Interfacial capacitance of graphene: Correlated differential capacitance and in situ electrochemical Raman spectroscopy study

Jin-Hui Zhong, Jun-Yang Liu, Qiongyu Li, Mian-Gang Li, Zhi-Cong Zeng, Shu Hu, De-Yin Wu, Weiwei Cai, Bin Ren

A R T I C L E   I N F O

Article history:
Received 13 December 2012
Received in revised form 3 April 2013
Accepted 3 April 2013
Available online 10 April 2013

Keywords:
Graphene
Interfacial capacitance
Quantum capacitance
Raman

A B S T R A C T

The origin of the low interfacial capacitance of carbon-based materials is a long standing puzzle. The space charge capacitance and the quantum capacitance models have been proposed to interpret the phenomena. However, the physical origin of the capacitance is still unclear. In this study, we performed the differential capacitance and in situ electrochemical Raman spectroscopic measurement of single layer graphene in aqueous solutions to study the origin of the interfacial capacitance of graphene. The capacitance was found to have a minimum value of $-4.5 \mu F cm^{-2}$ in NaCl solutions and increased linearly with respect to both sides of the minimum. The Raman parameters of single layer graphene, including the frequency and band width of the G band, the frequency of the 2D band and the intensity ratio of 2D to G bands ($I_{2D}/I_{G}$), show the similar potential dependent behavior as the capacitance curve. The clear correlation between the Raman parameters and the capacitance can be understood by the same physical origin of carrier concentration ($n$) of graphene. This study shows that the carrier concentration is a decisive factor that determines the quantum capacitance and thus the total capacitance of graphene in the electrochemical systems.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Carbon-based electrodes have been widely used in fundamental and applied electrochemistry including analytical chemistry, (bio)sensing, batteries and supercapacitor [1]. Apart from the ‘classical’ carbon materials such as graphite, glassy carbon and carbon black, some new allotropes, such as carbon nanotube (CNT) and graphene, have received much intensive attention because of their special electronic properties [2–8]. The utilization of graphene as an electrode material has opened up a new field in electrochemistry with much improved performances and provided an opportunity to understand the very elementary processes in the electrochemical interfaces [9,10]. It has been realized that the interfacial properties of an electrode play a crucial role in determining the overall performance of an electrochemical system. A longstanding puzzle about the interfacial properties of the carbon-based electrodes is the origin of the interfacial capacitance that is unusually small (<10 μF cm$^{-2}$) [11–13] compared with that of metallic electrodes (~20 μF cm$^{-2}$). Moreover, the capacitance curve of the carbon-based electrodes shows a symmetric V-shape with respect to the minimum, without the deep minimum and hump usually observed on metallic electrodes. The interfacial capacitance (μF cm$^{-2}$) and the specific surface area (m$^2$ g$^{-1}$) determine the energy storage capacity of an electrode material [14]. Thus a clear understanding of the interfacial capacitance of the carbon-based electrode is crucial for designing high energy storage devices and understanding other electrochemical processes. Yeager et al. carefully measured the differential capacitance of the basal plane of graphite in NaF solutions and proposed that the total capacitance is dominated by the space charge capacitance within graphite [11,12]. Gerischer suggested that it would be more appropriate to treat graphite as a metallic conductor with a low density of states near the Fermi level [15], which interpreted Yeager’s result reasonably. The space charge capacitance model based on the semiconductor theory suggests that the capacitance should increase with potential in a cosine form. This, however, could not fully describe the observed capacitance curve with a linear dependence on potential. In addition, owing to the high carrier concentration of graphite, the Debye
length is already comparable to the lattice dimension and the surface excess charge does not diffuse within graphite but tend to accumulate on the surface like in metallic electrodes [12]. Hence, it is highly questionable about the existence of the ‘space charge layer’ within graphite. Recently, the quantum capacitance was proposed to account for the interfacial capacitance of carbon-based electrodes, on the basis of the measurement of capacitance from a single layer graphene [13]. According to the proposed model, the quantum capacitance exhibits a symmetric linear dependence on potential with a minimum around the Dirac point, which agrees well with the experimental results. The difference between the experimental results and the theory for the minimum value of capacitance and the slope of the capacitance curve could be well explained by the charged impurities of graphene. However, up to now, both models rely solely on the measured differential capacitance and the proposed theories. As both models predict the dependence of the capacitance on the carrier concentration \( (n) \) [12,13], it will be persuasive if other techniques can be used to verify the two models and unlock the physical origin. Such an effort is important but has not been reported in the literature, which will allow us to have a solid understanding of the interfacial capacitance of graphene.

Raman spectroscopy has historically played an important role for the study and characterization of various carbon materials including carbon nanotube and graphene [16–19]. Rich structural and electronic information have been obtained by Raman spectroscopy, such as the crystallite size, nanotube diameter and chirality, number of graphene layers, doping, defects and the optical energy gap [16–19]. The frequency, band width and intensity of the Raman phonons of single layer graphene have been demonstrated to effectively monitor the doping (carrier concentration) of graphene [20]. We envision that there might be a correlation between the capacitance and the Raman spectra of graphene since they both depend on the carrier concentration \( (n) \). In general, doping of graphene induces the addition of charge carriers and the shift of the Fermi level \( (E_F) \). Electrochemical Raman spectroscopy provides an accurate and flexible control over the Fermi level and therefore the doping (carrier concentration) level of graphene by electrochemistry and monitors in situ the doping level by Raman spectroscopy [20]. The capacitance of graphene could be simultaneously measured within the same experimental setup. Hence, we would be able to verify the physical origin that determines the capacitance of graphene and other carbon-based electrodes. This stimulates us to combine Raman spectroscopy and the capacitance measurement to uncover the origin of the interfacial capacitance of graphene.

In this work, we performed the differential capacitance measurement and in situ electrochemical Raman (EC-Raman) spectroscopy study of the single layer graphene in 0.01 and 0.2 M NaCl solutions. A distinct correlation between the Raman parameters and the capacitance was observed. A same physical origin of carrier concentration was accounted for this correlation.

2. Experimental

2.1. Preparation of the single layer graphene electrodes

Large area single layer graphene (SLG) was grown on a 25 μm thick Cu foil (99.8% Alfa Aesar no. 13382) using methane and hydrogen as precursors by chemical vapor deposition (CVD) as reported previously [21,22]. The CVD growth was carried out in a two inch quartz tube furnace with a methane flow rate of 1 sccm (partial pressure of 50 mTorr) and a hydrogen flow rate of 10 sccm (partial pressure of 150 mTorr) at 1035 °C, following a 15 min hydrogen anneal (10 sccm, 150 mTorr). After growth, the as-grown graphene film was transferred to 300 nm SiO\(_2\)/Si substrate using a modified protocol [23]. The number of graphene layers was identified by Raman spectroscopy [24] as well as the optical contrast. Two metal leads (300 nm gold) were deposited on graphene and connected to outer electrical wires by a conductive silver paint. The resistance between the two leads was \( \sim 2 \, k\Omega \), indicating good electrical contact to graphene. The edges of graphene and the electrical contacts were both covered with epoxy leaving the basal plane of graphene with a defined geometric area (0.019 cm\(^2\)) exposed to electrolyte, see Scheme 1. This design allows the determination of capacitance only from the basal plane of graphene. The graphene was annealed at 250 °C under hydrogen atmosphere to remove any possible residuals that may influence the doping level of the graphene.

2.2. Electrochemical measurements

The cyclic voltammograms and electrochemical impedance measurements were carried out in three-electrode configuration on Autolab PGSTAT128N (Metrohm Autolab, the Netherlands). The graphene electrode was used as the working electrode (WE) and mounted on the bottom of a Teflon cell containing about 5 mL electrolyte. A piece of thin quartz window was mounted on the top of the cell to allow Raman measurements. A Pt wire was used as the counter electrode (CE) whose surface area is much larger than graphene thus the capacitance of CE can be neglected. A saturated calomel electrode (SCE) was used as the reference electrode (RE). All solutions were prepared with 18.2 MΩ cm, Milli-Q deionized water (Millipore Corp., USA). All the chemicals were spectral grade (NaCl, NaF and KCl from Sinopharm Chemical Reagent Co., Ltd., China; FeMeOH (hydroxymethylferrocene) from Alfa Aesar). Cyclic voltammograms were measured in a solution of 1 mM FeMeOH and 0.2 M KCl to characterize the quality of the graphene samples. The capacitance was determined by the electrochemical impedance method with a small ac perturbation (with an amplitude of 10 mV and a frequency of 18 Hz) applied on graphene. All the capacitance has been normalized to the geometric area of graphene (0.019 cm\(^2\)).

2.3. Raman spectroscopic measurements

Raman spectra were measured on Xplora (Horiba Jobin Yvon, France) with the 532 nm excitation and 1200 lines/mm grating. The laser power was kept at 1.5 mW to avoid significant perturbation to graphene or any possible damage of graphene. Normal
Raman spectra were recorded through a 100× objective (NA = 0.9) with an integration time of 2 s. The in situ electrochemical Raman spectra were recorded by a long working distance 50× objective (NA = 0.55). The acquisition time for each spectrum was 10 s. The detailed setup for the in situ electrochemical Raman measurement was shown in Scheme 1. The Raman spectra were fitted by Gaussian-Lorentzian function to extract the relevant parameters, including the frequency, band width and intensity (height) of the G and 2D bands of graphene.

3. Results and discussion

3.1. Characterization of a single layer graphene

The most dominant Raman signatures of sp² carbon materials are the G band at ~1584 cm⁻¹ and 2D band at ~2700 cm⁻¹. The G band originates from the in-plane stretching of the C–C bond, corresponding to the doubly degenerate E₂g phonon at the Brillouin zone center Γ [25]. The 2D band is due to a second-order process involving phonons near the K point in graphene [26]. The band at ~1350 cm⁻¹ is assigned to the D band appearing for graphite with defects (or disordered structure). Fig. 1a shows the Raman spectrum of graphene. The strong, single and sharp 2D peak (~2680 cm⁻¹) indicates the single-layer nature of graphene [24]. The absence of D band indicates the high crystallinity of graphene without noticeable defects. Fig. 1b shows the optical microscopic image of the single layer graphene with some barely visible wrinkles and double layer graphene on it. No impurities could be observed. The cyclic voltammogram (CV) of graphene in FcMeOH solution was shown in Fig. 1c. The peak to peak separation of ~80 mV indicates a quasi-reversible kinetics on graphene. Scanning electrochemical microscopy (SECM) has been employed to measure the electron transfer kinetics of an electrode material and image the electrochemical activity of graphene [27,28]. In order to determine the standard heterogeneous rate constant k₀ of the graphene sample, we performed the SECM feedback measurement in 1 mM FcMeOH and 1 M KCl aqueous solutions. The feedback current profile was then simulated as a function of k₀ following the Butler–Volmer kinetics by Finite Element Method (FEM) Modeling (COMSOL Multiphysics) [29]. The value of k₀ was found to be ~0.04 cm s⁻¹ that agrees well with the literature result of ~0.042 cm s⁻¹ on the pristine single layer graphene [30], suggesting the high quality of the graphene sample.

3.2. Differential capacitance study

Fig. 2a shows the cyclic voltammogram of graphene in 0.2 M NaCl at a scan rate of 100 mV s⁻¹. The near rectangular shape of CV indicates this potential window is located in the double layer region without any redox reaction. Fig. 2b plots the frequency dependent capacitance in 0.01 M NaCl solution. The frequency dispersion was small with a capacitance value of around 5 μF cm⁻² over a wide range of frequencies. The differential capacitance was determined by the ac impedance measurement within the potential window of double layer region. The potential was first scanned to the positive direction and the reverse scan produced similar results (data not shown). The capacitance curve measured in 0.2 M NaCl solution was shown in Fig. 3a. The minimum capacitance of ~4.5 μF cm⁻² is comparable to the values reported for graphite [11,12] and graphene [13]. It is well accepted that fluoride ion is not specifically adsorbed on electrode surfaces. As shown in Fig. 3b, the capacitance curves obtained in both 0.01 M NaF and NaCl solutions are almost identi-
measurement of stress-annealed pyrolytic graphite electrodes with the basal planes exposed to the electrolyte [11,12]. The minimum capacitance was around 3 μF cm⁻² in NaF solutions. A space charge capacitance \( C_s \) within graphite was proposed to interpret the results. Gerischer reexamined Yeager’s data and proposed that it is more appropriate to treat graphite as a metallic conductor with a low density of states, \( \delta(\varepsilon) \), near the Fermi level and the density of states could be estimated from the capacitance [15]. According to the expression of the space charge capacitance model, the capacitance should exhibit a minimum value, which matches with the experimental results. However, the shape of the capacitance curve (linear increase with potential) could not be well described by the space charge model in which the capacitance is expected to increase with potential in a cosine form [12]. Another problem is that the Debye length of graphite is comparable to the lattice dimension because of the high carrier concentration of graphite [12]. This makes the space charge capacitance model questionable as stated in the introduction. Recently, Tao and Li showed that the interfacial capacitance of graphene has a quantum origin, based on the measurement of the capacitance of the single layer graphene in both ionic liquid and aqueous solutions [13]. The minimum capacitance was found to be \( \sim 5 \mu \text{F cm}^{-2} \). Both theoretical and experimental results demonstrated that the quantum capacitance has a minimum value at the Dirac point where the carrier concentration has a minimum and increases linearly with respect to the minimum [13]. The model could well describe the capacitance curve of graphene with one side [13] or both sides [14] exposed to the electrolyte. The quantum capacitance of a perfect graphene could be given by [33]

\[
C_Q = \frac{2e^2 k_B T}{\pi (\hbar v_F)^2} \ln \left[ 2 \left( 1 + \cosh \frac{e V_{ch}}{k_B T} \right) \right]
\]

where \( h \) is the Planck constant, \( e \) the electron charge, \( k_B \) the Boltzmann constant, \( v_F \approx c/300 \) the Fermi velocity of the Dirac electron, and \( V_{ch} = E_F/e \) is the potential of graphene. When \( e V_{ch} \gg k_B T \), Eq. (2) reduces to [13]

\[
C_Q \approx \frac{e^2}{\hbar v_F} \frac{2}{\pi} \frac{e V_{ch}}{(\hbar v_F)^2} = \frac{2e^2}{\hbar v_F \sqrt{\pi} \sqrt{n}}
\]

where \( n \) is the charge carrier concentration. According to Eq. (3), the most important parameter for determining the quantum capacitance of a defined system is the charge carrier concentration (\( n \)). It would be highly persuasive if an alternative technique can be used to provide correlation of the carrier concentration with the applied voltage. Raman spectroscopy has been well utilized to study the electronic properties of graphene and almost becomes a must technique in graphene study. In particular, the doping levels (carrier concentration) of graphene could be routinely monitored by Raman spectroscopy [20]. Hence, Raman spectroscopy could be a distinct tool to gain a clear insight into the origin of the interfacial capacitance of graphene and other carbon-based materials [20,34–36].

3.3. In situ electrochemical Raman spectroscopic study

In situ electrochemical Raman spectroscopic measurement was performed in 0.2 M NaCl solution. The potential dependent Raman spectra of the single layer graphene were shown in Fig. 4. It is remarkable that both the peak position and the linewidth are highly dependent on the potential. The position and full width at half maximum (FWHM) of the G band was extracted and plotted as a function of potential in Fig. 5a and b, respectively. The frequency of the G band has its smallest value of \( \sim 1583 \text{ cm}^{-1} \) around \( -0.05 \text{ V} \). It shifts to higher wavenumbers (by \( \sim 15 \text{ cm}^{-1} \)) at potentials more positive and negative than this value, corresponding to the hole and electron doping, respectively. The upshift of the G band was due
Fig. 4. Potential dependent Raman spectra of single layer graphene in 0.2 M NaCl solution measured from −0.8 to 0.7 V vs. SCE. Dot: experimental data, black line: fitted curves by Gaussian–Lorentzian method. The blue dash line corresponds to the Dirac point. Right panel shows energy diagram of the Fermi surface with respect to the Dirac point for the hole (top) and electron (bottom) doping, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

to the non-adiabatic removal of the Kohn anomaly in graphene as a result of electrochemical doping [20,34,36]. The Kohn anomaly is the softening (downshift) of the $E_{2g}$ phonon (G band) induced by the strong electron–phonon coupling (EPC) in graphene and graphite [37]. The electrochemical doping of graphene removes the Kohn anomaly thus leading to the observed stiffen (upshift) of the G band. It should be noted that the frequency of the G band shows doublet minima rather than a single one (Dirac point at $−0.05$ V vs. SCE), which is due to the non-adiabatic effect [34,36]. The non-adiabatic effect should be considered in graphene because the general adiabatic Born–Oppenheimer approximation (ABO) is failed. The relaxation time of the G peak pulsation is too short ($\sim 3$ fs) to allow the relaxation of electrons to the adiabatic ground state as assumed in ABO [36]. Fig. 5b shows the FWHM of the G band, showing a larger band width when the potential approaches the Dirac point. The FWHM of the G peak is about $19$ cm$^{-1}$ for the undoped graphene and decreases for both electron and hole doping. The sharpening of the G peak is due to Pauli blocking of the decay of phonons into electron–hole pairs (Landau damping), when the electron–hole energy gap is higher than the phonon energy upon doping [36]. The damping of phonons will result in the broadening of the phonons [35,36]. The small wave vector G phonon could only decay into the electron–hole pairs also with a small wave vector (low Fermi energy) due to the conservation of energy and momentum [35]. Upon the electrochemical doping, the (absolute) Fermi energy of graphene is increased and thus the decay channel will be blocked, leading to the decrease of the band width (Fig. 5b). The decrease of the FWHM saturates (to $\sim 10$ cm$^{-1}$) when Fermi level shift exceeds half the phonon energy upon higher degree of doping because the Landau damping is allowed only when $|\hbar\varepsilon_F| < h\omega_{\text{ph}}/2$ to satisfy the Pauli principle [35,36]. Apart from the features of the G band, the frequency and intensity of the 2D band also depend strongly on doping [20]. Fig. 6a and b show the intensity ratio of the 2D to G bands ($I_{2D}/I_G$) and the frequency of the 2D band as a function of the electrode potential, respectively. The intensity ratio ($I_{2D}/I_G$) has a maximum at the Dirac point and decreases with doping [20], with the characteristic potential similar to other parameters. The dependence of the intensity on doping is much stronger for the 2D band than for the G band, with the former being reciprocal with the electron/hole scattering rate [38]. Electrochemical doping increases the number of carriers and thus the probability of the scattering event. As a consequence, the intensity of the 2D band decreases leading to the observed decrease of the intensity ratio ($I_{2D}/I_G$) with doping. The frequency of the 2D peak increases by $\sim 3$ cm$^{-1}$ for the low electron doping ($−0.05$ to $−0.4$ V) before decreasing to lower wavenumbers. This is slightly different from theoretical prediction in which the frequency of the 2D band is expected to decrease for electron doping [20]. The difference may arise from the electrostatic interaction between graphene and the electrolyte, which do not affect the G peak to the same extent because the G phonon is less sensitive to the external electrostatic potential [20].

We now focus on the trends of the variation for the above four Raman parameters, namely, the frequency of the G and 2D bands, the FWHM of the G band and the intensity ratio ($I_{2D}/I_G$). They show extrema at exactly the same potential, which corresponds to the Dirac point [20,34–36]. The similar potential dependent behavior for all the four parameters indicates the reliability of the results. The potential for the Dirac point is $−0.05$ V (vs. SCE) in 0.2 M NaCl solution (vertical dash lines for eye guidance in Figs. 5 and 6), which agrees well with the potential for the capacitance minimum, as could be clearly observed in Fig. 5b in which the capacitance curves were also plotted for reference. To further validate the correlation between the two sets of quantities (capacitance and the Raman parameters), we performed the capacitance and Raman measurements also in 0.01 M NaCl solution (see also Figs. 3, 5 and 6). They all show extrema at about $−0.13$ V vs. SCE (Dirac point) and the

Fig. 5. (a) The Raman shift and (b) the full width at half maximum (FWHM) of the G band as a function of the potential. The capacitance curves were also plotted in b as dot and dash lines for reference.
capacitance minimum corresponds well with the extrema of Raman parameters shown in Figs. 5 and 6. The potential for the Dirac point in 0.01 M NaCl is more negative than that of 0.2 M NaCl, which may due to the ion screening effect [39]. The total carrier concentration of graphene is contributed from both the gate potential induced doping and the charged impurity induced doping. The screening of the charged impurities in graphene would therefore result in the decrease of the total carrier concentration. A higher ionic concentration leads to more effective screening of the charged impurities. It should be also noted that the minimum capacitance in 0.2 M NaCl (4.67 μF cm⁻²) is larger than that of 0.01 M (4.58 μF cm⁻²) and 0.1 mM NaCl (4.31 μF cm⁻², data not shown) solutions. The upshift of the capacitance curve with the increasing electrolyte concentration is consistent with previous reports [12,13], which could be explained by the variation of the diffuse layer capacitance. The diffuse layer capacitance is proportional to the square root of the ionic concentration based on the Gouy–Chapman theory, which may contribute to the upshift of the capacitance at higher ionic concentrations [12].

3.4. The correlation between quantum capacitance and Raman parameters

The exact matching in the potential dependent behavior between the Raman parameters and the capacitance in both 0.01 and 0.2 M NaCl solutions suggests that these two sets of quantities may have a same physical origin. As stated above, the quantum capacitance depends on the potential (V_D) or the carrier concentration (n) of graphene. Raman spectroscopy, on the other hand, can provide the electronic properties of a material. In particular, sp² carbon materials have several distinct Raman modes (D, G, D', 2D and their combination frequencies) capable of discriminating different forms of sp² carbon structures, such as the carbon nanotube (and the diameter), graphene (and the number of layers) and graphite [16–19]. The frequency and FWHM of the G band have been demonstrated theoretically [34] and experimentally [20,35,36] to be sensitive to the doping. The dependence of the frequency and FWHM of the G band, the frequency of the 2D band and the intensity ratio (I_{2D}/I_G) on doping have been discussed above (Section 3.3). Now we consider a theoretical description for the dependence of the G band frequency on doping. The other parameters also have their own theoretical description [20,34,36,38]. The band structure of graphene exhibits isotropic linear dispersion near Dirac points (K and K'). For neutral graphene, the Fermi surface is located at the Dirac point (Fig. 4). The Fermi level (E_F) and the carrier concentration (n) could be well tuned through the gate voltage or the electrochemical potential, which induces electron or hole doping and shifts the Fermi level higher or lower than the Dirac point, respectively (Fig. 4). Upon doping, the Fermi level in graphene changes as [20,35]

\[ E_F(n) = \frac{\hbar |V_F|}{\sqrt{\pi n}} \]  

The frequency shift (Δω) of the G band (as compared to undoped graphene, ω₀) could be expressed as [36]

\[ h \Delta \omega = \frac{\hbar A \langle D_{2g}^2 \rangle_F}{\pi M_0 Q(hv_F)^2} |E_F| = \alpha' |E_F| \]  

in which \( \alpha' = 4.39 \times 10^{-3} \), and \( A \) is the unit cell area, \( M \) is the carbon mass, \( \langle D_{2g}^2 \rangle_F \) is the deformation potential of the E_{2g} mode and \( \langle D_{2g}^2 \rangle_F = D^2/4 \) [35,40] where \( D \) is the electron–phonon coupling strength. Combining Eqs. (4) and (5) we obtain:

\[ \Delta \omega = \alpha' |V_F| \frac{1}{\sqrt{\pi n}} \]  

which clearly shows the dependence of Δω on the carrier concentration (n) of graphene as observed experimentally [20,35,36]. Since both the quantum capacitance (C_Q) and frequency shift (Δω) depends on the carrier concentration (n), we could further combine Eqs. (3) and (6) to obtain the relation between C_Q (μF cm⁻²) and Δω (cm⁻¹) as:

\[ C_Q = \frac{4e^2}{h v_F^2 \alpha'} \Delta \omega \]  

By calculating the equation using the numerical values we obtain

\[ C_Q = \Delta \omega \times 10.15 \left( \frac{\mu F \ cm^{-2}}{cm^{-1}} \right) \]  

which indicates the quantum capacitance has a linear relationship with the frequency shift of the G band by a constant slope of 0.105. To check the validity of this relation (Eq. (8)), we roughly estimate the quantum capacitance as follows. Taking the quantum capacitance of graphene into consideration, the total capacitance could be expressed as:

\[ \frac{1}{C_T} = \frac{1}{C_Q} + \frac{1}{C_{il}} + \frac{1}{C_{diff}} \]  

For simplification, the compact layer capacitance (C_Q) was treated as a textbook value of 20 μF cm⁻² (supposed that it will not change with potential [13,14]) and the diffuse layer capacitance can be neglected. As shown in Fig. 3a, the quantum capacitance increases linearly with potential by a slope of ∼30 μF cm⁻² V⁻¹. The dependence of C_Q (μF cm⁻²) on Δω (cm⁻¹) was plotted in Fig. 7a for the results from both 0.01 and 0.2 M
Fig. 7. (a) Plot of the quantum capacitance \(C_Q\) against the frequency shift of the G band \(\Delta \omega\), the data for the positive branch (0.05–0.3 V) of the capacitance curves was used for fitting. (b) The mean slopes (in both 0.01 and 0.2 M NaCl solutions) for \(C_Q\) (\(\mu F cm^{-2}\)) \~\(\Delta \omega\) (\(cm^{-1}\)) and \(C_G\) (\(\mu F cm^{-2}\)) \~\(E\) (\(V\)) curves under various values of the compact layer capacitance \(C_{hl}\). The small scattering of the data suggests the almost identical slope for both electrolytes.

NaCl solutions, which gives almost identical slopes of 0.83 and 0.84, respectively, reflecting that it is reasonable to neglect the diffuse layer capacitance. Note that the data within the potential region \(E \geq 0.05\) V was used for fitting because Eq. (5) is only valid when \(|E| \gg \hbar \omega c/2\) (high degree of doping) [36]. The slope values are much higher than the calculated value of 0.105. The difference is reasonable considering the uncertainty in \(C_H\) and \(C_{diff}\) when estimating the quantum capacitance, which may also account for the larger slope for the \(C_Q\) \~\(E\) (potential) curves \((-30\ \mu F cm^{-2} V^{-1}\) ) than the predicted value for the ideal graphene \((-23\ \mu F cm^{-2} V^{-1}\) ) [13]. However, this value of \(-30\ \mu F cm^{-2} V^{-1}\) is still questionable because for graphene with charged impurity the slope should be smaller than that of the ideal graphene [13]. This urges us to reconsider the value of the compact layer capacitance \(C_{hl}\).

Very high \(C_Q\) values (up to 100–150 \(\mu F cm^{-2}\)) have been found in gold and silver electrodes in concentrated electrolytes, which was ascribed to the reorientation of the water molecules adjacent to the electrode surfaces [41]. The electric double layer of diamond and graphene electrodes were also proposed to be dominated by the ordered water (or the hydroxyl ions) in the inner Helmholtz plane [31,32], in which both hydroxyl (OH\(^-\)) and hydronium (H\(_3\)O\(^+\)) ions were found to adsorb specifically on the graphene surface [32]. To remove the uncertainty in predicting the \(C_H\) on graphene surface, we plot the slopes of \(C_Q\) \~\(\Delta \omega\) and \(C_Q\) \~\(E\) curves against a series of the \(C_H\) values in Fig. 7b. Indeed the slopes decrease and saturate when \(C_H\) is larger than 200 \(\mu F cm^{-2}\). If we consider a \(C_H\) of 100–200 \(\mu F cm^{-2}\), the \(C_Q\) \~\(\Delta \omega\) curve gives a slope value of \(-0.3\), which is much closer to the calculated result. Under this condition, the slope for \(C_Q\) \~\(E\) curves is \(-13\ \mu F cm^{-2} V^{-1}\), indicating a certain amount of charged impurities in graphene [13]. The effective charged impurity concentration \(n^*\) was estimated to be \(-10^{11} cm^{-2}\) (at \(C_H = 100 \mu F cm^{-2}\)), in line with literature report value [13]. We also note that even under a high value of \(C_H\), the slope for \(C_Q\) \~\(\Delta \omega\) curve is still higher than the calculated value. This could be partially explained by the deviation of \(\langle F_D^2\rangle\) (possibly accounting for the doping effect, see Ref. [42] and Note 38 therein) and \(D\) value (due to the imperfect structure of graphene sample) from the theoretical model. Note also that the deviation from linearity of the G band frequency shift (Fig. 5a), the influence of the intrinsic defects (wrinkles and grain boundaries) on the capacitance, and the impact of the interaction between graphene and electrolyte on the Raman parameters not captured by the present theoretical model, may also be considered to fully explain the deviation of slope. Nevertheless, the slopes for 0.01 and 0.2 M NaCl solutions are almost identical (Fig. 7), indicating that the linear relationship between the quantum capacitance and the frequency shift of the G band is valid. This further confirms the hypothesis that these two sets of values have the same physical origin of carrier concentration \(n\), which is also associated with the Fermi level and the density of states (DOS) of graphene [20,33,34]. The carrier concentration could be tuned by the gate voltage, the electrochemical potential or the chemical doping of graphene [43]. The observed distinct correlation between the Raman parameters and the capacitance in different NaCl concentrations indicates that the carrier concentration is a decisive factor that determines the quantum capacitance and thus the interfacial capacitance of graphene.

4. Conclusions

Differential capacitance of single layer graphene was measured by the electrochemical impedance method. The capacitance has a minimum value of \(-4.5 \mu F cm^{-2}\) in NaCl solutions and increases linearly with respect to the minimum. In situ electrochemical Raman spectroscopic measurement was carried out. The frequency and FWHM of the G band, the frequency of the 2D band and the intensity ratio of the 2D to G band \((I_{2D}/I_G)\) all show strong dependence on potential, as in the case of the capacitance curve. The excellent correlation between the Raman parameters and the capacitance was observed in different electrolyte concentrations. The linear relationship between the quantum capacitance \(C_Q\) and the frequency shift of the G band \(\Delta \omega\) was also found for both 0.01 and 0.2 M NaCl solutions with almost identical slopes. The same physical origin of charge carrier concentration \(n\) of graphene was accounted for both quantum capacitance and Raman parameters. The combination of the electrochemical and spectroscopic methods provides abundant information that would be helpful for understanding the electrochemical interfacial processes. This study shows that the interfacial capacitance of graphene has an additional quantum capacitance component, which is determined by the carrier concentration \(n\). On the basis of these results, the modulation of the electronic properties (such as by chemical doping) of graphene itself should be taken into account when designing graphene-based devices.

Acknowledgements

This work was financially supported by Ministry of Science and Technology of China (2011YQ03012406) and National Science Foundation of China (21021120456, 20825313, 21021002 and 21227004). We would like to thank Prof. Dong-Ping Zhan for the inspiring discussion.
References


