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A symmetrical bi-electrode electrochemical technique for high-efficiency transfer of CVD-grown graphene

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Abstract

Graphene transfer is a critical process in the journey from CVD-grown graphene to device application. The current transfer techniques use a chemical-etching method to oxidize the metal catalyst, which is heavily time-consuming and involves a high material cost. In this study, a highly efficient symmetrical bi-electrode technique has been developed to simultaneously delaminate the CVD-grown graphene from the metal catalyst at both the anode and cathode of the electrolytic cell. Raman spectra, UV-visible transmittance, and four-probe measurements confirm that this transfer process is nondestructive and can produce similar electrical properties to those produced by the conventional metal-etching transfer method. This bi-electrode transfer technique possesses the advantages of high efficiency, recyclable use of metal catalyst, and high electrical conductivity, and it can be potentially applied for industrial applications.

Keywords: graphene, electrochemical, transfer, CVD

 Online supplementary data available from stacks.iop.org/Nano/25/145704/mmedia

(Some figures may appear in colour only in the online journal)

1. Introduction

Graphene has attracted great attention since its first discovery in 2004 [1]. Graphene exhibits various extraordinary properties, such as single atomic thickness [1], high transparency [2], remarkable tensile strength [3], and high intrinsic carrier mobility [4], which have made it a promising material during the past decade. Rapid and extensive scientific studies on graphene physics and chemistry have revealed a great number of possible applications in various fields, from electronics and biomedicine [5, 6] to energy storage (super-capacitors [7], solar cells [8], batteries [9], and fuel cells [10]). So far, various methods have been reported to fabricate graphene, such as micromechanical cleavage [1] (Scotch tape method), chemical exfoliation [11], epitaxial growth of SiC [12], and chemical vapor deposition (CVD) growth on metals [13, 14]. Among these methods, CVD is the leading technique in producing

large-area (30 in) [15], high-quality graphene, which shows immense potential for electrical and photovoltaic application. In the CVD synthesis of graphene, the carbon precursor (such as methane, acetylene, benzene) undergoes a decomposition reaction on catalyst metals. The carbon atoms dissolve and segregate as graphene (on a Ni surface), or adsorb and reassemble into graphene (on a Cu surface) when the environment cools down rapidly.

For further application, the CVD-grown graphene (CVD-graphene) needs to be transferred from the metal substrate onto a target device substrate. It is important to note that most of the quality degradation occurs during the transfer process, due to the tearing and ripping of the graphene sheets. Currently, the widely used transfer processes are based on the complete etching of metal substrates [16, 17]. Polymethylmethacrylate (PMMA) is spin-coated on graphene as a supporting material and then the underlying metal is etched away in an oxidant

solution, such as an iron salt solution or ammonium persulfate, and finally the PMMA is removed in acetone. We denote this process as the conventional metal-etching transfer method. This method not only takes a long time (up to one day or more) to etch away the metal, but it also leads to inevitable damage to the graphene because of the different surface tension of the graphene and the aqueous solution. Recently, Cheng *et al* [18] and Kian Ping Loh *et al* [19] reported an electrochemical delamination to exfoliate graphene from the metallic growth substrates by *in situ* generating H₂ bubbles at the graphene/metal interface. However, the exfoliation only occurred on the cathode and thus the efficiency was relatively low. Besides, no resistance data of the graphene films obtained were shown in their studies.

In this paper, we demonstrate a novel symmetrical bi-electrode method for graphene transfer with much higher efficiency. In addition to the graphene/copper separation occurring at the cathode by continuous H₂ generation, an identical graphene/copper stack is used as the anode, and a second graphene film can be delaminated by the accelerated dissolution of the anodic copper substrate. We examine the quality of the transferred graphene by detailed analysis using Raman spectroscopy, optical microscopy (OM), scanning electron microscopy (SEM) and four-probe measurements. By this method, two nondestructive films can be obtained from a single process in only 20 min.

2. Experiment

2.1. Graphene growth procedures

In a typical experiment, the graphene was grown on a 25 μm thick copper foil (Alfa Aesar, 13382#) by ambient pressure chemical vapor deposition at a temperature of 1000 °C using methane as the carbon source, according to a previously reported method [13]. Before the growth, the copper foil was annealed at 1000 °C for 30 min under a hydrogen flow rate of 200 sccm. Thereafter, the flow rate of H₂ was reduced to 40 sccm and a gas mixture of CH₄ (6 sccm) and Ar (1300 sccm) was introduced into the tube furnace. After 10 min of growth, the system was rapidly cooled to room temperature by maintaining the gas flow rate.

2.2. Electrochemical graphene transfer from a Cu substrate

A Cu substrate covered with as-grown graphene was spin-coated with PMMA (46 mg ml⁻¹ in chlorobenzene) at a rotating speed of 4000 r min⁻¹ for 30 s and cured at room temperature for 1 h. Two PMMA/graphene/Cu stacks, each of size 2 × 1.5 cm², were immersed in (NH₄)₂S₂O₈ (0.1 M) solution at a separation distance of 15 mm; these acted as the anode and cathode, respectively (see figure S1 available at stacks.iop.org/Nano/25/145704/mmedia). A direct current voltage of 2 V was applied, and the delamination process was completed in about 20 min. Thereafter, the two PMMA/graphene films obtained were rinsed several times with deionized (DI) water and then adhered to a quartz substrate. The PMMA was washed off with acetone and the transferred films were finally dried at 100 °C for 1 h in vacuum.

A typical conventional metal-etching transfer method was also adopted to get the transferred graphene onto a quartz substrate, and all the subsequent treatments were kept the same as those in the symmetrical bi-electrode electrochemical transfer process so as to ensure the comparability of different samples.

2.3. Material characterization

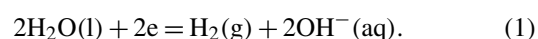
The field-emission scanning electron microscopy (FE-SEM) analysis of graphene on Cu foils was performed on an S-4800 microscope (Hitachi, Japan) at an acceleration voltage of 1.0 kV. The Raman spectra of graphene were collected using a 532 nm laser under ambient conditions with a Raman microscope (Thermo Scientific Raman DXR), and the laser spot size was ~0.6 μm. The electrochemical transfer process was performed on a CHI-660C electrochemical workstation in air at room temperature. The UV-visible (UV-vis) spectrum of the transferred CVD-graphene was obtained with a PerkinElmer Lambda 950 UV-vis spectrometer. The x-ray photoelectron spectroscopy (XPS) characterization of the transferred CVD-graphene was measured with a Thermo Scientific ESCALAB 250Xi x-ray photoelectron spectrometer. The resistance measurement was carried out by using a Loresta-EP MCP-T360 four-probe instrument (Mitsubishi Corporation). Work function measurement was undertaken on a Kelvin probe (Cross-Tech Development Co. Ltd).

3. Result and discussion

3.1. Symmetrical bi-electrode electrochemical transfer processes

The conventional metal-etching transfer method [20] requires long-time copper oxidation in an etching solution: one day or more at room temperature. In contrast to the time-consuming wet-etching process, we accelerated the oxidation and dissolution of the copper substrate by utilizing the PMMA/graphene/Cu stack as the anode of an electrolytic cell (shown in figure 1); this could be demonstrated by the current evolution curve of the reaction time in figure 2. The slow current decline of step 1 in figure 2 revealed that the Cu substrate on the graphene was becoming thinner and thinner. When the Cu foils became discontinuous thin islands, the current dropped suddenly, as step 2 shows. In step 3, the conductive graphene film can serve as the support electrode to realize the subsequent electrochemical etching of the Cu substrate. The current gradually approached zero as the discontinuous Cu islands on the graphene surface were completely etched away, while the conductive graphene film ensured a persistent electrochemical process, so the current cannot actually be zero. Finally, the electrochemical reaction stopped, and the whole process only needed 20 min to realize a complete transfer.

A delaminating reaction occurred simultaneously on the cathode of the electrolytic cell. As the PMMA/graphene/Cu electrode was cathodically polarized at -2 V, a water reduction reaction took place to produce H₂ at the graphene/copper interface. The reaction can be represented as follows:



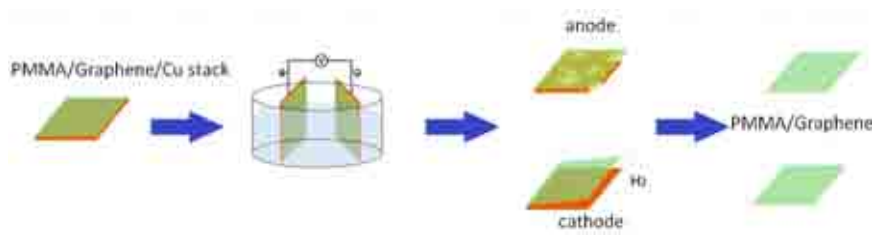


Figure 1. Illustration of the symmetrical bi-electrode electrochemical graphene transfer process from the Cu substrate.

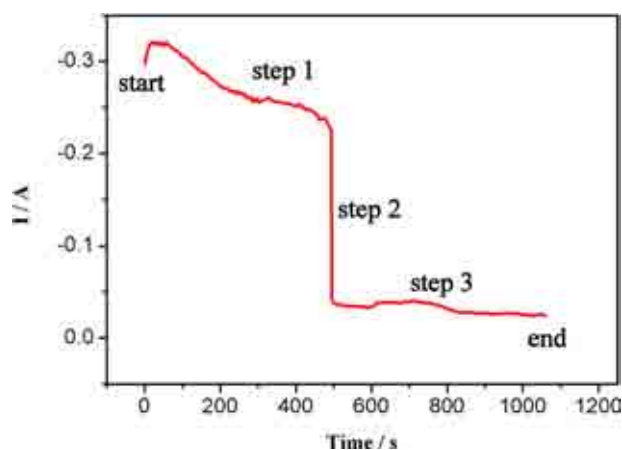


Figure 2. Current evolution curve of the reaction time at electrolytic potential 2 V.

The hydrogen bubbles provide a continuous driving power to separate the graphene from the copper foil at its edges. The electrolytic solution permeated persistently into the interface as the graphene/Cu edges separated.

The selection of a proper electrolyte with appropriate concentration is very critical for the transfer of graphene films. The copper at the anode is oxidized to Cu_2O or CuO at the electron-deficient anode. In order to gradually remove these oxides from the anode without damaging the graphene surface, a weak acidic environment is needed to change the Cu_2O or CuO into soluble Cu^{2+} ions. Therefore we adopted $(\text{NH}_4)_2\text{S}_2\text{O}_8$ aqueous solution as the electrolyte, instead of the alkaline solution used in the individual cathode transfer process by Cheng *et al* [18]. A $\text{pH} < 7$ aqueous system is needed to make sure that the oxidized Cu ions dissolve into the electrolyte, as mentioned before, while the solution acidity should be controlled in an appropriate range. In a strongly acidic system, the gas generation reaction at the cathodic graphene/Cu interface was fierce, which made the H_2 gather together to form big bubbles and break up quickly. This process cannot provide a continuous driving force for delamination. Besides, on the anode side, too high acidity leads to a rapid and uneven oxidation rate of copper ions and creates a mass of damages and defects on the transferred graphene films. A low hydrogen ion concentration can ensure a sequential and minute H_2 generation along the electrode's edge, which can strip the graphene off gradually from the copper foil. As the electrochemical transfer reaction proceeds, the concentration of Cu^{2+} (generated at the anode side) in

the system keeps increasing and the Cu^{2+} ions are reduced by receiving electrons on the cathode. This side reaction creates a competitive effect between Cu^{2+} and H^+ . By taking these factors into account, we determined the optimum concentration of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ to be at 0.1 M.

On the other hand, the PMMA coating of the graphene is important for the whole transfer process both at the cathode and the anode, as it acts as a supporting layer so that the graphene film will not roll or tear during the separating process. The peeled off graphene sheet is easily torn apart due to the bubbling force, and once they are released from the solution the graphene sheets would scroll up immediately without the PMMA coating.

3.2. Characterization of bi-electrode electrochemically transferred graphene

The morphology of as-grown graphene on copper foils was characterized by scanning electron microscopy (SEM), and examples are shown in figures 3(a) and (b). In the images we can see that several black spots exist on the foils (pointed out by red arrows) which are considered to be the nucleating centers of carbon sources, and they prefer to form on the Cu grain boundaries, as figure 3(a) shows. Graphene grows and forms domains around the nucleating centers. These domains will grow larger with prolonged reaction time and finally touch each other to form a continuous and integral graphene layer on the copper foils. Besides, the graphene growth will not be terminated when the domains have formed single-layer graphene. We can clearly observe the color difference around the nucleating centers in figures 3(a) and (b). According to our previous studies, these contrast differences represent the layer thickness of the graphene: the darker domains represent thicker ones. This reveals that carbon atoms keep depositing around the nucleating centers to form graphene islands even though the copper foil substrate is fully covered with mono-layer graphene [21], but these islands cannot join neighboring islands to form a complete second layer of graphene over the copper foil substrate. This graphene domain growth process can be probably explained by the Stranski–Krastanov growth mode [22]. Figures 3(c) and (d) show optical microscopy (OM) images of a few-layer graphene film electrochemically transferred onto a quartz substrate from the anode and the cathode, respectively. We can find a number of white points on the OM images, which refer to the carbon nucleating centers. The remaining regions are covered by single-layer

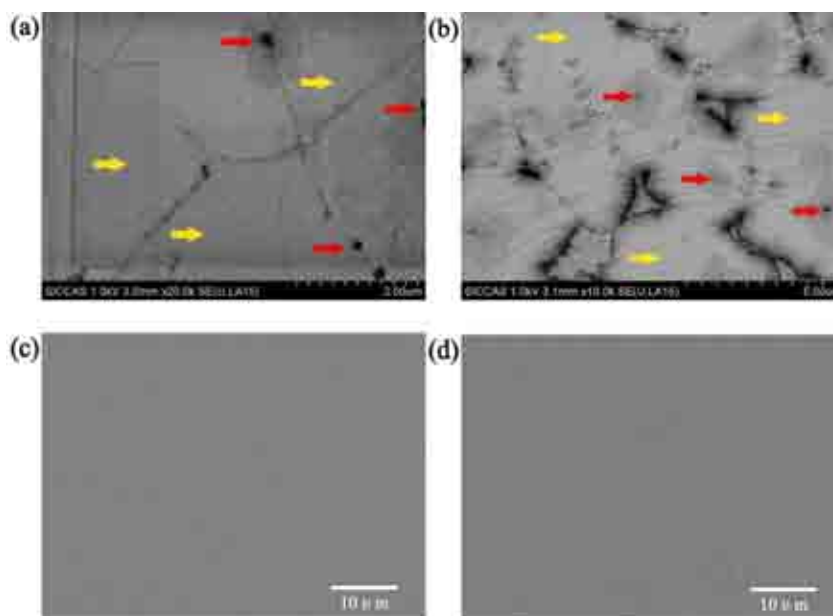


Figure 3. (a) and (b) Scanning electron microscopy (SEM) images of CVD-graphene grown on Cu foils; and typical optical microscopy images of (c) anode transferred graphene and (d) cathode transferred graphene.

or double-layer graphene, and no obvious impurity or defect is found.

Raman spectroscopy can be used to obtain information on the quality, thickness, and doping concentration of graphene [23, 24]. As reported previously, an intense and narrow G band, a weak D band, and a very intense 2D band are typical features of continuous single-layer or few-layer graphene. We performed Raman measurements on the graphene transferred to a quartz substrate by bi-electrode electrochemical transfer methods; the results are shown in figures 4(a) and (b). The D band (at about 1350 cm^{-1}), corresponding to the defect and disorder level in graphene, is negligible in both samples (see figure S2 available at stacks.iop.org/Nano/25/145704/mmedia). The intensity ratios of the D band to the G band (I_D/I_G) are both less than 15% for anode transferred and cathode transferred samples. This result reveals that the gained graphene has high quality and is not degraded by our electrochemical transfer process. The full width at half maximum (FWHM) of the 2D band of graphene on the quartz substrate is in the range $25\text{--}40\text{ cm}^{-1}$, which is comparable to that of micro-cleavage graphene from graphite, also indicating that the process to transfer the graphene is nondestructive.

Besides, the intensity ratio of the 2D band to the G band (I_{2D}/I_G) is in the range 1–2, indicating the one-layer or two-layer nature of our graphene samples. We used the Raman mapping method to make an effective characterization of the graphene surface homogeneity. A $200\text{ }\mu\text{m} \times 100\text{ }\mu\text{m}$ area of transferred graphene was selected, and we performed a continuous line-by-line scanning with a step of $20\text{ }\mu\text{m}$. Then results of these scanning points made up a visual image to describe the information of detected graphene region. Figures 4(c) and (d) show the 2D-band intensity to G-band

intensity (I_{2D}/I_G) ratio distribution trend (represented by color change), which refers to the layer variation of the scanned graphene sample. The statistical histograms presented in figures 4(e) and (f) reveal that both the anode and the cathode electrochemically transferred samples on a quartz substrate achieve a high coverage rate of one-layer to two-layer graphene, which is around 80–90%.

UV–vis spectroscopy measurements were carried out to evaluate the optical transparency of the graphene films on quartz substrates. As shown in figures 5(a) and (b), the UV–vis spectrum displays a high transmittance of the films, at about 95–96%, in the visible wavelength ranging from 450 to 600 nm, which is consistent with the one-layer or two-layer nature of graphene as determined by Raman spectroscopy, and comparable to that of samples transferred by the conventional metal-etching method [20]. This indicates that no significant impurities were introduced during the transfer process, which can also be proved by the XPS characterization (shown in figure S4 available at stacks.iop.org/Nano/25/145704/mmedia) of the anode and cathode graphene samples. The inset image in figure 5 is a photograph of graphene films transferred to a quartz substrate.

3.3. Comparison of electrochemically transferred graphene with conventional metal-etching transferred graphene

A four-point probe measurement was conducted to evaluate the quality of anode transferred, cathode transferred, and conventionally transferred graphene films, as shown in figure 6(a). The sheet resistance of anode transferred and cathode transferred graphene films is $\sim 2000\text{ }\Omega/\square$, and that of conventionally transferred graphene is $\sim 1400\text{ }\Omega/\square$. The result reveals that graphene samples obtained by electrochemical

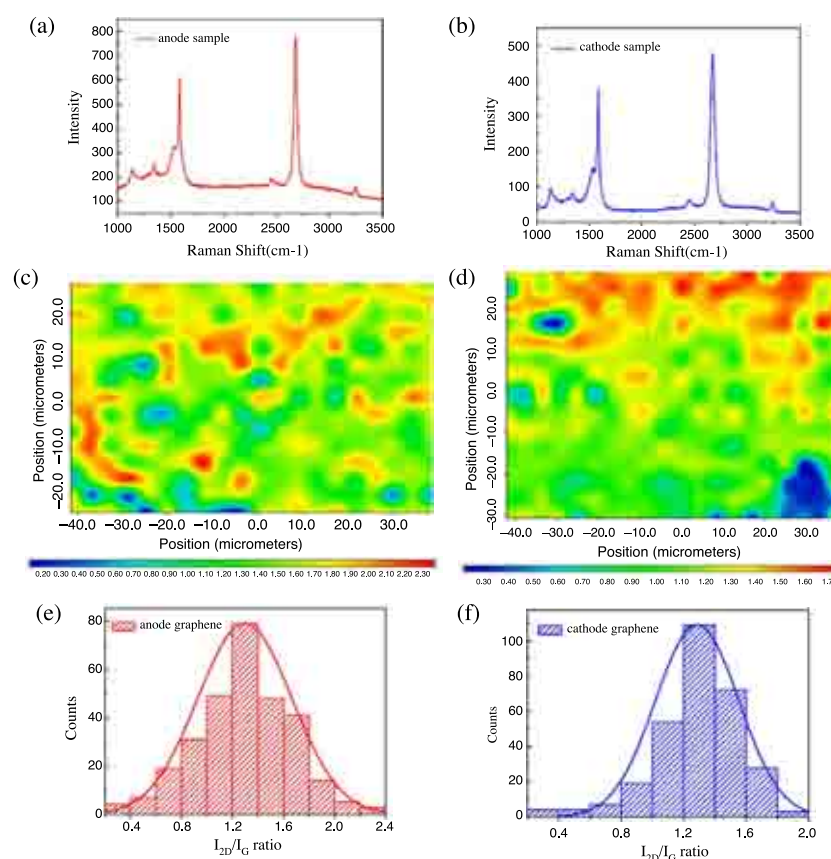


Figure 4. Typical Raman spectra, selected-region 2D to G Raman mapping, and statistical histogram of the 2D/G ratio with Gaussian fits for the electrochemically transferred graphene films on quartz substrates, from the anode ((a), (c), (e)) and from the cathode ((b), (d), (f)).

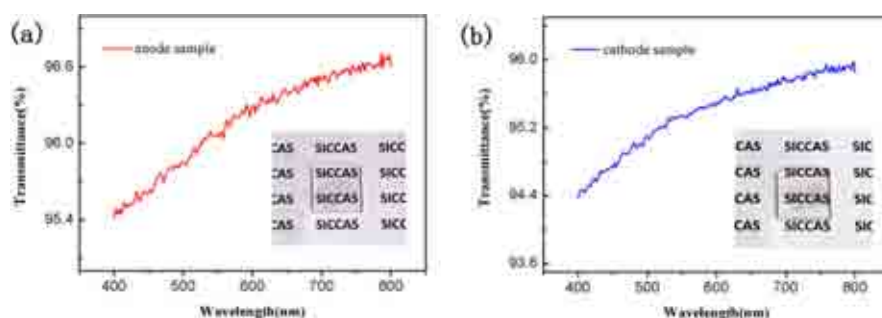


Figure 5. UV-vis spectrum of two-polar electrochemically transferred graphene on a quartz substrate: (a) from the anode and (b) from the cathode. The inset image is a photograph of the graphene films.

methods exhibit similar electrical property to that obtained by the conventional metal-etching method. In addition, the anode sample has smaller resistance variations of resistance than conventionally transferred graphene. Because the conventional metal-etching method leads to a slow and inhomogeneous oxidation and dissolution of the copper foil, the long-time contact between graphene and the aqueous solution causes the obviously broad resistance distribution. In contrast, the electrochemical method can realize an approximate electron exchange rate over the whole PMMA/graphene/Cu stack in about 20 min, and so obtains a narrow resistance distribution and uniform graphene films.

So we can see that the accelerated electrochemical-etching process did not lead to an obvious quality reduction of the

graphene films. The bi-electrode electrochemical technique we developed can noticeably reduce the transferring time, meanwhile maintaining a graphene quality that is comparable to that of films transferred by the conventional metal-etching method.

The Raman 2D-band position of graphene is very sensitive to its doping type and level because of the electron-phonon coupling in graphene [25–27]. Figure 7 shows the 2D-band position of the Raman spectra for the anode transferred, cathode transferred, and conventional metal-etching transferred samples. Graphene films transferred by the conventional metal-etching method show features of p-doping due to the sulfuric doping [26], with the 2D band located at ~ 2690 cm⁻¹, red-shifted compared to the 2665 cm⁻¹ for as-

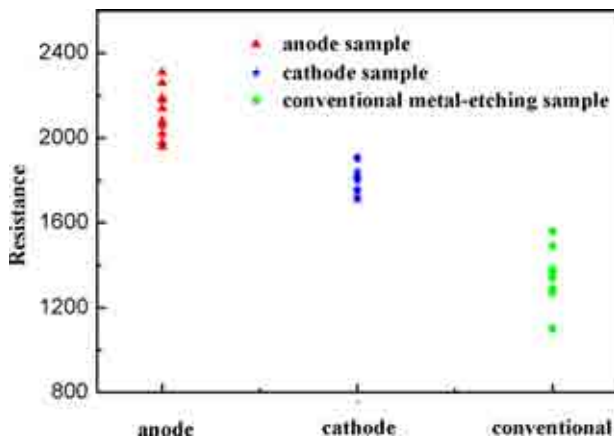


Figure 6. Resistance distribution of three different transferred graphene films; each sample was measured at ten points.

grown graphene on copper [18]. In contrast, in our experiment, the Raman spectra of the anode transferred and cathode transferred graphene films reveal features different from those of conventional metal-etching transferred graphene. The 2D band of anode transferred graphene films upshifts to 2697 cm^{-1} , while the 2D band of cathode transferred graphene films downshifts to 2680 cm^{-1} . These results indicate that the two types of graphene transferred by our electrochemical method show distinct doping features. In detail, the anode transferred graphene films show a 7 cm^{-1} upshift compared with those of graphene films transferred by the conventional metal-etching method, indicating a heavier p-doping level. This is because an etching process with 2 V potential at the positive electrode

may promote the electron loss of the graphene and copper foils. In contrast, the cathode transferred graphene films have a 10 cm^{-1} downshift, which indicates a lighter p-doping level compared to the conventional metal-etching transferred graphene. The reason might be that the graphene/Cu stack at the cathode might gain a mass of electrons on the cathode side of the electrolyte. These features indicate that the electrochemical process can change the doping of graphene in different ways [28]. We made a work function measurement of the anode and cathode by using a Kelvin probe, and the result showed that the cathode sample's work function was 0.05 eV smaller than the anode sample's. This tendency is consistent with result reported by Yu *et al* [29] that the work function of graphene can be adjusted as the gate voltage tunes the Fermi level across the charge neutrality point. Such graphene films with different doping degree can be potentially used for different purposes, as they may have different work functions.

We have also examined the subsequent re-use of copper foils after the electrochemical bubbling transfer process on the cathode side. We removed the copper foils as the transfer process finished and repeated the CVD-graphene growth procedure. The Raman spectra of graphene grown on the original and second-use (i.e., re-used) copper foils show the existence of typical single-layer graphene, and no obvious structural changes were observed in the graphene films, as shown in figure 8 (Raman mapping results are shown in figure S3 available at stacks.iop.org/Nano/25/145704/mmedia). Therefore, the copper foils can be repeatedly used in our method.

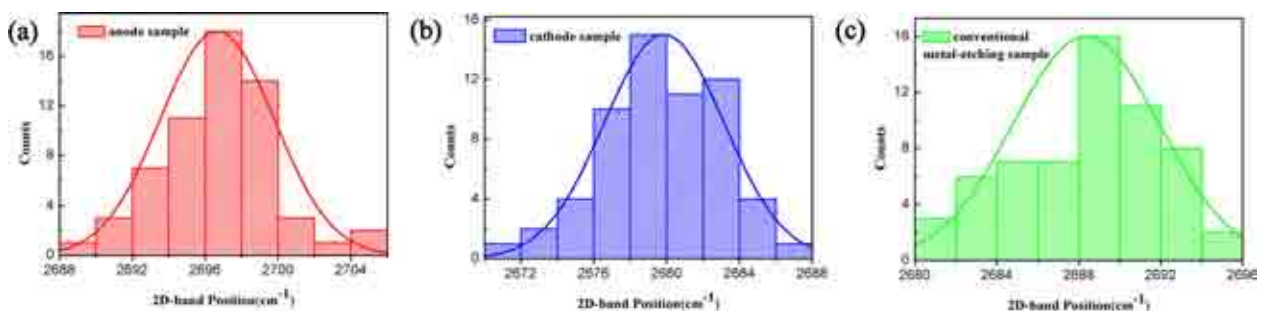


Figure 7. Statistical histogram of the 2D-band positions with Gaussian fits derived from 60 Raman spectra. (a) anode sample, (b) cathode sample, (c) conventional metal-etching sample.

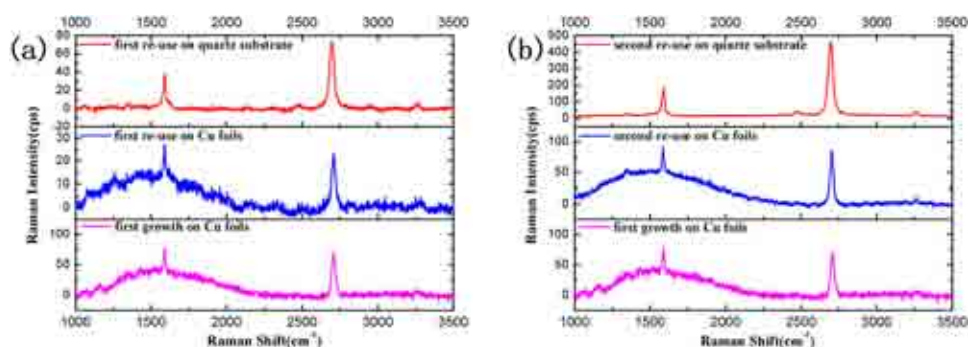


Figure 8. Raman spectrum comparison of CVD-graphene on the original and re-used cathode Cu foil. (a) First use and (b) second use.

4. Conclusion

In conclusion, a promising high-efficiency symmetrical bi-electrode electrochemical method was developed for transferring CVD-grown graphene from Cu foil to other target substrates. Both the H₂ release at the cathode and the accelerated copper etching at the anode were employed to accomplish the delamination of two films simultaneously. With proper selection of the electrolyte and concentration, the electrochemically transferred graphene films demonstrate electrical resistance properties similar to those obtained using the conventional metal-etching transfer method. The doping effects of the transferred graphene were also studied. This bi-electrode transfer process can achieve high-quality and different doping level graphene with few defects and cracks. The graphene films obtained demonstrate similar resistance values to those obtained from conventional metal-etching transfer methods. The electrochemical transfer process can be a low-cost and efficient replacement for traditional chemical etching of metal catalysts, and it has a promising future for large-scale device production.

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