



Supporting Information

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Uniform Functionalization of High-Quality Graphene with Platinum Nanoparticles for Electrocatalytic Water Reduction

Raffaello Mazzaro,^[a, b] Alessandro Boni,^[a] Giovanni Valenti,^{*[a]} Massimo Marcaccio,^[a] Francesco Paolucci,^[a, c, d] Luca Ortolani,^[b] Vittorio Morandi,^{*[b]} Paola Ceroni,^[a] and Giacomo Bergamini^{*[a, c, e]}

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PCA-G synthesis

6,7 mg of PCA were added to 20 ml of a 2mg/mL solution of Graphite powder in methanol. The solution was bath sonicated for 45 at RT, then 80 ml of DW were added. The solution was sonicated for 24 h keeping the temperature under 20°C, then it was settled overnight. The surnatant was removed and the solution was topped off with DW. The pH of the solution was adjusted to 7 in order to completely deprotonate the PCA and increase the solubility. After 2h sonication, the solution was centrifuged three times at 10000 RPM and the precipitate was redispersed in DW.

After the last centrifugation step, the solution was decanted for three days and the surnatant was stored.

The Raman spectrum for the PCA-G sample exhibits the typical features of a graphene-based material. The D-band at 1350cm⁻¹ reflects the degree of defects and disorder on graphene, while the G-band at 1580cm⁻¹ represents the planar vibration of the sp² carbon network. From the intensity ratio of these two peaks (I_D/I_G) we can obtain some information about the density of defects of graphene, and the small I_D/I_G value of 0.073 is a proof of a low defect density on our material after the exfoliation procedure with PCA.

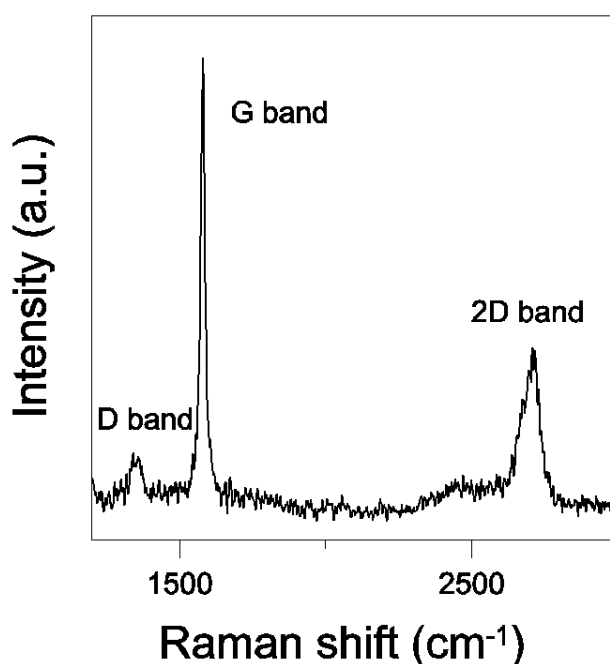


Figure S1. Raman spectra of the exfoliated PCA-G material.

NMP-G synthesis

A 2mg/ml solution of Graphite powder was bath sonicated for 12h keeping the temperature under 20°C, then the solution was centrifuged at 3000 RPM for 20 min. and decanted for three days. The supernatant was stored. 2ml of the solution were filtered onto a 0,2 mm PTFE membrane, then washed with acetone, isopropyl alcohol and water. The solid cake topped filter was then sonicated inside 10 ml of DW to transfer graphene into the solution.

Figure S2 shows the comparison of the typical absorption spectra of PCA-G and NMP-G. The concentration of graphene dissolved was calculated through Lambert-Beer equation, by considering the extinction coefficient provided by ref. 23 and reported on the graph.

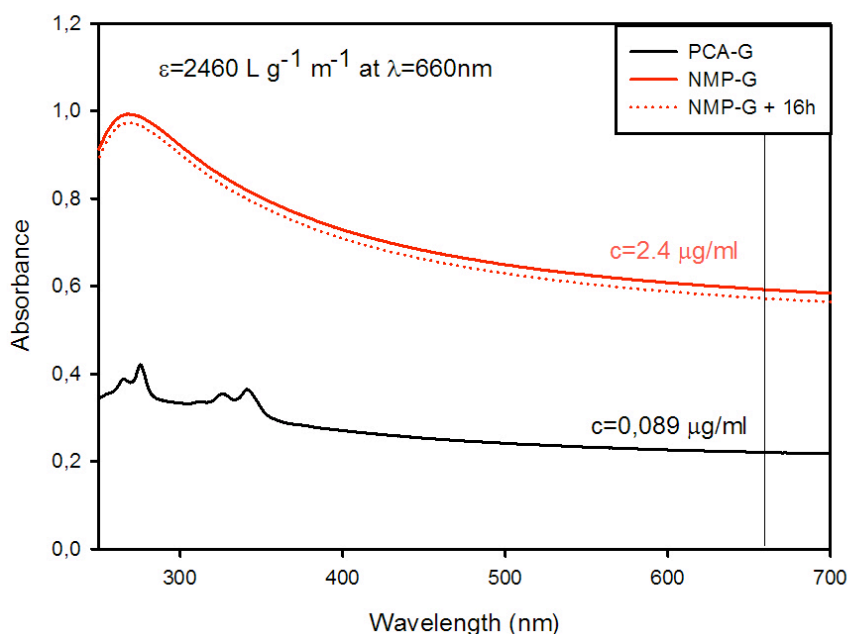


Figure S2. Absorption spectra of PCA-G (black) and NMP-G (red). The structured bands centered at 345 and 280 nm for PCA-G spectrum were due to the presence of PCA, which is impossible to remove due to the synthetic procedure. The dotted line shows the absorption of NMP-G after 16 h, showing a good stability.

Pt nanoparticles synthesis

50 μl of K_2PtCl_4 $6 \cdot 10^{-3}$ M water solution was added to 10 ml of an exfoliated graphene dispersion (PCA-G and NMP-G, respectively). To this solution 8 μl of a $6 \cdot 10^{-2}$ M freshly prepared solution of NaBH_4 were added in order to reduce the platinum salt to Pt^0 . A small excess of NaBH_4 was added to balance the small consumption due to the spontaneous production of hydrogen bubbles inside aqueous solution. The synthesis was followed by UV-Vis spectroscopy, and Fig S3 shows an example of the absorption spectra taken during the synthesis of the Pt nanoparticles inside NMP-G sample.

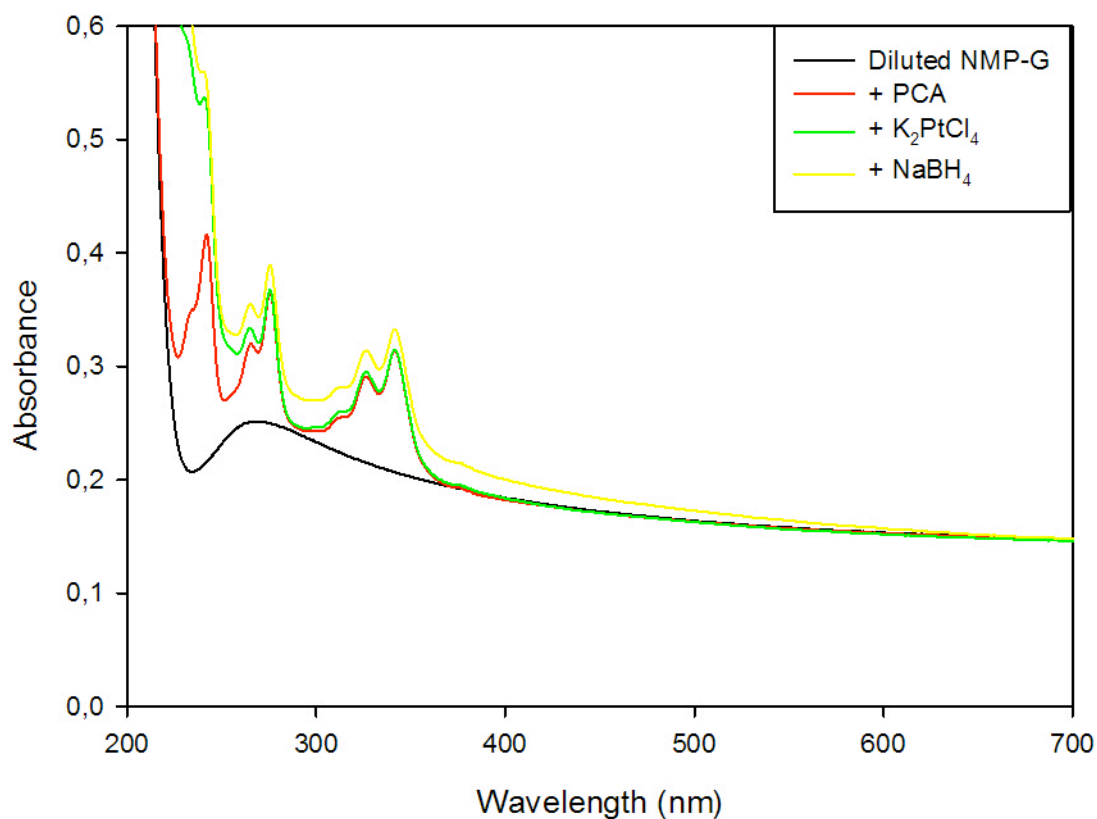


Figure S3. Absorption spectra of the NMP-G sample during the synthesis of the Pt nanoparticles. The addition of the PCA (red) is necessary only for NMP-G sample. The addition of the reducing agent (yellow), after the one of the Platinum salt (green), induced the increase of a scattering-like band in the UV zone, typical of small Pt nanoparticles.

Pt-graphene composite electrochemistry

The stability of the NMP-G Pt material was tested running a chronoamperometry experiment for 30 minutes, during which we applied a constant potential of -0.8V (versus SCE). The cathodic current reaches the stationary state, and we do not observe any appreciable loss of activity during the course of the measure.

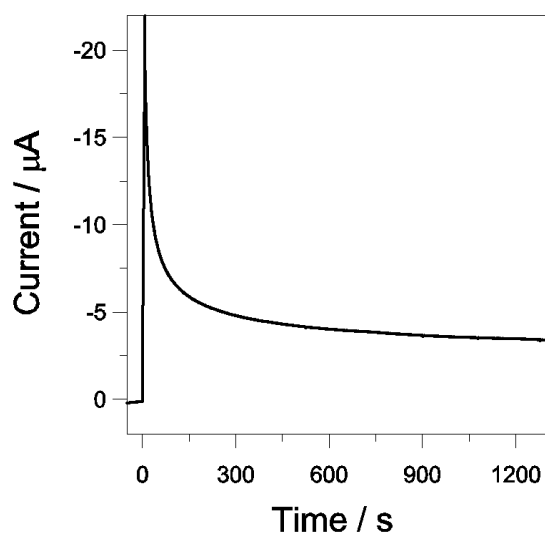


Figure S4. Cathodic current vs. time for the NMP-G Pt material. Applied potential: -0.8V versus SCE.

The chronoamperometric experiments allowed us to measure the charges related to the process $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$, i.e. the amount of products generated at the electrode, by the integration of the cathodic current during the various potential steps. The integrated charges, that takes into account the capacitive contribution, were thus used to obtain the quantification of the catalytic activity.

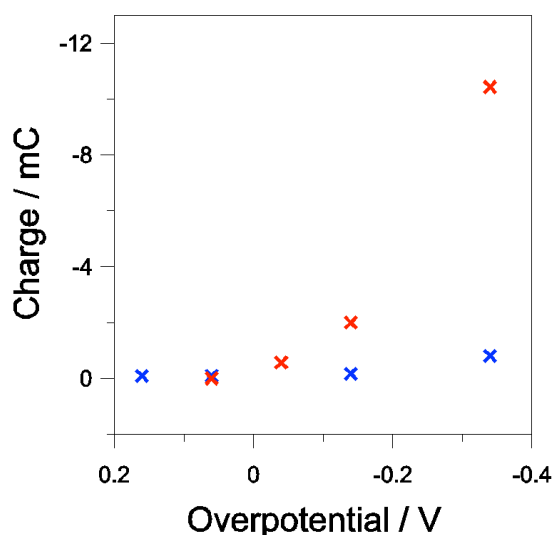


Figure S5. integrated charges from the CA potential steps for the NMP-G Pt (red line) and NMP-G (blue line) samples. Phosphate Buffer solution at pH=6.8, $v = 0.1$ V/s, Ar saturated solution.

The quantification of the electroactive catalyst it has been done measuring the charge related to the redox process $\text{Pt} + \text{H}_2\text{O} \rightarrow \text{PtO} + 2\text{e}^- + 2\text{H}^+$ by means of cyclic voltammetry in acid and oxidizing solution (H_2SO_4 0.05 M). The integration of the CV curve in the potential region around +1.0 V gives a value of the integrated charge of $5 \mu\text{C}$ and it is used as the normalizing factor Q_{Pt} in the calculation of the turnover number. Since both HER and Pt oxidation are bi-electronic process, any further corrective factor has not been introduced in equation 1 (see main text)

$$\text{TON} = \frac{Q_{\text{GraphPt}} - Q_{\text{Graph}}}{Q_{\text{Pt}}} \quad (1)$$

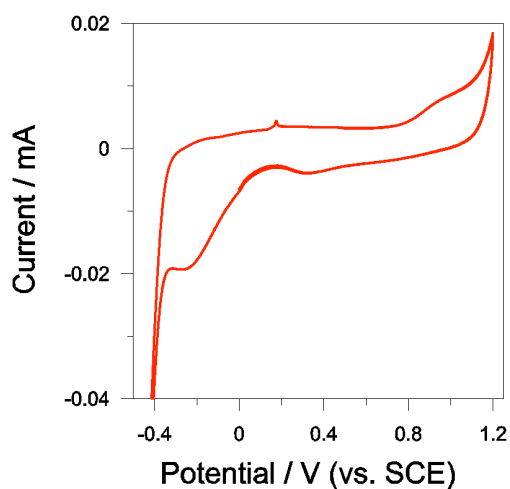


Figure S6. CVs of the NMP-G Pt in H_2SO_4 0.05M. $v = 0.05$ V/s. The integration of the CV curve in the potential window 0.7 V – 1.2 V gives a charge of $1.7 \mu\text{C}$.