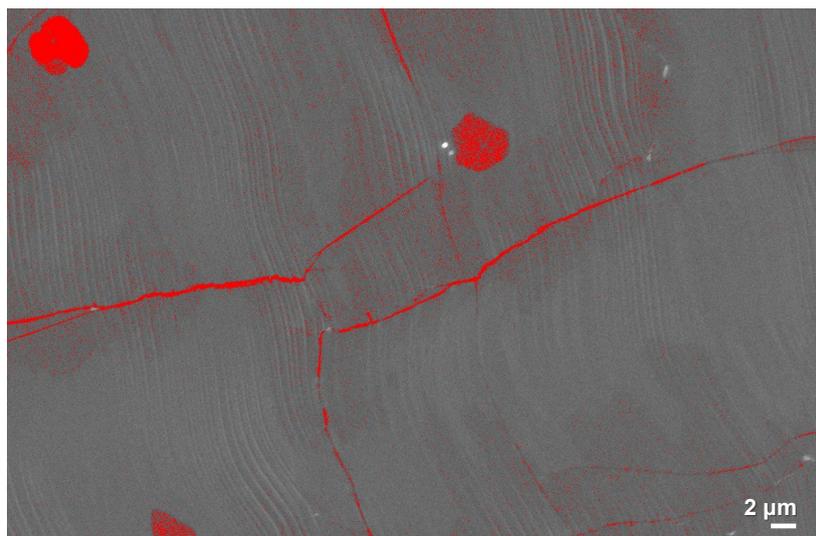


SI 1. Schematic representation of the experimental set-up for the electrodeposition of metal NPs of CVD-Gr

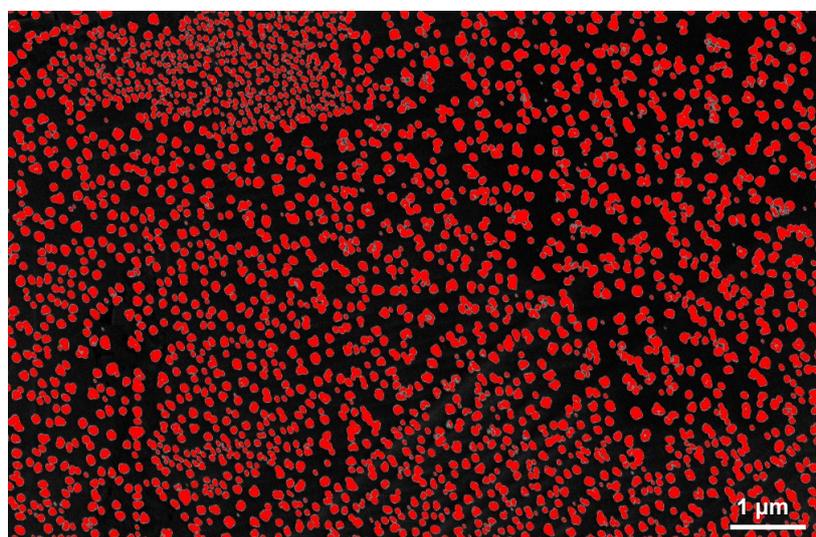


SI2. Additional SEM images corresponding to (a/b/c) fully covered CVD-Gr and (d/e/f) partial covered sample of CVD-Gr on copper, at different magnifications.

SEM images were analysed by ImageJ.¹ The contrast difference between exposed copper regions, monolayer graphene and bilayer graphene allows the different regions to be identified by thresholding the images (see the example below in SI3) which allows rapid and robust quantification of the percentage coverage and percentage of the graphene regions that are bilayer/multilayer. ImageJ was also used to quantify the size and particle distribution of the electrodeposited NPs on CVD-Gr (see the example below in SI3). Several images were analysed for each sample, and comparison with low magnification images were made to ensure that the results were representative.



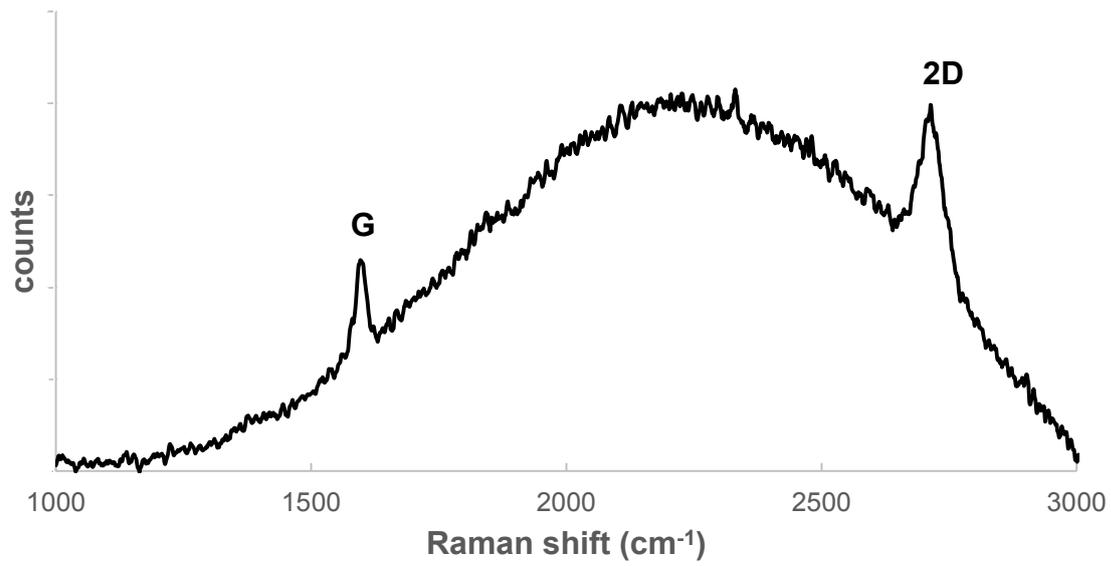
(a)



(b)

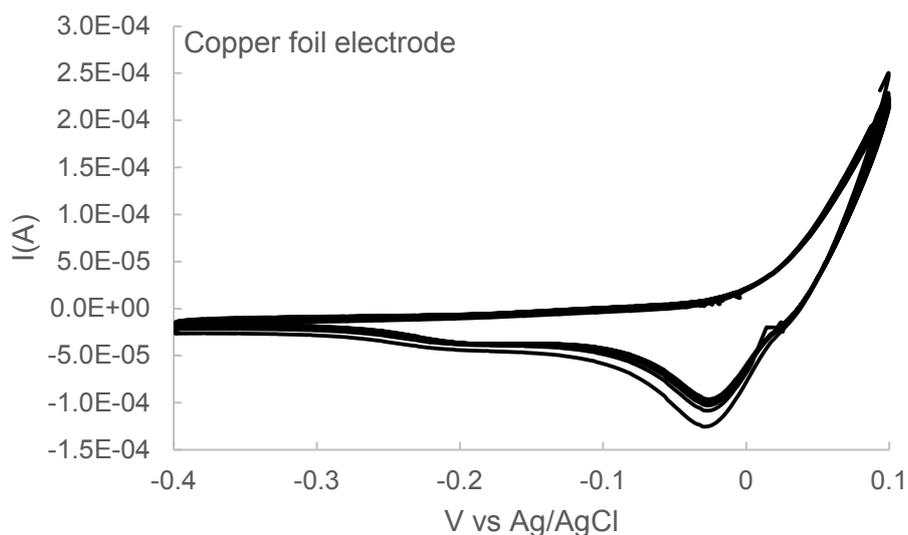
SI3. a) SEM image of a fully covered CVD-Gr in which the threshold has been modified to highlight the wrinkles and bilayer regions. b) Typical SEM image of a CVDGr-AgNPs sample in which the threshold has been adjusted to highlight the AgNPs.

¹ C.A. Schneider, W.S. Rasband and K.W. Eliceiri, *Nature Methods*, 2012, **9**, 671-675



SI4. Raman spectrum of a CVD-Gr working electrode recorded at 514 nm excitation wavelength.

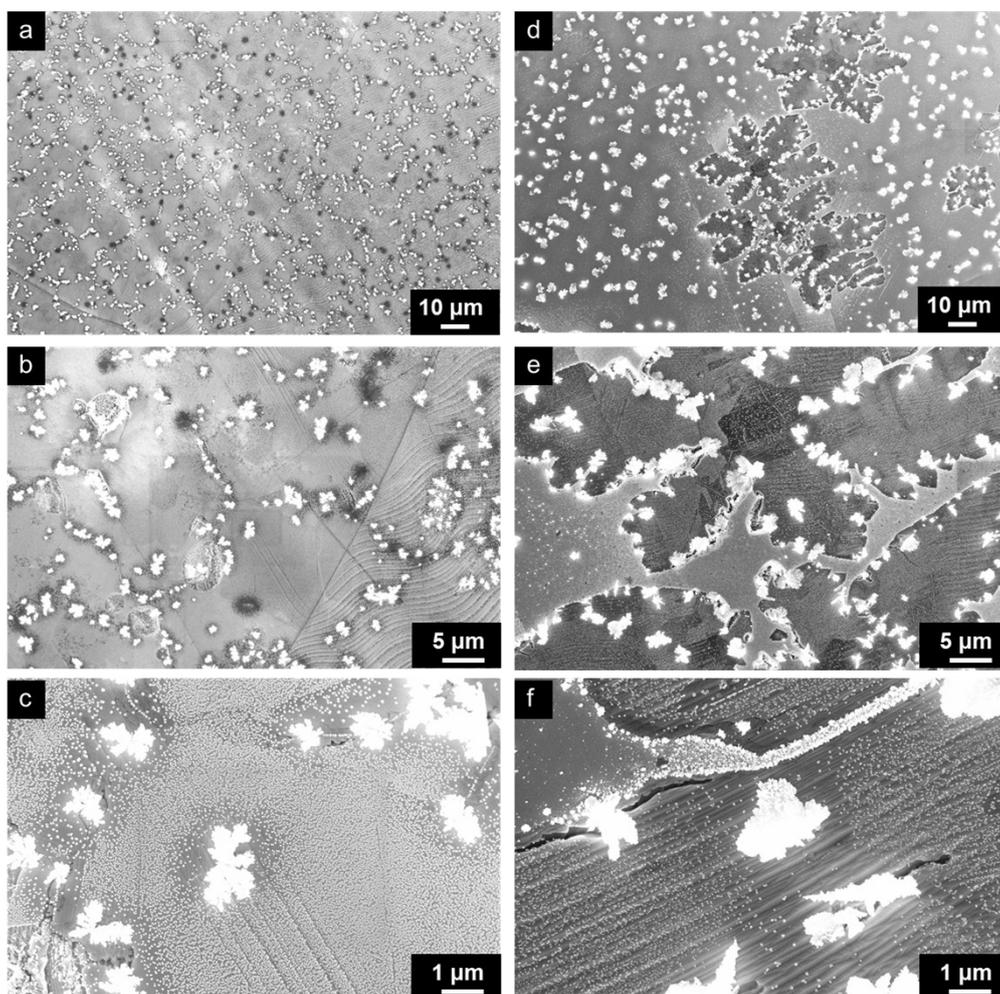
A control experiment using a clean copper foil as the working electrode was also performed. As shown in Figure SI 5, an irreversible reduction peak is observed close to 0 V. This peak is not observed when using CVD-Gr as working electrode (Figure 1 main text), thus confirming that the electrochemical signal is dominated by Gr as we have already demonstrated in our previous report.² However, the observation of a reduction peak at almost 0 V when using a copper electrode, suggests that a competitive process may occur during electrodeposition process (refer to main text and SI 6).



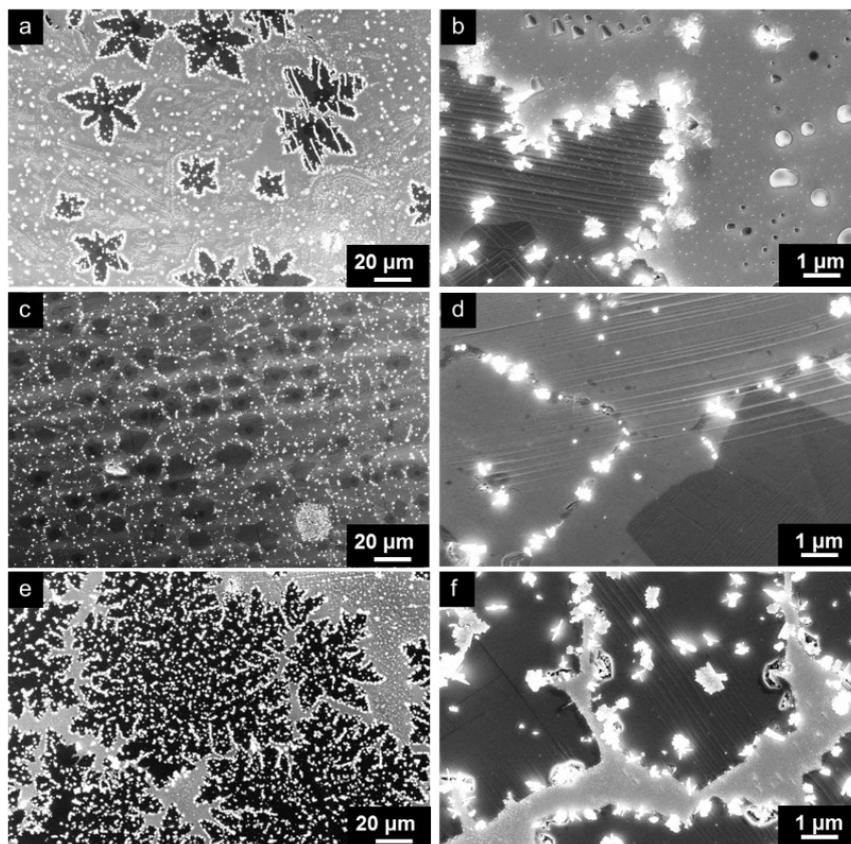
SI 5. Cyclic voltammograms at 0.1 V s^{-1} for the reduction of 0.7 mM AgNO_3 in 0.2 M KNO_3 using copper foil as working electrode. The measurements were taken over electrodes with a constant surface area of 0.05 cm^2 (see experimental section and SI 1)

² C. Bosch-Navarro, Z. P. L. Laker, J. P. Rourke and N. R. Wilson, *Phys. Chem. Chem. Phys.*, 2015, **17**, 29628–29636.

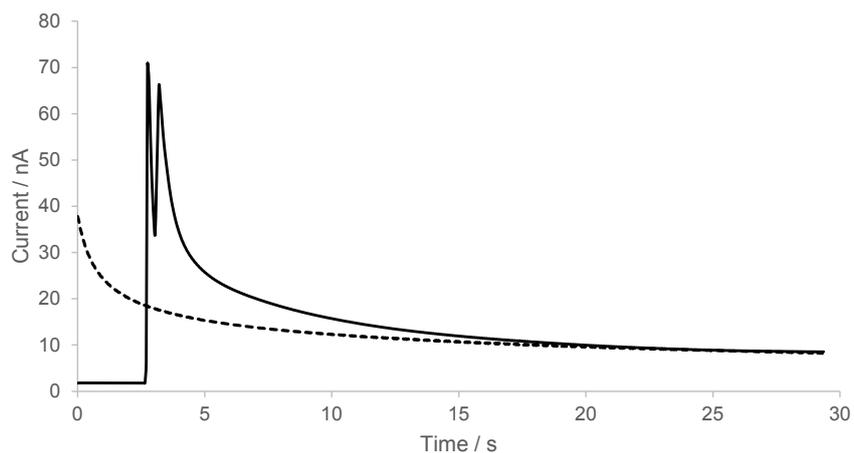
In order to understand the different phenomena that occur during the electrodeposition process, some control experiments were performed. First the electrodeposition experiment was repeated by employing a CVD-Gr sample showing almost no Gr coverage (a typical SEM image of this sample can be seen in SI 2d-f). After the electrodeposition process, the Gr islands were completely decorated with AgNPs, while on the edges of the Gr sheets, and also over the copper substrate some big bundles of NPs were observed (SI 6d-f). This features suggest that two different electrochemical processes are taking place, one induced by the Gr layers and another one promoted by the presence of copper.



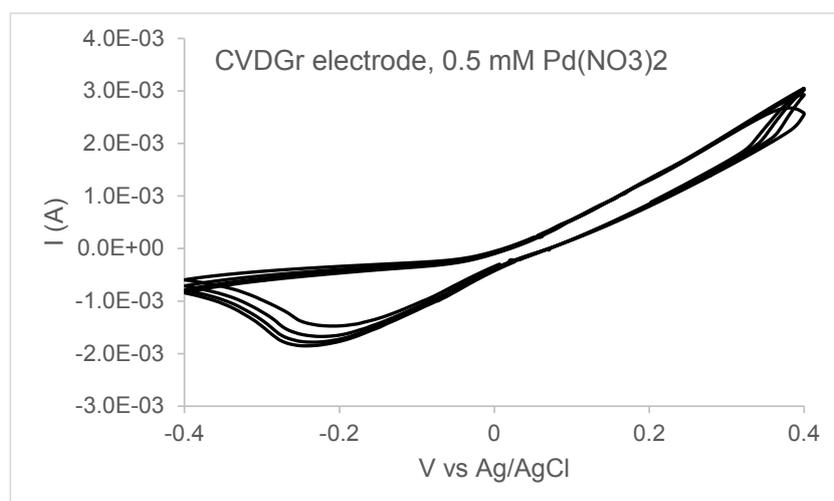
SI 6. Additional SEM images of (a/b/c) full covered CVD-Gr after electrodeposition of AgNPs at three different magnifications, and (d/e/f) partial covered CVD-Gr after the electrodeposition of AgNPs at three different magnifications. The SEM images were acquired after the electrodeposition process carried out by applying a voltage of -0.4 V during 30 s. The working solution consisted in 0.7 mM of AgNO_3 in 0.2 M KNO_3 .



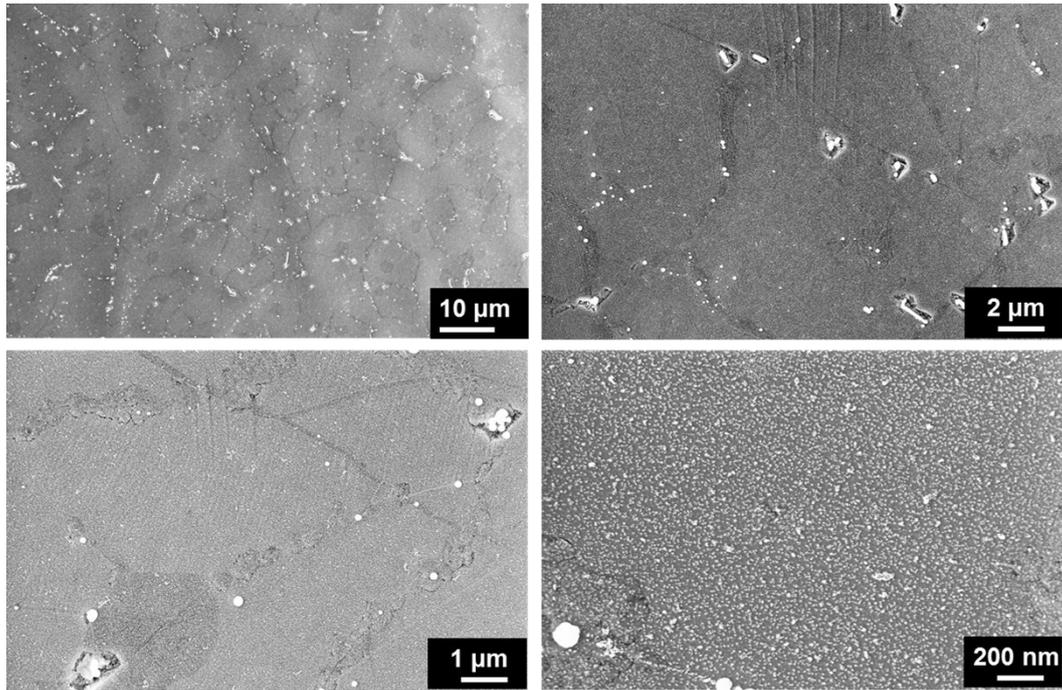
SI7. SEM images taken after the electroless process carried on during 2 s on (a/b) Partial covered CVD-Gr on copper, (c/d) Full coverage CVD-Gr on copper. In (e/f) the SEM images corresponding to a full covered CVD-Gr after electroless deposition of AgNPs during prolonged periods of time (*i.e.* 60 s) are shown. The working solution consisted in 0.7 mM of AgNO₃ in 0.2 M KNO₃.



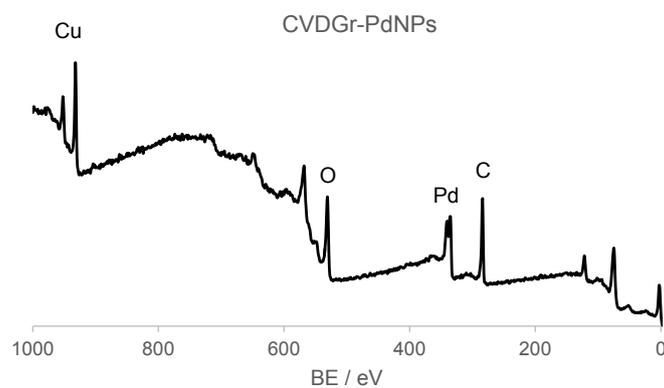
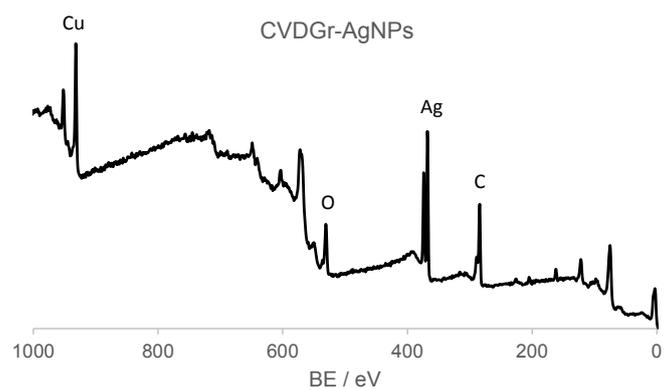
SI8. Current versus time for the electrodeposition of AgNPs. The solid line corresponds with the protocol followed to avoid the occurrence of electroless deposition, and thus, it corresponds with just the electrodeposition process. The dashed line represents both processes (*i.e.* electroless deposition and electrodeposition). In both cases CVD-Gr was used as working electrode, and the potential of the electrode was stepped from 0.0V to -0.46 V (versus Ag/AgCl) for 30 s. The solution contained 0.7 mM AgNO₃ in 0.2 M KNO₃



SI9. Cyclic voltammograms at 0.1 V s⁻¹ for the reduction of 0.5 mM Pd(NO₃)₂ in 0.2 M KNO₃ using CVD-Gr as working electrode



SI 10. Additional SEM images of a full covered CVD-Gr after electrodeposition of PdNPs at four different magnifications. The SEM images were acquired after the electrodeposition process carried out by applying a voltage of -0.4 V during 30 s. The working solution consisted in 0.5 mM of Pd(NO₃)₂ in 0.2 M KNO₃.



SI 11. Survey X-ray photoelectron spectroscopy spectra of CVDGr-AgNPs (*top*) and CVDGr-PdNPs (*bottom*) showing the presence of Ag and Pd, respectively. The XPS spectra were acquired after the electrodeposition process carried out by applying a voltage of -0.4 V during 30 s. The working solution consisted either of 0.5 mM of Pd(NO₃)₂ or 0.5 mM of AgNO₃ in 0.2 M KNO₃.