

Suitable alkaline for graphene peeling grown on metallic catalysts using chemical vapor deposition



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ABSTRACT

In chemical vapor deposition, the higher growth temperature roughens the surface of the metal catalyst and a delicate method is necessary for the transfer of graphene from metal catalyst to the desired substrates. In this work, we grow graphene on Pt and Cu foil via ambient pressure chemical vapor deposition (AP-CVD) method and further alkaline water electrolysis was used to peel off graphene from the metallic catalyst. We used different electrolytes i.e., sodium hydroxide (NaOH), potassium hydroxide (KOH), lithium hydroxide (LiOH) and barium hydroxide Ba(OH)₂ for electrolysis, hydrogen bubbles evolved at the Pt cathode (graphene/Pt/PMMA stack) and as a result graphene layer peeled off from the substrate without damage. The peeling time for KOH and LiOH was ~6 min and for NaOH and Ba(OH)₂ it was ~15 min. KOH and LiOH peeled off graphene very efficiently as compared to NaOH and Ba(OH)₂ from the Pt electrode. In case of copper, the peeling time is ~3–5 min. Different characterizations like optical microscopy, Raman spectroscopy, X-ray photoelectron spectroscopy and atomic force microscopy were done to analyze the as grown and transferred graphene samples.

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1. Introduction

Graphene, honeycomb lattice structure of sp²-bonded carbon atoms, harnessed the scientific community from the time of its experimental discovery [1,2], The exfoliated graphene from the highly oriented pyrolytic graphite (HOPG) and its successful transfer to other substrates open the possibility of graphene electronics [1,3] but to synthesize large area of graphene is not possible with exfoliation technique. Since then many techniques have been used to synthesize graphene but the most advantageous technique which is cost effective, consistent in quality of graphene and scalable to large area is chemical vapor deposition (CVD) [4–6]. In CVD, metallic substrates are used as catalysts for graphene growth and later graphene would be transfer to the desired substrate. A variety of catalytic substrates like Cu [4], Ni [5,6], Pt [7], Ir [8], Ru [9] and Au [10] have been used for graphene growth.

For graphene device fabrication, the controlled transfer of graphene from the growth substrate to the desired substrate is

very crucial. The advances in nanofabrication facilitate the structure of device but there is no specific method which provides submicrometer precision during transfer and aligning of structures on the device. The most opted method for transfer is the wet etching technique where the polymer covered graphene catalyst would be etched in suitable etchant. The shortcomings of this method are the damage to the graphene surface, metal residue and etching of expensive metals like Pt. In order to avoid wet etching technique, electrochemical delamination was used by Wang et al. [11] and Gao et al. [7] to peel off graphene from the metallic substrate by utilizing hydrogen bubbles produced during electrolysis. Recently, Wang et al. [12] used delamination technique to peel off graphene-polyamide stack from copper foil using electrolysis of aqueous sodium sulphate (Na₂SO₄) electrolyte [13], they also apply the same method to peel off graphene oxide from the metal substrate and simultaneously reducing the oxygen content in graphene oxide. Frame assisted graphene peeling via the electrolysis of NaOH also showed promising results in minimizing the wrinkles and the holes in the graphene during transfer [14]. Comparative study of potassium sulphate (K₂SO₄) and NaOH electrolytes was done for peeling of PVC/graphene from copper. The effect of electrolytic potentials and electrolytes concentration was observed in the sheet resistance of graphene [15]. A similar approach was used to peel off

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graphene stack from metal catalyst by using $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2 + \text{H}_2\text{O}$ solution [16]. Upon combining $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2 + \text{H}_2\text{O}$ at 80°C a vigorous bubbling reaction took place because of the rapid dissociation of H_2O_2 into H_2O and O_2 (gas) in the presence of NH_4OH . When bubbling starts, graphene stacks were immersed in the solution and the oxygen bubbles seep between graphene stack and the metal and gradually spreads across the whole surface and detach the stack. Moreover, a facile method was also used where the polymer/graphene/metal (Pt, Cu) stack was immersed in a hot bath until the water soak inside the interface between the graphene and the metal and as a result, the polymer supported graphene left the substrate [17].

In our report, we presented the use of different electrolytes that are suitable for peeling of graphene from growing substrates. The electrolysis of alkaline water is one of the simplest way of achieving hydrogen bubbles. We successfully peeled off graphene from metallic catalysts by electrolysis of different alkaline and compare the delamination time of peeling of graphene by different electrolytes.

2. Experiments

2.1. Growth of graphene on Pt and transfer

Graphene was grown on Pt foils in AP-CVD system using CH_4 (99.995% purity, Messer), H_2 (99.999% purity, BOS) and Argon (99.999% purity, Messer) gases. The $50\ \mu\text{m}$ thick 99.995% pure Pt foil of $20 \times 20\ \text{mm}$ dimensions were cleaned with acetone, isopropanol and deionised (DI) water followed by dipping in diluted (1:10) nitric acid for 3 min. The Pt samples were rinse with DI water; blow dried and loaded inside the furnace. The CVD system was evacuated down to $\sim 5 \times 10^{-2}$ mbar pressure and Ar gas was entered at a flow rate of 300 sccm for 10 min to purge the system. H_2 gas was introduced at the rate of 50 sccm before heating. The Ar flow was stopped at 200°C and H_2 flow was increased from 50 to 150 sccm at 800°C and kept fixed until experiment ends. CH_4 was introduced into the system at 1040°C with a flow rate of 1.2 sccm for 3 h. After growth, furnace was opened to quickly cool down the samples. Further the graphene/Pt foils were coated with C9-PMMA electron beam resist for mechanical support during transfer. 1 molar solutions of different alkaline NaOH, KOH, LiOH and $\text{Ba}(\text{OH})_2$ were prepared by adding alkaline salts in DI water. The solution of 0.2 molar $\text{Ba}(\text{OH})_2$ was used to peel off graphene because 1 M solution was so concentrated in $\text{Ba}(\text{OH})_2$ case. The PMMA/graphene/Pt substrate was given the negative potential and another piece of Pt foil was given positive potential. The hydrogen bubbles produced in alkaline tried to attach the negatively biased Pt and peels the graphene/PMMA layer from the Pt [7]. The graphene/PMMA stack was scooped out from alkaline and cleaned few times in DI water and transferred to SiO_2 covered Si substrate. The sample was left overnight in air to dry. After drying, samples were heated at 180°C on a hot plate followed by vacuum drying at 70°C for 3 h. The samples were dipped in acetone to dissolve the PMMA layer, followed by a nitrogen blow dry.

2.2. Growth of graphene on Cu and transfer

Graphene was grown on Cu foils in AP-CVD system using CH_4 (99.995% purity, Messer), H_2 (99.999% purity, BOS) and Argon (99.999% purity, Messer) gases. The $25\ \mu\text{m}$ thick 99.995% pure Cu strips of $100 \times 20\ \text{mm}$ dimensions were cleaned with acetone, isopropanol and deionised (DI) water followed by dipping in acetic acid for 3 min. The Cu strips were rinsed with methanol; blow dried and loaded inside the furnace. The CVD system was evacuated down to $\sim 5 \times 10^{-2}$ mbar pressure and Ar gas was entered at

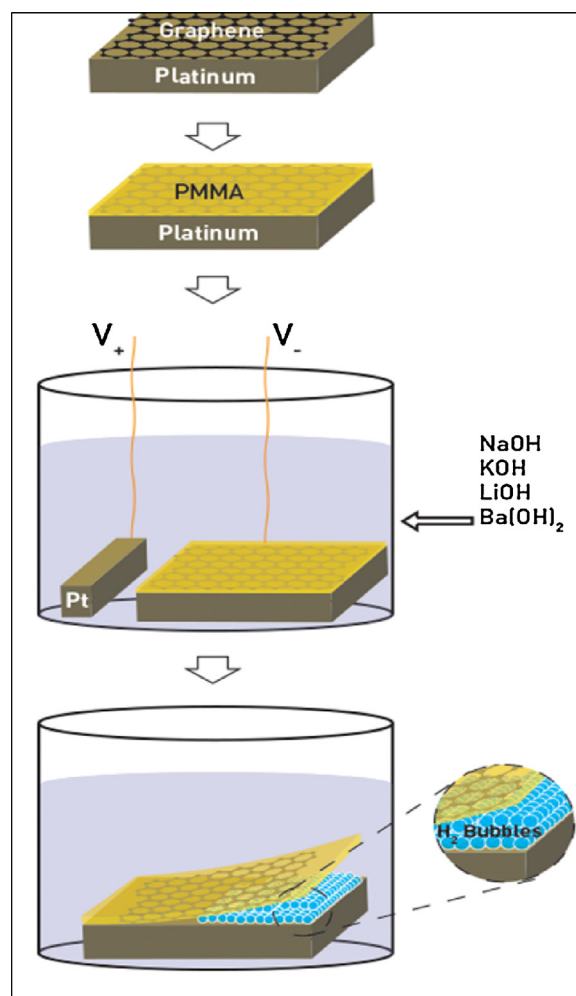


Fig. 1. The detailed schematic of the experimental procedure.

a flow rate of 140 sccm for 10 min to purge the system. H_2 gas was introduced at the rate of 10 sccm before heating and Ar flow was stopped at 100°C . CH_4 was introduced into the system at 1000°C with a flow rate of 15 sccm for 35 min. After growth, furnace was opened to quickly cool down the samples. The Cu strip was cut into $20 \times 20\ \text{mm}$ dimensions for the graphene transfer from Cu to SiO_2/Si substrate and the above mentioned procedure of electrolysis was followed. For graphene transferred to polymer we used a lamination method introduced by Martins et al. [18]. Further the graphene/Cu strips were laminated with PVC sheets and cut into pieces. PVC/graphene/Cu sample was given the negative potential and another piece of Cu foil was given positive potential. The hydrogen bubbles produced in alkaline tried to attach the negatively biased Cu and peels the PVC/graphene layer from the Cu. The PVC/graphene stack was scooped out from alkaline and cleaned few times in DI water followed by a nitrogen blow dry. We also peeled off PVC/graphene stack from Pt using bubbling technique. The schematic of the process is shown in Fig. 1.

Nikon Eclipse LV 100 optical microscope was used for basic information about the graphene samples. Renishaw inVia Reflex microRaman spectrometer with 532 nm laser source is used to measure the Raman spectra at different points for different samples. eZ-AFM from NanoMagnetics Instruments [19] was employed for AFM imaging and elastic modulus measurements. A Thermo Fisher K-alpha electron spectrometer with a monochromatic Al K α X-ray source ($h\nu = 1486.6\ \text{eV}$) was used for the chemical information of elements.

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