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Electrochemical interfacial capacitance in multilayer graphene sheets: Dependence on number of stacking layers

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ABSTRACT

We engineered the number of stacking layers of multilayer graphene sheets by selective post-treatments. The most probable number of layers of graphene was determined according to specific surface area. The interfacial capacitance of multilayer graphene sheets relates to the number of layers. This result is attributed to the dependence of space charge layer capacitance on the number of layers.

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1. Introduction

Graphene-monolayer of carbon atoms arranged in a honeycomb lattice – is a prevalent building block in many carbon materials [1,2]. As a novel model for theoretical study, unusual electronic properties have been discovered in graphene. Previous studies have shown the dependence of the electronic structure of graphene on its number of layers [3–5]. Most of these results fall in the topic of nanoelectronics. Electrochemistry, however, fails to play its role until recently [6,7]. Electrochemical interfacial capacitance, defined as the capacitance per surface area ($F\text{ m}^{-2}$), is a function of electric double layer capacitance, which is determined by the electronic structure of specified electrode. Insights into the relationships between number of layers and interfacial capacitance of graphene sheets can provide electrochemical approaches to study the electronic structure of graphene and optimize the capacitance of graphene materials as supercapacitor electrode.

Up to date, many efforts have been devoted to the interfacial capacitance of carbon electrodes. The higher interfacial capacitance on edge plane than basal plane of bulk graphite was observed years ago [8]. New insights are recently thrown into the effects of surface chemistry (boron [9], oxygen [10], nitrogen [11,12] and phosphorus [13]) and micropore size on interfacial capacitance of diverse carbon electrodes [14–16]. Besides, the interfacial capaci-

tance of porous carbon electrode is limited as the pore wall thickness is reduced [17]. We herein address the dependence of interfacial capacitance on number of layers of multilayer graphene sheets.

2. Experimental

Reduced graphene oxide sheets were chemically exfoliated from natural flake graphite powder (Sinopharm Chemical Reagent Co. Ltd.) [18]. Post-treatments in argon (g), hydrogen (g), ammonia (g) and hydrazine (l) were performed to modify the surface chemical environment of reduced graphene oxide sheets and hence tailor the stacking thickness. Gaseous treatments were conducted at 400 °C for 4 h, while liquid treatment was refluxed at 100 °C for 24 h. The samples are denoted as r-GO (reduced graphene oxide sheets), GAr (400 °C, Ar), GH (400 °C, H₂), GN (400 °C, NH₃) and GHy (100 °C, hydrazine).

The graphene samples were characterized by SEM (FEI Nova NanoSEM 430, 15 kV). Specific surface area (SSA) and porous parameters were determined using Micromeritics ASAP 2010 M instrument at liquid nitrogen temperature. X-ray photoelectron spectroscopy (XPS) analysis was performed on ESCALAB 250 instrument with Al K α radiation (15 kV, 150 W) under a pressure of 4×10^{-8} Pa. X-ray diffraction (XRD) was conducted on D-MAX/2400 instrument (Cu K α , $\lambda = 0.154056$ nm).

The graphene electrodes were prepared by mixing with carbon black and PTFE at a weight ratio of 90:5:5. All the measurements were finished in a three-electrode test cell with 6 M KOH or 1 M

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Table 1
Surface chemical properties, SSA, total pore volume (V_{total}) and interfacial capacitance (C) of the pristine and modified chemically exfoliated graphene sheets.

Sample	C1s _{XPS} (at.%)	O1s _{XPS} (at.%)	N1s _{XPS} (at.%)	SSA ($\text{m}^2 \text{g}^{-1}$)	V_{total} ($\text{cm}^3 \text{g}^{-1}$)	C-KOH (F m^{-2})	C-H ₂ SO ₄ (F m^{-2})
r-GO	90.93	9.07	0	106	0.3	0.65	–
GAr	91.74	8.26	0	170	0.47	0.72	0.46
GH	92.47	7.53	0	163	0.45	0.64	–
GN	90.72	6.98	2.3	136	0.41	0.67	0.54
GHy	89.91	8.29	1.8	22	0.07	2.79	1.45

H₂SO₄ electrolytes. The cyclic voltammograms were collected on Solartron 1287 electrochemical instrument at 5 mV s^{-1} . The CV potential ranges were -1 to 0.1 V vs. Hg/HgO in KOH electrolyte and -0.2 to 0.8 V vs. SCE in H₂SO₄ electrolyte with a Pt plate as counter electrode. The gravimetric capacitance of the electrodes was calculated according to $C_g = (\int i dV)/(vmV)$, where i is the current density during charging or discharging, V is the potential, v is the potential sweep rate, and m is the mass of the paper electrodes. The interfacial capacitance was calculated by dividing the gravimetric capacitance with the specific surface area of the corresponding graphene samples.

3. Results and discussion

3.1. Surface chemistry and physical texture characterizations

XPS reveals a decreased oxygen atomic concentration in the sequence of r-GO > GAr ~ GHy > GH > GN (Table 1). Hydrazine is considered to unlikely reduce carboxylic groups but can react with lactones and anhydrides to form hydrazides and with quinones

to form hydrazones [19,20]. However, it is believed that only the formation of hydrazone can remove oxygen [19]. Oxygen groups can be removed by thermal treatment [21]. Ammonia can be thermally decomposed to yield atomic hydrogen for oxygen removal [22]. Consequently, the oxygen population in GH and GN is smaller than that in GHy and GAr. The SSA and total pore volume (V_{total}) were increased after gaseous treatments, but decreased considerably after hydrazine reflux (Table 1). Correspondingly, the hysteresis loops for graphene were expanded or narrowed (Fig. 1a). These results indicate the textural expansion/shrinkage after post-treatments of r-GO. The SSA of the present graphene samples are substantially smaller than the theoretical SSA of $2620 \text{ m}^2 \text{g}^{-1}$ of single layer graphene, which indicates the severe restacking of graphene sheets after solvent removal, as confirmed by the SEM image of GAr in Fig. 1a.

3.2. Determination of the most probable number of layers

1. The theoretical specific surface area of graphene monolayer is $2620 \text{ m}^2 \text{g}^{-1}$.

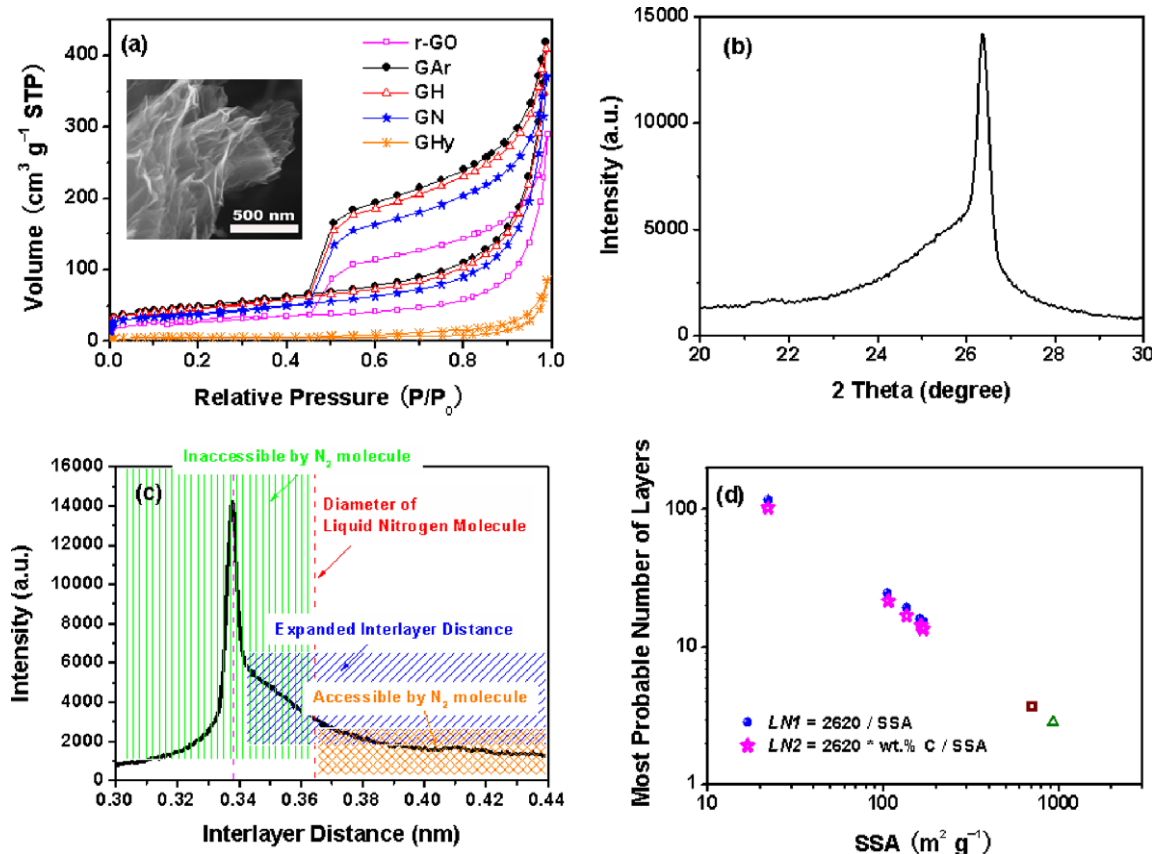


Fig. 1. (a) Nitrogen cryosorption isotherms of graphene. Inset SEM image shows the stacking status of graphene in GAr with the highest SSA in this work. (b) The raw XRD curve, and (c) the converted curve of interlayer distance by Scherrer equation of GAr. (d) Relation between the SSA and number of layers of solvent-free graphene according to relations LN1 and LN2. The empty square and triangle marks show the number of layers of chemically modified graphene samples [6,7], according to relation LN1.

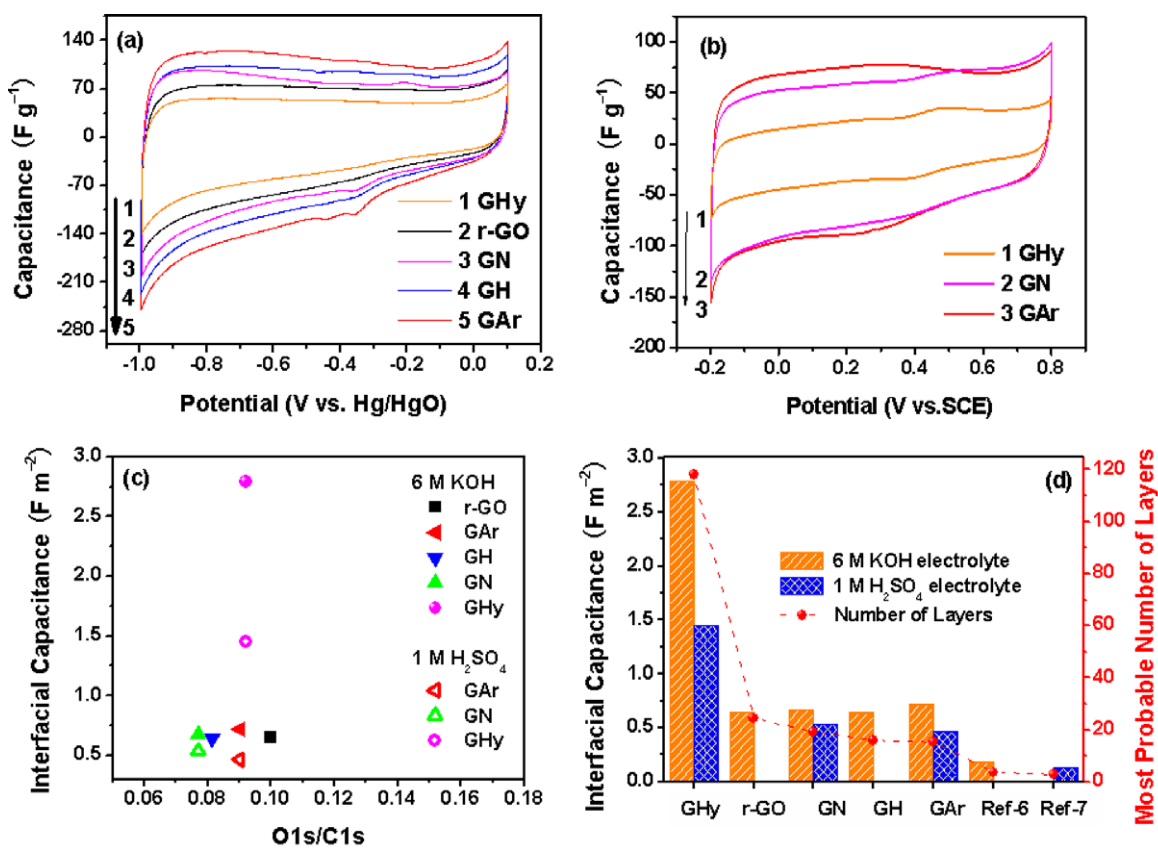


Fig. 2. Cyclic voltammograms of graphene recorded in (a) 6 M KOH and (b) 1 M H₂SO₄ electrolytes at 5 mV s⁻¹. (c) Relation between the oxygen concentration and interfacial capacitance of solvent-free graphene. (d) Relation between the interfacial capacitance and number of layers of solvent-free graphene. The data obtained from literature [6,7] are given for a comprehensive insight.

- The interlayer distance of two graphene monolayer in graphite (0.335 nm) is smaller than the kinetic diameter of a liquid nitrogen molecule (0.364 nm). The theoretical specific surface area of a multilayer graphene sheet is the value of 2620 m² g⁻¹ divided by the number of layers. One can thus estimate the number of layers of solvent-free graphene by dividing 2620 m² g⁻¹ with the measured SSA.
- The interlayer distance of solvent-free graphene was measured by XRD (Fig. 1b and c). The asymmetry of the (0 0 2) peak is due to graphene sheets with relatively large interlayer distance. According to Fig. 1c, the interlayer distance of graphene ranges from 0.34 to 0.44 nm, most of which (>70%) is inaccessible by liquid nitrogen molecule. Therefore, the most probable number of layers (>70%) is dividing 2620 m² g⁻¹ with the measured SSA.
- Considering the presence of oxygen/nitrogen in chemically derived graphene, the weight ratio of carbon should be considered when calculating the most probable number of layers.

Two formulas (*LN1* and *LN2*) are proposed to derive the number of layers of graphene (Fig. 1d), where *LN2* is corrected with carbon weight ratio. The number of layers decreases as the SSA is increased.

3.3. Interfacial capacitance and number of layers

Cyclic voltammetry profiles (Fig. 2a and b) collected in both alkaline and acidic electrolytes indicate the contributions from electric double layer capacitance and pseudocapacitance to the

interfacial capacitance. From Fig. 2c and Table 1, we can find that GN has a comparable interfacial capacitance with r-GO/GAr/GH owing to their close oxygen ratios, disregarding the presence of nitrogen. It is known that highly concentrated nitrogen in carbon electrode can produce pseudocapacitance [11,12]. However, the quite low amount of nitrogen in GN contributes little to the interfacial capacitance. Quite interestingly, GHy exhibits a greatly higher interfacial capacitance (2.79 F m⁻²), four-folds of those of the rest samples (0.64–0.72 F m⁻²). Taking into account of the extremely lower nitrogen atomic ratio (N/C = 0.022) in GHy, it is unreasonable to achieve such a high interfacial capacitance only through enhanced redox reactions from nitrogen. Meanwhile, the quite close population of oxygen in the GHy to the rest, especially GAr, should contribute comparable pseudocapacitance, and neither explains its anomalous higher interfacial capacitance. These results suggest that the deviation of pseudocapacitance arising from the different surface chemical environment is neglectable. Consequently, the difference in electric double layer capacitance dominates the deviations in interfacial capacitance.

The electric double layer interfacial capacitance depends on the Helmholtz layer capacitance and space charge layer capacitance of an electrode. The Helmholtz layer capacitance is a function of electrolyte type and concentration, and can be treated identically for all the samples prescribed to the same electrolyte. Space charge layer capacitance (C_{sc}) can be expressed as [17]

$$C_{sc} \propto \beta/\delta$$

where β is the stacking thickness of graphene sheets and can be calculated according to $\beta = (LN-1) \times d$; d is the most probable interlayer distance of graphene sheets determined from X-ray

diffraction (0.34 nm, Fig. 1c); δ is the screening length of electric field in the electrode.

During the restacking of solvent-removed graphene, the number of layers (i.e., the stacking thickness) increases, while the stacking sequence becomes random. Since the energy deviation between *ABA* and *ABC* stacking sequence is quite close, the screening length of restacked graphene sheets is solely dominated by the number of layers [4]. The screening length increases in thicker graphene sheets because of the decreased charge carrier concentration [4]. However, only 3–4 times increment in screening length was found when the number of layers of graphene increased from three or four to bulk graphite [4,23]. On the contrary, the stacking thickness dramatically increases by 5–45 times in the present case, as known from Fig. 1d. Consequently, the space charge layer capacitance is positively determined by the number of layers, and hence the total interfacial capacitance. A comparison made in Fig. 2d among different graphene samples consolidates this point.

The meaning of our work lies in increasing the interfacial capacitance of modified graphene sheets by reducing the screening length or promoting the stacking thickness. Since gravimetric capacitance is the product of interfacial capacitance multiplied by SSA, modified graphene sheets with a high SSA can be more suitable for supercapacitor applications.

4. Conclusions

In this contribution, we engineered the number of layers of graphene sheets by selective treatments. The number of layers of graphene was determined according to specific surface area. The interfacial capacitance of multilayer graphene sheets is found to depend on the number of layers. This result is attributed to the dependence of space charge layer capacitance of graphene on the number of layers, where the two factors of screening length and stacking thickness play dominantly. This work opens up the understanding of the electronic structure of multilayer graphene via an electrochemical way, and probably initiates interests in the field of electrochemical electronics of graphene.

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