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A green, simple and cost-effective approach to synthesize high quality graphene by electrochemical exfoliation via process optimization

High-quality graphene was manufactured by electrochemical exfoliation method. The comparison of graphene and rGO exhibits tremendous differences including morphology, defects level. The correspondence of D/G ratio with different current density were detailed record, that is, with the rising of current density, the more defects can be observed. In addition, through tuning various synthetic parameters, we found out that current density plays an important role in the process.

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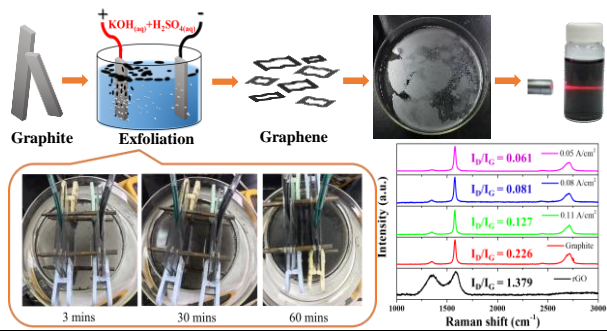
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A green, simple and cost-effective approach to synthesize high quality graphene by electrochemical exfoliation via process optimization

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The research is focus on manufacturing graphene nanosheets by electrochemical exfoliation method (EC-graphene). Through tuning the synthetic parameters, such as the composition of electrolytes, concentration of electrolyte, KOH/H_2SO_4 ratio as well as applying voltages and current density to study the relationship between characterization and synthetic parameters. The corresponding characterizations, including physical and chemical properties of as-synthesized GNS are studied by scanning electron microscope (SEM), high resolution transmission electron microscope (HR-TEM), X-ray diffraction (XRD), atomic force microscopy (AFM), Raman spectroscopy (Raman), Fourier transform infrared spectroscope (FTIR) and X-ray photoelectron spectroscopy (XPS) are systematically carried out in this study. Among these synthetic parameters, current density play a very important role on this exfoliation process. Under the optimal current density of $0.11A/cm^2$, we successfully synthesize high quality of GNS with a D/G ratio of 0.061, which is much superior to those of others groups' reported value. The results indicate that a green, simple and cost-effective exfoliation process have been successfully build up in this study.

1. Introduction

Graphene, a novel material with merely a single layer of carbon atoms in two-dimensional lattice, was discovered in 2004 by A. K Geim and K. S. Novoselov through mechanical method[1], has been attracted tremendous attention for a wide variety of applications. This material possesses unique physical properties, such as intrinsic carrier mobility (200,000 $cm^2V^{-1}s^{-1}$), excellent mechanical strength (~1,100 GPa), superior thermal conductivity (~5,000 $Wm^{-1}K^{-1}$), high electrical conductivity (10^{-6} $\Omega\cdot cm$) and nearly transparent in visible light (97.7%).[1-4] All of the properties mentioned above make graphene as one of the most promising material which has potential application in electronic, photonic, composite material and several other fields.

Synthesis of graphene has been investigated through several ways: (1) Mechanical exfoliation exhibits quite great quality, but is impossible to scale up production[1,5]; (2) Chemical vapor deposition using copper or nickel as catalysts can grow large-area and high-quality graphene[6-10]. However, this technique needs to manipulate under severe conditions which implicate expensive cost for providing reasonable price. (3) Chemical exfoliation based on Hummers' method can produce graphene derivatives in large quantity.[11-14] Through oxidation of graphite flakes into graphene oxide (GO) and then reduction by chemical or thermal treatment has become a familiar process by reason of benefit of quite low-cost compared to other methods. However, lots of strong chemicals such as sulfuric acid, hydrochloric acid or potassium permanganate will be applied in this process which is non-environmentally friendly and hazardous due to possibility of explosion[15], what's more, the high defects and oxygen functional groups exist in reduced GO (rGO) make it physical properties scarcely comparable to graphene. In other words, the shortcoming of this process is harmful yield. In Comparison with chemical exfoliation, we demonstrate a one-step method to obtain high-quality graphene nanosheets through electrochemical exfoliation which is safer, more time-saving and more environmental-friendly than chemical exfoliation. Moreover, it was reported that electrochemical-exfoliated possess a better quality.[16]

In this research, low-contamination and high quality graphene were manufactured by electrochemical exfoliation method. High purity graphite plates were imposed with DC to exfoliate the electrodes, then shattered the exfoliated-graphite with sonication. A series of analyzing and discussing toward low-defect, few-layers and large lateral size graphene.

2. Experimental section

2.1. Sample preparation

In the past, expandable graphite was prepared by the chemical intercalation of sulfuric acid followed by instantly high temperature, where the graphite was expanded by gaseous species released from intercalant.[17-18] For this reason, we

considered that adoption of sulfuric acid as an electrolyte is a well beginning. However, some researches indicate that only use sulfuric acid to exfoliate graphite into graphene will generally produce high defect level because of intense oxidation. To improve this phenomenon, potassium hydroxide was added to lower the acidity of the electrolyte solution.[9] Another literature demonstrate that merely employ potassium hydroxide as an electrolyte will exhibit excellent quality of graphene.[16]

In the experiment, we combine both compounds mentioned above (sulfuric acid and potassium hydroxide) as electrolytes, then focus on the concentration of solution, applied voltages and electrode distance. First, we found out the optimal parameters with the best graphene production, then carry on further analyses. Table 1 presents the experimental design of electrochemical exfoliation process of graphite in our study. The parameters we chose including voltages, composition of electrolyte, distance between two graphite electrodes. First, in accordance of different weight proportion to blend specific electrolyte and paralleled the graphite plates as shown in Figure 1a, then electrodes were connected to DC power supply with wires and emerged in the solution, which was continuously stirred by magnet to reduce concentration polarization

Table 1 Experimental parameters of electrochemical exfoliation graphite in this study.

Experimental parameters			
Voltages (V)	12	15 *	18
Concentration of KOH (wt%)	30 *	35	45
Concentration of H_2SO_4 (wt%)	-	13.5 *	23.8
Distances (cm)	2.5	3.5	4.5 *

phenomenon. By means of cooling system, which was applied on the outer side of electro-bath, to avoid raising of temperature. After beginning of electrolysis, the silver-like substances gradually appeared and reunited on the surface of electrolyte solution, as shown in Figure 1b. Collecting silver-like substances with scoop and removing the electrolyte through considerable water washing until the filtrate is around neutral. As a results, exfoliated-graphene was obtained. Final, we treated the samples with sonication to turn exfoliated-graphene completely into EC-graphene. Therefore, highly dispersed graphene solution with observable Tyndall effect were obtained, as shown in Figure 1c. After crossover parameters study in Table 1, we found that when the electrolyte solution deployed with weight percentage of 30% $KOH_{(aq)}$ and 13.5% $H_2SO_{4(aq)}$, the distance of graphite plates at 4.5 cm and applied voltage of 15 V, will demonstrates the best exfoliation efficiency. In order to identify the crucial parameters which dominates the whole process, further experiments were carried out. We fixed the electrolyte formula followed by adjusting voltages and electrolysis area. All of data and results were presented in Table 2. From the Table 2, we can obviously observe that current density is a key factor in the exfoliation process where 0.11 A/cm^2 is a critical point. When current density is less than 0.11 A/cm^2, exfoliation effect is not significant because the silver-like substances produce slowly, which implicates the consumption of lots of time. On the other hand, when current density is greater than 0.11 A/cm^2, intense reaction will produce numerous of silver-like substances. However, extreme exfoliation usually occurs along with relatively large graphite fragments, which attached to silver-like substances will be uneven of graphene quality. After 8 hours of electrochemical exfoliation including water washing and sonication, we found that the production of graphene is around 0.335 g.

Table 3 displays the comparison of relative literature on electrochemical exfoliation graphene, including electrochemical procedure, electrolyte and other important parameters. Among all of the references, our research exhibits the best quality, which can be inferred from the minimum D and G ratio (around 0.061) based on Raman spectrometer.

Table 2 The observed phenomena of electrochemical exfoliation in different experimental conditions.

Voltages (V)	Currents (A)	Electrode area (cm^2)	Current density (A/cm^2)	Results and notes
6	0.84	35.2	0.05973	Silver-like substances emerged after a long time
9	1.80	35.2	0.04290	Almost nothing exfoliated
9	6.38	106.8	0.05114	Silver-like substances is quite rare
12	6.90	85.1	0.08108	Silver-like substances existed
15	9.49	85.1	0.11328	Large amounts of silver-like substances
18	12.02	89.38	0.13448	Lots of black and silver-like substances exfoliated

Table 3 Electrochemical exfoliation GNS or GO comparison of procedure, electrolyte and other important parameters.

Electrochemical procedures	Electrolytes	Products	I_D/I_G ratio	O/C ratio	References
Anodic oxidation	NaOH+H$_2$O$_{2(aq)}$	GNS	0.67	0.06	[19]
Anodic oxidation	PSS$_{(aq)}$	GNS	0.6	-	[20]
Anodic oxidation	TBA$_{(aq)}$	GNS	0.64	0.09	[21]
Anodic oxidation	Ionic liquid$_{(aq)}$	GNS	0.1	High	[22]
Cathodic reduction	NaCl$_{(aq)}$+DMSO+Thinion	GNS	0.1	0.08	[23]
Cathodic reduction	HClO$_{4(aq)}$	GNS	0.1	-	[24]
Cathodic reduction	PC	GNS	<0.1	-	[25]
Anodic oxidation then cathodic reduction	H$_2$SO$_{4(aq)}$	GNS	0.6	-	[9]
Anodic oxidation then cathodic reduction	H$_2$SO$_4$(aq) or H$_3$PO$_{4(aq)}$	GO	0.71	-	[26]
Anodic oxidation then cathodic reduction	Ionic liquid$_{(aq)}$	GNS and GO	0.3 (GN) 0.75 (GO)	-	[27]
Anodic oxidation then cathodic reduction	H$_2$SO$_{4(aq)}$+KOH$_{(aq)}$	GNS	0.061	-	This study

Figure 1. (a) Experimental set-up of electrochemical exfoliation system; (b) Silver-like substances floated on the electrolyte solution. (c) Highly dispersion of EC-graphene suspension with Tyndall effect were obtained after exfoliation process.

2.2. Sample characterization

Field emission scanning electron microscopy (SEM, Hitachi S-4100), High resolution transmission electron microscopy (HR-TEM JOEL-2000FX), Atomic force microscopy (AFM, Bruker ICON2-SYS) Raman spectrometer (Horiba iHR320, Olympus BX41, 532 nm excitation laser), X-ray diffraction (XRD, Bruker D8 Avance), Fourier transform infrared spectroscope (FT-IR, Bruker Tensor-II) and X-ray photoelectron spectroscopy (XPS Thermo K-alpha) were carried out for functional groups identification.

3. Results and discussion

Figure 2 unveils XRD patterns of EC-graphene (black), graphite (red) and rGO (blue). It is clearly shows graphite exist a high intensity characteristic peak at 26°. However, in comparison with that of graphite, the characteristic peak of graphene at 26° disappears, which is replaced by a broad and weak mound, representing that no matter we utilize either electrochemical or chemical approaches, well-exfoliated graphene can be obtained.
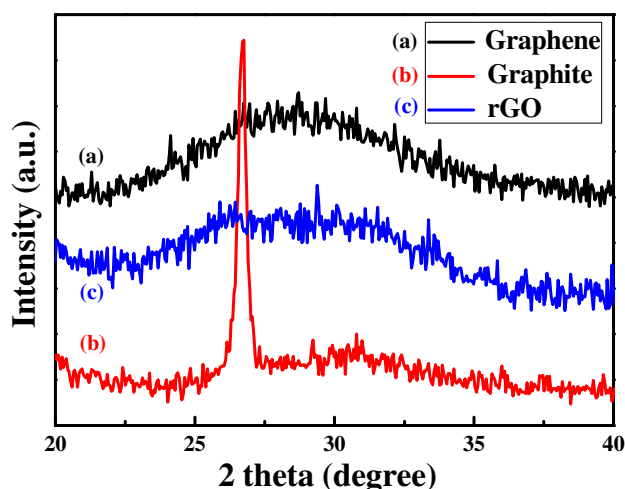
Figure 2. XRD patterns of (a) EC-graphene, (b) chemical exfoliated-graphene and (c) graphite

Figure 3a shows the FT-IR spectra of EC-graphene and rGO based on Hummers method after 300°C thermal treatment. The weak peaks at 2927 and 2947 cm^{-1} indicate the asymmetric and symmetric vibrations of C-H groups. The appearance of peaks at 1674 cm^{-1} in both EC-graphene and rGO are attributed to C=C groups. It can be observed clearly that the former peak is sharper than the latter one, which can be inferred that GNS exists stronger C=C groups. There are peaks at 1299 and 1312 cm^{-1} are attributed to stretching vibration of C-O groups and a weak peak for GNS at 1263 cm^{-1} can be ascribed to C-O-C group. The existence of a weak peak at 1510 cm^{-1} is C-C stretching in the aromatic ring, which disclosed the hexagonal carbon structures were detected. However, low intensity of the peak also revealed that C-C groups were quite minor in EC-graphene. FT-IR results confirm the presence of oxygen-containing functional groups in both EC-graphene and rGO. For the further investigation of the evidence of formation, XPS analysis were implemented as shown in Figure 3b. The presence of the XPS C1s binding energy in figure at 284.1 eV in is due to C=C functionalities with sp^2 carbon. The oxygen functional groups such as C-O and COOH at the binding energy of 285.8eV and 288.6 eV can also be observed. The XPS survey spectrum unveiled relative percentage of carbon and oxygen with binding energy at 284 and 533 eV showed that the sample consisted of 89.64% carbon and 10.36% oxygen. From FT-IR and XPS analysis, we can confirm that compared to rGO, EC-graphene exists better C=C groups and fewer oxygen.

Figure 4 shows the surface morphologies of EC-graphene and rGO for comparison. Figure 4a firstly gives the SEM image of electrochemical exfoliation. As we can see, the surface of graphene is quite smooth, flat and clear. The color of the silicon substrate stage at bottom left corner is almost identical to the samples, indicating that high transparency and few-layers of graphene were obtained. On the contrary, reduced GO (rGO), which reduce under 1000°C thermal treatment, was manufactured from chemical exfoliation based on Hummers method exhibits porous block structure, which is quite different from the former, as shown in Figure 4b. The common point of

two samples are the existence of little wrinkles and curling at the border. The reason for this phenomenon is that graphene itself tries to maintain stable state thermodynamically and the oxygen functional groups bounded around the edge. Figure 4c shows SEM image of sediments in the electro-bath. We can observe that even if the samples is the flaked structure, the graphene stacks between layers apparently. The thickness distribution is also inferior to the samples in Figure 4a. This is the reason why we only collect the upper floating sliver substances, due to maintaining the quality of graphene. Figure 4d exhibits TEM image of sample on the Cu-grid. The GNS are nearly transparent and showed uniform thickness distribution with lateral size about 2.85 µm. The HR-TEM image in Figure 4e shows the edge of suspended film always fold back and the ordered lattice are clearly observed. The image demonstrated that the layer of EC-graphene was about 6 layers. In addition, a selected area electron diffraction (SAED) pattern in Figure 4e. The well-defined diffraction spots prove crystalline structure and low defects inside EC-graphene.
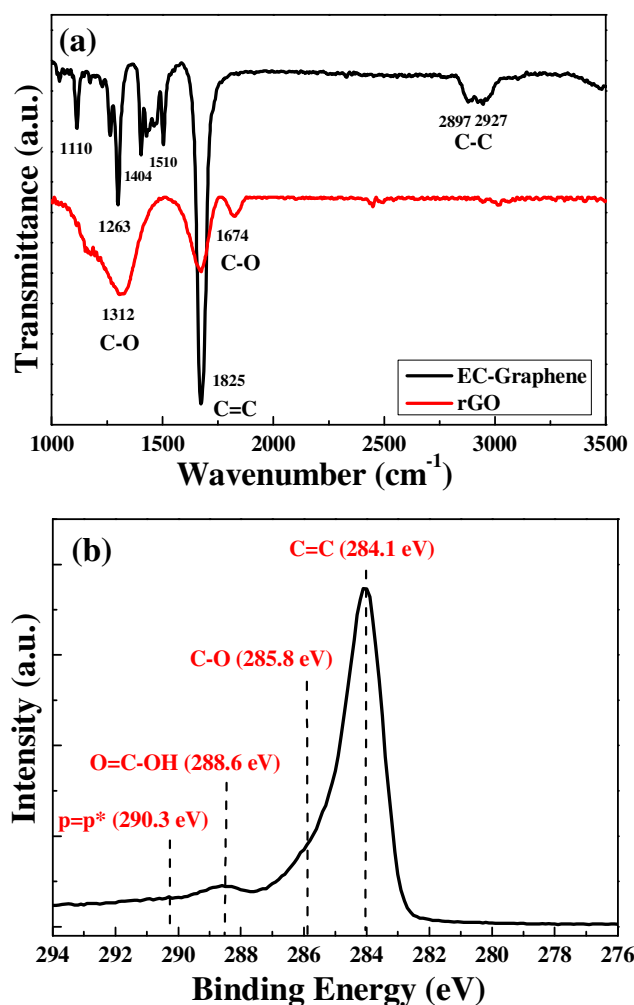

Figure 3. (a) Fourier transform infrared spectra of EC-graphene and rGO; (b) X-ray photoelectron spectrum of EC-graphene.
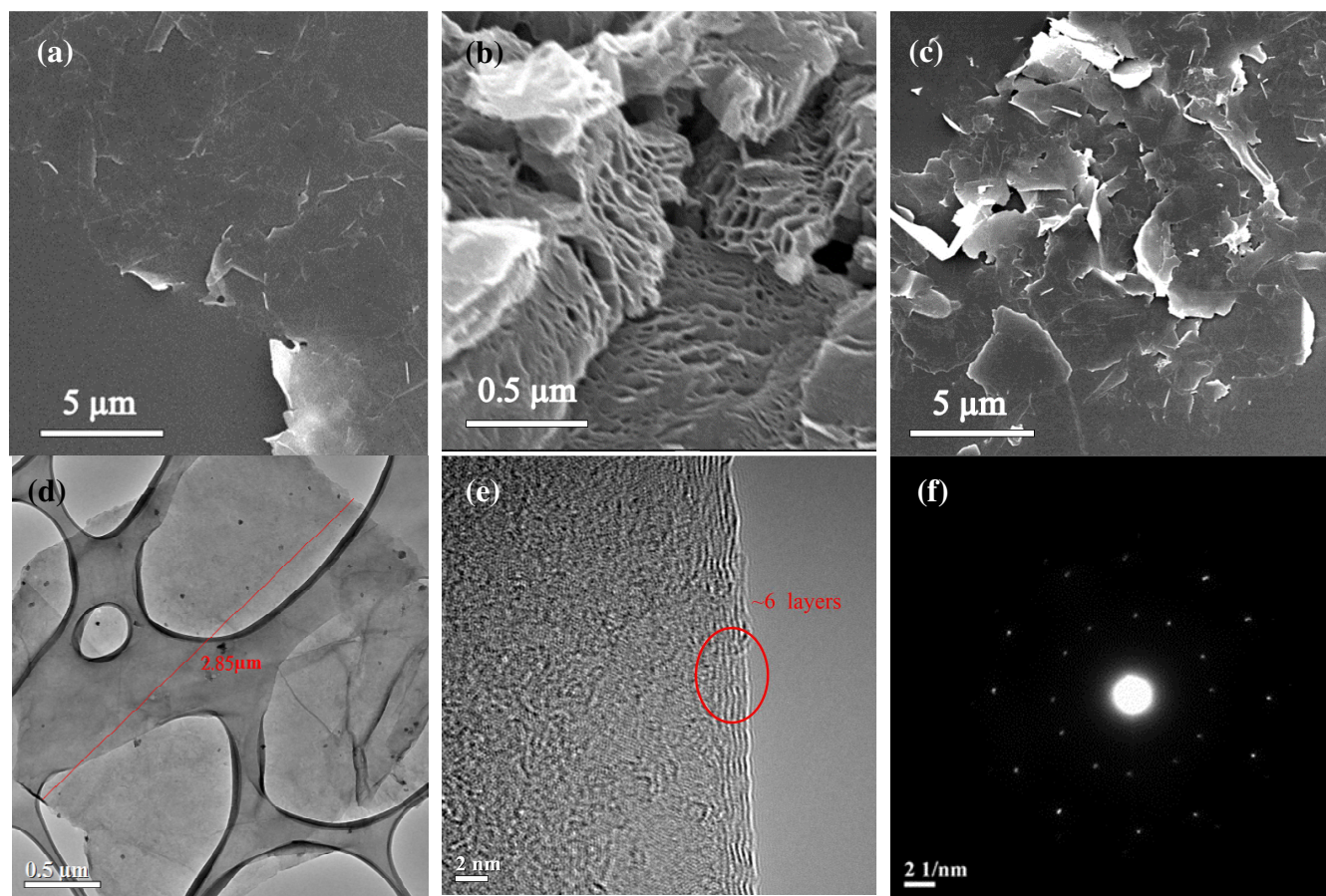
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Figure 4. SEM images of (a) EC-graphene, (b) rGO based on Hummers method, (c) sediments of electrochemical exfoliated-graphene without sonication (d) TEM image of GNS, (e) HR-TEM image of EC-graphene and (f) SAED pattern.
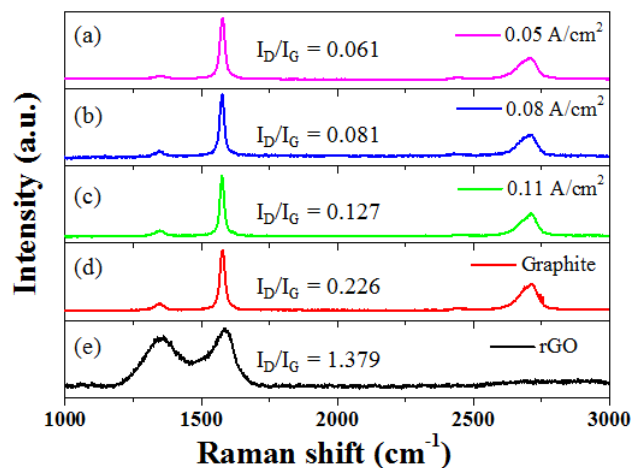

Figure 5. Raman spectra of EC-graphene under different current density: (a) 0.05 A/cm^2; (b) 0.08 A/cm^2; (c) 0.11 A/cm^2; (d) graphite and (e) rGO.

Raman spectroscope is a convenient and non-destructive approach to examine distortion and defects degree of graphite-based materials. As we know, two characteristic peaks generally named by D (~1355 cm^{-1}) and G (~1580 cm^{-1}) bands were observed in graphite-based materials. The G band represents the first order scattering of the E$_{2g}$ photons observed for sp^2 carbon domain, while the D band corresponds to breathing mode or j-point photons of A$_{1g}$ symmetry associated with disorder band of structural defect, amorphous carbon or edge. The intensity ratio of D band to G band (I$_D$/I$_G$) is usually used as a measure of disorder. Figure 5 exhibits Raman spectra (excited by 532 nm laser light) of electrochemical exfoliated-graphene under different current density in (a)-(c). It is evident that with increasing current density, the I$_D$/I$_G$ ratio becomes stronger and stronger, which might be due to destroy and damage of graphitic structure under large current density. The structural defects of GNS, thus, were observed in the Raman spectra. On the contrary, I$_D$/I$_G$ ratio of chemical exfoliated-graphene is

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about 1.38, which is at least 10 times less than that of the former sample, as shown in Figure 5e. From this analysis, we can reasonably assert that electrochemical EC-graphene possess a better quality than that of rGO.
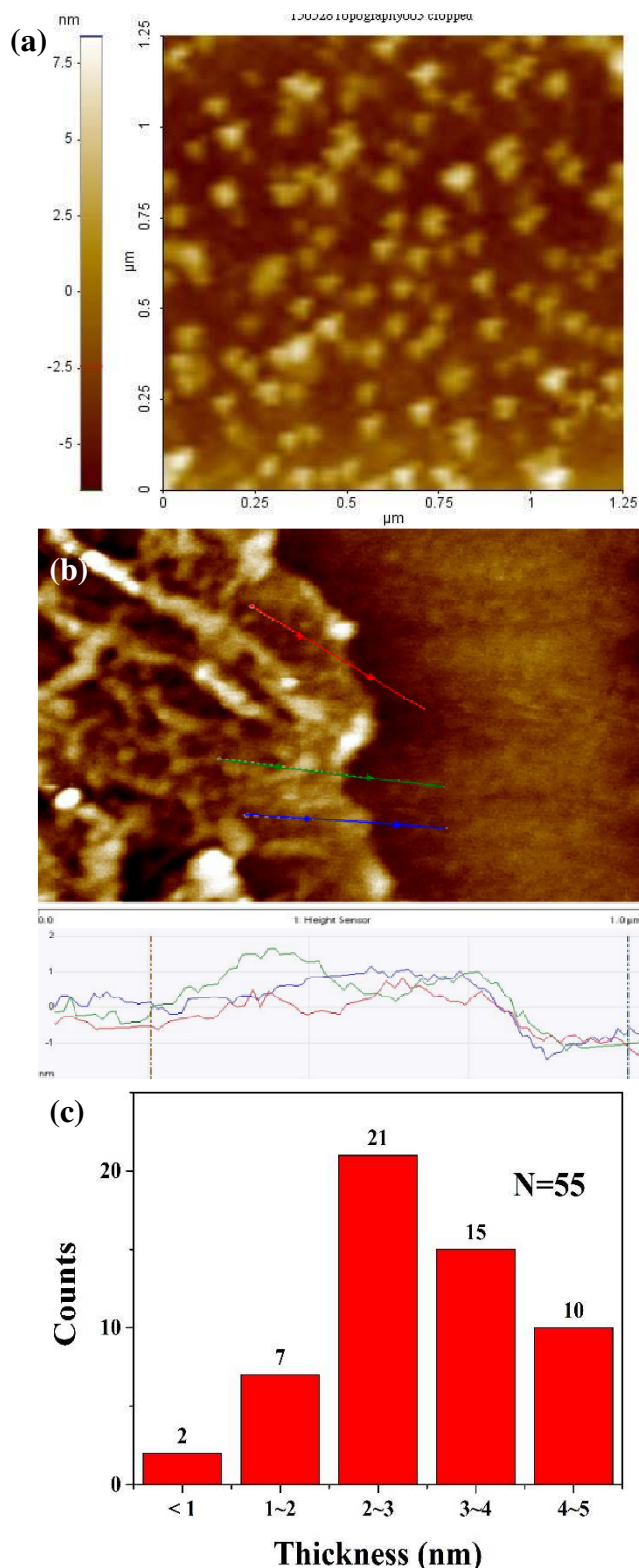
Figure 6 AFM images of (a) EC-graphene drop-cast, (b) line scan and (c) thickness distribution of EC-graphene.

Figure 6a shows typical AFM images for GNS drop-cast on silicon wafer, the flakes with almost identical thickness can be observed. Here, we randomly chose line-scan for the sample as shown in Figure 6b. Apparently, the average thickness of sample is around 2 nm. The statistical thickness distribution for sample exhibits in Figure 6c exhibits that most of the GNS we obtained were 2~3 nm, which is around 6 layers of graphene. The result is in consistent with TEM images shown in Fig. 4e. Through AFM analysis, we firmly believe that through electrochemical method, few layer graphene can obtain easily.

4. Conclusions

In behalf of taking into account the quality and productive cost, the tendency of manufacturing graphene is directly exfoliating the graphite into graphene in the future, for retaining the structural integrity. Electrochemical exfoliation is one of the methods which matched the tendency. Through a series of research, we found that when current density is around 0.11 A/cm^2, the best exfoliated efficiency will occurred then a detailed analysis were executed. SEM and TEM exhibited morphology of electrochemical-exfoliated graphene existed uniform thickness distribution and smooth surface. The AFM analysis demonstrated the thickness of EC-graphene is around 2~3 nm, which indicated around 6 layers of graphene were obtained. This results is in accordance with HR-TEM analysis. In Raman spectra, D/G ratio of EC-graphene is solely 0.061, which is 11 times less than rGO, showed that EC-graphene has barely defects. FT-IR introduced different oxygen functional groups on EC-graphene and rGO. XPS gave further information of EC-graphene with relative percentage of carbon and oxygen on the samples also verify the conclusion of Raman spectra. Through electrochemical exfoliation method, high quality graphene solution is also a considerable number of applications in the future.

Acknowledgments

Notes and references

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