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Large-scale quantification of CVD graphene surface coverage†

Adriano Ambrosi, a Alessandra Bonanni, a Zdeněk Sofer b and Martin Pumera a

The extraordinary properties demonstrated for graphene and graphene-related materials can be fully exploited when a large-scale fabrication procedure is made available. Chemical vapor deposition (CVD) of graphene on Cu and Ni substrates is one of the most promising procedures to synthesize large-area and good quality graphene films. Parallel to the fabrication process, a large-scale quality monitoring technique is equally crucial. We demonstrate here a rapid and simple methodology that is able to probe the effectiveness of the growth process over a large substrate area for both Ni and Cu substrates. This method is based on inherent electrochemical signals generated by the underlying metal catalysts when fractures or discontinuities of the graphene film are present. The method can be applied immediately after the CVD growth process without the need for any graphene transfer step and represents a powerful quality monitoring technique for the assessment of large-scale fabrication of graphene by the CVD process.

Introduction

Due to its unusual and fascinating properties graphene has attracted the interest of the scientific community in numerous research fields in recent years. 1–3 Defined as a two-dimensional, single atomic layer material of sp2-bonded carbons, graphene has shown exceptional electronic, physical and chemical properties since its first isolation. 4–5 It has been demonstrated that the adoption of graphene could bring improved performances and significant advantages in electronic, energy storage or conversion, sensing and medicine applications. 6–11 Various synthetic methodologies have been developed for the production of graphene and graphene-related materials which however generated graphenes with different structural, physical and chemical properties to be considered for each specific application. 12–13 The mechanical exfoliation of highly oriented pyrolytic graphite (HOPG) first proposed in 2004 produces high quality graphene sheets that can be adopted for fundamental transport property studies. 4 Since it is time-consuming and not scalable, this method cannot be used for large-scale practical applications. Another top-down method, consisting of chemical oxidation and exfoliation of graphite (natural or synthetic), demonstrates excellent scalability possibilities, but since the produced graphene presented structural defects with variable new entities and functionalities, only applications requiring bulk quantities of graphene, like sensing, composite materials, energy-storage and production devices may be considered. 9 For applications such as electronics, material coatings or condensation heat-transfer, a large area of nearly pristine single- or few-layered graphene is required. Chemical vapor deposition (CVD) emerged as the most promising procedure for large-scale fabrication of high quality graphene for such applications. 14 Although the growth of graphene by CVD has been demonstrated on platinum, iridium and ruthenium metal surfaces, 15–17 the most remarkable results were achieved during the last few years using nickel or copper as catalytic surfaces. 18–21 In particular, the impressive work carried out by Bae and co-workers who demonstrated a roll-to-roll fabrication of a 30-inch monolayered graphene on copper with subsequent successful incorporation to a touch-screen panel is worth mentioning. 19

Beside the electronic applications, homogeneous and large-area graphene have been proposed for other interesting applications such as corrosion-inhibiting or oxidation-inhibiting coating. 24–26 For such applications it is crucial not only to control the number of graphene layers grown on the metal but also and more importantly to ensure complete surface coverage avoiding any possible disruption or structural “hole”. Despite great progress made recently in the synthesis of graphene by CVD, 25,27 some issues still remain unsolved and become even more important when it comes to large-scale production. It is known for example that due to the different solubility of carbon atoms in Ni and Cu at high temperature, the resulting graphene prepared with these metals presents different structural features. Ni can dissolve more carbon atoms than Cu, thus the precipitation of carbon atoms often generates areas with multilayered graphene on the Ni metal during the cooling process. Cu, in contrast, allows only a small amount of carbon atoms to
dissolve and therefore the graphene growth terminates when the whole surface substrate is covered.\textsuperscript{15,14} This resulted in the generation of mono-layered graphene of only about 87–90\% on the Ni surfaces and about 95\% on the Cu foil, while the remaining of the surfaces were scattered with multi-layered graphene or structural deficiencies (holes).

Besides, even when a mono-layer is synthesized, it is of polycrystalline nature which appears as several grains easily distinguishable by the well defined boundaries.\textsuperscript{29} The presence of these grain boundaries has been demonstrated to cause detrimental effects on the electronic, thermal and mechanical properties of the prepared graphene.\textsuperscript{24,25,29–31} In addition, for large-scale synthesis, technical issues, such as the formation of a temperature gradient inside the reactor, or some defects of the catalyst surfaces, may result in an inhomogeneous growth of the graphene.\textsuperscript{19}

A high-throughput technique is therefore necessary for industrial applications to monitor and control the quality of the graphene grown by CVD. For laboratory applications, characterization of graphene is generally performed using Raman spectroscopy\textsuperscript{22,31} and atomic force microscopy (AFM).\textsuperscript{21} These techniques offer atomic-scale resolution but are extremely time-consuming, limited to only micrometer-size regions and require expensive instrumentation as well as qualified personnel. Large area graphene defect analysis can also be performed by exploiting its optical transparency by optical microscopy, which however requires long image processing and with no quantitative result. We describe herein, a simple, scalable and reliable method to rapidly evaluate the presence of structural discrepancies at the macro and microscale level on large-area CVD graphene grown onto Ni and Cu surfaces. This method relies on the inherent electrochemistry of Cu and Ni. Based on the fact that a single crystal of mono-layered graphene is impermeable to atoms as small as He,\textsuperscript{34} any signal generated by passed-through ions from the underlying metal (Ni or Cu) can be directly correlated to a “fracture”, “hole” or “discontinuity” in the graphene structure. We have developed an electrochemical method to rapidly quantify the surface coverage of the CVD-grown graphene onto Ni or Cu surfaces, by measuring the inherent redox signals of the underlying Ni or Cu metal. Our method is able to quantify the graphene surface coverage between 0 and 100\%, can be easily scaled-up to larger sizes, requires simple and low-cost instrumentation as well as can be applied immediately after the cooling step of the CVD process without the need for transferring the graphene to other surfaces.

**Experimental**

**Materials**

Cu foil, Ni foil and Si/SiO\textsubscript{2}/Ni film plates with and without CVD-grown graphene were purchased from Graphene Laboratories Inc., Calverton, NY. Potassium ferrocyanide, potassium chloride and sodium hydroxide were purchased from Sigma-Aldrich, Singapore.

**Apparatus**

Cyclic voltammetric measurements were performed on a \textmu\textsuperscript{3}AutoLab type III electrochemical analyzer (Eco Chemie, The Netherlands) connected to a personal computer and controlled by General Purpose Electrochemical Systems Version 4.9 software (Eco Chemie). Electrochemical Impedance Spectroscopy measurements were performed on an Autolab 302 electrochemical analyzer (Eco Chemie, The Netherlands) and using ferro/ferricyanide (10 mM) as a redox probe in KCl (0.1 M) solution. All electrochemical potentials in this paper are stated versus an Ag/AgCl reference electrode.

X-ray photoelectron spectroscopy (XPS) was performed with a Phoibos 100 spectrometer and a monochromatic Mg X-ray radiation source (SPECS, Germany). Both survey and high-resolution spectra for C 1s were collected. Raman spectra were obtained by using a confocal micro-Raman LabRam HR instrument from Horiba Scientific in backscattering geometry with a CCD detector, a 514.5 nm Ar laser and a 100\times objective mounted on a Olympus optical microscope. The calibration is initially made using a silicon reference at 520 cm\textsuperscript{\textminus}1 and gives a peak position resolution of less than 1 cm\textsuperscript{\textminus}1.

Scanning Electron Microscopy (SEM) images were obtained by using a JEOL 7600F SEM (JEOL, Japan) operating at 2 kV in GB high mode.

**Synthesis of graphene film on copper foil**

The growth of graphene was achieved on a Cu substrate in a quartz hot wall reactor. The copper substrate of 25 micron thickness was obtained from Alfa Aesar (99.99998\% purity) and cleaned with hot acetone before use. The graphene deposition was performed at 1000 °C and a pressure of 60 Pa. The heating at deposition temperature was performed in a hydrogen atmosphere with a heating rate of 7 °C min\textsuperscript{\textminus}1. The copper substrate was subsequently held for 30 minutes at the deposition temperature in a hydrogen atmosphere (50 ml min\textsuperscript{\textminus}1). The graphene deposition was performed in a methane–hydrogen atmosphere (5 cm\textsuperscript{3} min\textsuperscript{\textminus}1 H\textsubscript{2}, 15 cm\textsuperscript{3} min\textsuperscript{\textminus}1 CH\textsubscript{4}) for 30 minutes. The purity of hydrogen and methane was 99.9999% and 99.995% respectively.

**Results and discussions**

The method that we describe here is based on the inherent redox activity of Cu and Ni, as shown in Fig. 1. A homogeneous surface coverage of the metal catalyst by single- or multi-layered graphene impedes the accessibility of the metallic surface to interact with the external environment, thus acting as a protective layer.\textsuperscript{24} A discontinuity in the graphene layer (hole or fracture) exposes the metal surface to the solution undergoing oxidative or reductive processes which could be detected electrochemically. As such, electrochemistry is a sensitive and powerful tool to investigate the quality of CVD-grown graphene by measuring the redox behaviors of the exposed metal substrates.

The electrochemistry of Ni and Cu metals in alkaline solutions\textsuperscript{35–37} is well known due to the common applications of these metals in electrocatalysis,\textsuperscript{38–41} batteries,\textsuperscript{42} capacitors,\textsuperscript{43} and corrosion studies.\textsuperscript{44–48} We have recently proposed a method to quantify bioavailable Ni impurities within carbon nanotube2
samples based on the electrochemical behavior of Ni ions in alkaline solutions.\textsuperscript{49,50}

Measuring the amount of Ni (Fig. 1A) or Cu (Fig. 1B) from the portions of metal substrates that are unprotected by the graphene films, the graphene surface coverage can be calculated. We first investigated the electrochemistry of bare Ni foil, Si/SiO\(_2\)/Ni film and Cu foil, which did not have any CVD-grown graphene deposited, in alkaline solution (0.1 M NaOH). Typical cyclic voltammetric measurements of these three bare surfaces were obtained (Fig. S2, of ESI\textsuperscript{†}). Both the Ni film on the Si/SiO\(_2\) wafer and bare Ni foil showed, as expected, a very similar trend. In alkaline solution, Ni metals spontaneously generate a thin film of Ni(OH)\(_2\) on their surfaces.

Such an Ni(OH)\(_2\) layer can be oxidized further to NiOOH and reduced back to Ni(OH)\(_2\) by potential scanning according to the reaction:

\[
\text{Ni(OH)}_2 \rightarrow \text{NiOOH} + \text{H}^+ + \text{e}^- \tag{1}
\]

Successive potential cycling causes the thickening of the Ni(OH)\(_2\) layer with consequent increment of the corresponding oxidative and reductive peaks, until the thick layer of Ni(OH)\(_2\)/NiOOH blocks further exposure of the fresh Ni metal to the alkaline solution.\textsuperscript{51}

By taking into consideration only the anodic peak, which represents the oxidation of Ni(OH)\(_2\) to NiOOH, we can observe that the amount of charge exchanged during this process (area of the peak) before reaching saturation increases linearly with the natural logarithm of the number of scans (Fig. S2A and B\textsuperscript{†}). This relationship was utilized and taken into consideration for quantitative evaluation of the graphene surface coverage as explained later in the text.

The electrochemical behavior of the Cu foil was investigated under the same experimental conditions to give a voltamogram with two anodic peaks (a\(_1\) and a\(_2\)) at about \(-0.4\) V and \(-0.5\) V, which corresponded to reactions (2) and (3), respectively, as follows:

\[
2\text{Cu} + 2\text{OH}^- \rightarrow \text{Cu}_2\text{O} + \text{H}_2\text{O} + 2\text{e}^- \tag{2}
\]

\[
\text{Cu}_2\text{O} + 2\text{OH}^- \rightarrow 2\text{CuO} + \text{H}_2\text{O} + 2\text{e}^- \tag{3}
\]

On the reversed potential scan, two cathodic peaks appeared (c\(_1\) and c\(_2\)) at about \(-1.1\) V and \(-0.7\) V, which resulted from the reversal of reactions (2) and (3), respectively.\textsuperscript{44} It is important to note that successive potential cycling did not significantly alter the recorded signals for the Cu foil. A stable contour was obtained after the first scan (Fig. S2C\textsuperscript{†}), as demonstrated by the
constant value of charge exchanged during the cathodic reactions (peak c₁ and c₂). A total of 50 repetitive cyclic voltammograms were recorded for each of the bare metal surfaces. After the electrochemical characterization of the bare metal surfaces, we proceeded to alter the active metal surface area artificially by masking the metal with a transparent tape punctured with a specific hole size. As such, the metallic surface was intentionally partially blocked to simulate the presence of a graphene film with a well-defined and controlled surface coverage.

The use of a plastic adhesive tape to simulate the physical barrier offered by the graphene layer is justified by several published works which demonstrate the ability of graphene films to prevent electrochemical corrosion of Cu and Ni metals in aqueous media,25 or their oxidation.24,25

Fig. 2 shows representative cyclic voltammograms recorded using different metal active surface areas. Fig. 2A highlights the cyclic voltammograms recorded for each of the Si/SiO₂/Ni films with varying areas of exposed metal surfaces of 17 mm², 5 mm², 1.7 mm² and 0.5 mm² for I, II, III and IV, respectively. Optical images of the Si/SiO₂/Ni films masked with transparent tapes are also included as inset.

Different schemes can be adopted to correlate the electrochemical signals with the active metal surface areas as illustrated in Fig. S3 of the ESI.† A correlation between the area of the anodic peak (charge for the oxidation of Ni(OH)₂ to NiOOH after ten scans and the projected graphene surface coverage was selected as a calibrated reference here. Ten cyclic voltammetric scans allowed for an accurate quantification in less than 5 min of measurement time. Based on the correlation, there is an excellent linear relationship between the anodic peak area and the projected graphene surface coverage on the Si/SiO₂/Ni film, as shown in Fig. 2C (red dot).

Similarly, Fig. 2B shows the cyclic voltammograms recorded with different active surface areas of the Cu foil. In this case, since the signal stabilized after a few scans, the 4th scan can be used as a representative for the corresponding surface area. Given that both the cathodic signals were more intense than the anodic peaks, they can be used for the actual quantification (Fig. S3B†). We propose to measure the peak c₁ area (charge for the reduction of Cu₂O to CuO) which is linearly proportional to the projected graphene surface coverage on the Cu foil as shown in the linear plot of Fig. 2C (blue circle). Subsequently, the plots for Ni and Cu metal surfaces in Fig. 2C were adopted to evaluate the actual graphene surface coverage of commercial CVD-grown graphene samples. We tested commercial CVD graphene samples fabricated using standardized procedures and employed Ni foil, Si/SiO₂/Ni film and Cu foil as catalytic surfaces.53 The CVD graphene sample grown on the Ni foil consisted of a multi-layered graphene film (Ni-foil-ML-G). Due to its multi-layer structure, this sample should represent an example of a Ni foil with full graphene coverage and therefore electrochemical signals generated by the Ni metal should not be recorded. Fig. 3A compares the cyclic voltammograms of the bare Ni foil, a damaged Ni-foil-ML-G and a Ni-foil-ML-G as-received. It is clear that the presence of the graphene film protects the Ni foil, which therefore cannot interact with the external alkaline solution. The purposely damaged graphene film resulted in an intermediate signal that lay between that of the bare Ni foil and the original Ni-foil-ML-G. Interestingly, a detailed view of the cyclic voltammogram recorded for one of the Ni-foil-ML-G samples analyzed revealed an extremely low redox signal generated by Ni(OH)₂ (inset graph inside Fig. 3A). This means that, even for a multi-layer CVD graphene sample, some cracks or holes might be present, leaving the Ni metal underneath partly exposed. By measuring the anodic peak area (oxidative charge) and subsequently matching against the linear plot in Fig. S3A† we estimated a total exposed metal area of approximately 70 × 70 μm which corresponded to a surface

![Fig. 2](image-url)

**Fig. 2.** Electrochemical signals recorded with bare Si/SiO₂/Ni films or Cu foil metal surfaces (in the absence of graphene) with different exposed metal surfaces. A transparent tape with different apertures was masked on the metal surface to simulate different graphene defect openings: (I) 17 mm², maximum exposed surface using o-ring, (II) 5 mm², (III) 1.7 mm², (IV) 0.5 mm² (inset in A and B; scale bar, 2 mm). (A) Representative cyclic voltammograms (10th CV scan) recorded using the bare Si/SiO₂/Ni film with exposed metal surfaces of I to IV. (B) Representative cyclic voltammograms (4th CV scan) recorded with Cu foil with exposed metal surfaces of I to IV. (C) Plot of the charge for the anodic peak as in (A) (red dot) or the cathodic peak c₁ as in (B) (blue circle) vs. the corresponding graphene surface coverage. For 100% coverage the value of 0 μC was assigned and included in the plot. Electrolyte solution: NaOH 0.1 M; reference electrode: Ag/AgCl.
coverage of about 99.97% for this particular sample over a 17 mm² total area analyzed. Fig. 3B shows optical images (upper part) and the corresponding microscopic images obtained using a conventional optical microscope (lower part) of the samples tested.

We have also characterized the samples by using XPS and Raman spectroscopy before and after the electrochemical measurements. These were done to evaluate possible major structural and surface modification/damage caused by prolonged potential scans in alkaline solution (see also Fig. S6 of the ESI†). Fig. S5 of the ESI† shows SEM images of Cu-foil-graphene and Si/SiO₂/Ni-film-graphene samples as received and after the electrochemical analysis confirming that no significant damage or change occurred. It can be seen in Fig. 3C(a) that the Ni-foil-ML-G sample presented an XPS spectrum without any Ni 2p₃/₂ signal, which indicated that the graphene film thickness should be more than 10 nm. This was deduced since the approximate depth limit attainable by the XPS analysis was 10 nm. The sample was therefore clearly multi-layered with more than 30 graphene layers. It can also be seen that no damages or changes were noted after the voltammetric treatment in alkaline solution as Ni was again not detected by XPS analysis (Fig. 3C(b)). As expected, the G and 2D bands did not appear on the bare Ni foil spectrum (no graphene) (Fig. 3D(c)).

The CVD graphene sample fabricated using the Si/SiO₂/Ni film as a catalytic surface provided single- to few-layered graphene films which have also been previously adopted for the fabrication of transparent electrodes.²⁸,²³ It is known that Ni catalysts produce non-uniform graphene films that display typical conformation of a patchwork as confirmed by optical microscopy (Fig. 4C) and Raman spectroscopy (Fig. 4D). Patches of irregular graphene thicknesses presented different color intensities and were characterized by Raman analysis which gave varying intensities of the G and 2D bands (see also Fig. S4 and S5 of the ESI†). Darker spots corresponded to multi-layered graphene with a G/2D ratio greater than 1 (Fig. 4D(b)), while the almost transparent portions indicated single to bi-layered graphene with a G/2D ratio <1 (Fig. 4D(c and d)). Electrochemical treatment was subsequently carried out on the commercial CVD graphene sample prepared on the Si/SiO₂/Ni film to evaluate its graphene surface coverage. Fig. 4A shows representative cyclic voltammograms obtained using the bare Si/SiO₂/Ni film surface (black line) and the Si/SiO₂/Ni-G sample. It can be seen that the presence of graphene significantly reduced the electrochemical signal of the Ni metal, which was however still detectable. The measured anodic peak area (charge related to the oxidation of Ni(OH)₂) was subsequently matched against the plot in Fig. 2C.
for the Ni surface to give an average graphene surface coverage value of 97.7 ± 0.7% among the samples analyzed. This meant that about 0.4 mm² over a surface of 17 mm² remained uncovered without any grown graphene. The result was also confirmed qualitatively by XPS analysis (Fig. 4B).

The Ni 2p₃/₂ core-level spectrum of the bare Si/SiO₂/Ni film presented a signal at about 852.6 eV due to the Ni metal and a signal at about 856 eV due to NiO/Ni(OH)₂ (Fig. 4B(a)). After the electrochemical treatment (50 CV scans in alkaline solution), the NiO/Ni(OH)₂ signal became predominant while the contribution from the Ni metal was almost negligible (Fig. 4B(b)). The CVD graphene sample as-received gave a Ni 2p₃/₂ spectrum with only an intense signal at 852 eV, which was due to the Ni metal. The absence of a signal at 856 eV indicated that the graphene film protected the Ni metal effectively from natural/spontaneous oxidation in the presence of atmospheric oxygen (Fig. 4B(c)). However, after the electrochemical treatment, a signal at 856 eV became apparent indicating that a portion of the surface was oxidized with the consequent growth of a Ni(OH)₂ layer²⁴ (Fig. 4B(d)).

Extremely uniform graphene films have been obtained using Cu foil as a catalyst. It was shown that over 95% of the graphene grown onto Cu is monolayered.¹⁹ We tested commercial CVD graphene samples prepared using high-quality Cu foil to evaluate the graphene coverage over a large area. It can be seen in Fig. 5A that the electrochemical signal of Cu-foil-G in alkaline solution has a much lower intensity compared to the signal from the bare Cu foil. Again, the graphene film (mostly monolayer) acts as a protective shield that impedes the oxidation of the Cu metal.²⁴ Using the plot in Fig. 2C, we could correlate the cathodic peak area (peak c₁) recorded for the Cu-foil-G sample to an average graphene coverage of 98.1 ± 0.6% over a 17 mm² surface area. The Cu-foil-G was thus estimated to have an uncovered metal surface of about 0.3 mm². To provide further evidence on the sensitivity of the method, we applied it on a home-made bilayered graphene film grown on a Cu foil (Cu-foil-G). It can be seen in Fig. 5A that the cyclic voltammograms recorded presented signals of lower intensities than the commercial mono-layered graphene sample. Based on the plot in Fig. 2C, we estimated a graphene coverage of 99.4 ± 0.4%, which corresponded to an exposed Cu area of only 0.1 mm².

XPS analyses were also performed to investigate the oxidation state of Cu as presented in Fig. 5B. The bare Cu-foil sample showed broad Cu 2p₃/₂ and Cu 2p₁/₂ peaks which resulted from the contribution of Cu metal (932.6 eV and 952.5 eV) as well as oxidized Cu species such as CuO (933.7 eV and 953.4 eV) and Cu(OH)₂ (934.7 eV and 954.5 eV) (Fig. 5B(a)). It can also be seen that the electrochemical treatment accelerated the oxidation of the Cu metal as demonstrated by the increased intensities of the peaks corresponding to CuO and Cu(OH)₂ (Fig. 5B(b)). On the other hand, the Cu-foil-G sample showed only sharp and intense peaks corresponding to Cu metal (932.6 eV and 952.5 eV) indicating that the graphene layer protected the Cu foil from oxidation²⁴ (Fig. 5B(c)). However, small signals corresponding to CuO and Cu(OH)₂ were observed after the electrochemical treatment in alkaline solution, which highlighted the presence of small exposed portions of the Cu metal (Fig. 5B(d)). Fig. 5C shows the optical images of Cu-foil (upper part) and Cu-foil-G (lower part) before and after the electrochemical treatment (30 CV scans). Surface modifications due to the potential scans were clearly visible only on the bare Cu foil which underwent oxidation. No
significant changes were visible on the surface of the Cu-foil-G sample after the electrochemical treatment as confirmed also by SEM analysis (Fig. S5 of the ESI†). Raman spectroscopy was also carried out to characterize the samples and to study possible surface alterations as consequences of the electrochemical treatment. It can be seen in Fig. 5D(c) that the CVD graphene sample was mostly mono-layered with a G/2D peak ratio of <1, as normally achieved with Cu catalyst. Similar to the XPS analysis, some traces of surface modifications were also detected using Raman spectroscopy. In fact, after the electrochemical treatment, an increased signal at about 200 cm⁻¹ as compared to the original sample was recorded which could be assigned to Cu₂O (214 cm⁻¹) (Fig. 5D(d)). The Raman spectrum of the bare Cu-foil also presented signals between 200 and 600 cm⁻¹ only after the electrochemical process which facilitated the oxides formation (Fig. 5D(b)).

Electrochemical impedance spectroscopy (EIS) was subsequently used to characterize the CVD graphene layers grown on both Ni and Cu substrates. Due to the outstanding sensitivity of EIS to probe interfacial phenomena, the technique is especially suited for surface studies.

Impedance measurements were recorded before and after repeated CV scans in sodium hydroxide in order to evaluate the ability of the graphene film to act as a protective layer of the metal surface. Fig. 6A represents Bode plots (log|Z| vs. logf) of CVD graphene on the Si/SiO₂/Ni film before and after the CV treatment. A Randles equivalent circuit was used for data fitting and interpretation. The circuit comprises of the capacitance of the double layer which is in parallel with the resistance of the graphene or graphene/metal oxide–hydroxide layer; both elements are in series with the resistance of the solution. Due to the non-homogeneity of the layer on the metal substrate in contact with an electrolyte, the interface is better described by a constant phase element (CPE) instead of a capacitor.⁶⁰ As shown in Fig. 6A, the resistance of the solution is the predominant factor at high frequencies, and provided a slope of zero for the Bode magnitude data. At intermediate frequencies, the capacitance of the graphene film coating generated considerable impedance which increased linearly with decreasing frequency (slope in the range from −0.71 to −0.88) while the phase angle lies between −55° and −85°. This response was typical for systems with a predominantly capacitive behavior.⁵⁷,⁵⁸

After the electrochemical treatment, a smaller total impedance and larger capacitance values (as from the fitting: C_{all}(Ni-film-G) = 2.68 μF cm⁻² and C_{all}(Ni-film-G-CV) = 22.65 μF cm⁻²) were obtained indicating that the Ni-film surface was not totally covered and protected by CVD graphene (Fig. 1A). This implied the presence of defects and holes on the graphene layer, which allowed for NiO–Ni(OH)₂ to grow from the Ni-film during the repetitive scans in NaOH solution and thus altered the capacitive behavior of the material surface. Similar conclusions can be drawn by analyzing the Bode plots of the CVD graphene grown on a Cu foil (Fig. 6B). Similarly, after the electrochemical treatment, the total impedance decreased and was accompanied by a significant capacitive alteration (as from the fitting: C_{all}(Cu-foil-G) = 13.06 μF cm⁻² and C_{all}(Cu-foil-G-CV) = 49.12 μF cm⁻²), which indicated the presence of minor defects and holes in the graphene coating.

When similar experiments were performed using the Ni-foil with a grown multi-layered graphene film (Fig. 6C), an almost
negligible change in the total impedance and capacitance were observed (as from the fitting: $C_{\text{all}}(\text{Ni-foil-MLG}) = 2.32 \ \mu\text{F cm}^{-2}$ and $C_{\text{all}}(\text{Ni-foil-MLG-CV}) = 2.45 \ \mu\text{F cm}^{-2}$). This indicated a better coverage of the metal surface which remained unaltered after the electrochemical treatment, thus confirming the results previously observed with the cyclic voltammetric measurements.

**Conclusions**

The excellent sensitivity of the electrochemical method described allows for a rapid and large-scale quantification of graphene surface coverage after the CVD growth process on Ni and Cu catalysts. We have demonstrated that the signal generated by the underlying Ni or Cu metal in alkaline solution can be directly correlated to fractures, holes or discontinuities in the graphene films. This provides an opportunity to rapidly evaluate the efficiency of the CVD growth process right after the cooling step without the need for any mechanical transfer of graphene. We foresee that this method could be easily scaled up and combined to industrial fabrication processes, such as roll-to-roll transparent electrode fabrication.

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