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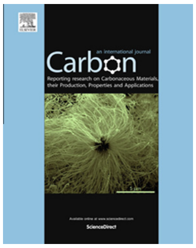

One-step etching, doping, and adhesion-control process for graphene electrodes

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ABSTRACT

Enhancing the electrical conductivity and reliability of graphene electrodes is critical for the practical realization of graphene-based electronics, since these factors influence the electrical performance of devices. To achieve such improvements in graphene electrodes requires additional processes such as doping and surface treatments, which inevitably complicate device fabrication. Here, we introduce a novel, straightforward one-step etching method, in which a catalytic copper substrate is etched in imidazole-containing ammonium persulfate solution, of simultaneously enhancing the electrical and adhesion properties of graphene grown on copper foil by chemical vapor deposition. Applying one-step etching method, the sheet resistance of monolayer graphene with 270 Ω/sq is obtained, while the adhesion of graphene is improved by 20%. Moreover, the electrical conductivity of graphene remained improved after storage for 30 days in ambient conditions without any passivation layers, and the graphene was almost transparent with transmittance of 97.7% at 550 nm. The enhancement of the electrical and adhesion properties of graphene originated from the synergistic adsorption of imidazole and etched Cu ions, which results in p-doping of graphene.

1. Introduction

Since the discovery of graphene, much effort has focused on utilizing its unique electrical, optical, and mechanical properties in practical applications [1–5]. Graphene has shown great potential for the development of high-performance flexible, transparent electronic devices [6,7]. In these devices, graphene electrodes are located at the best stage in the possible application timeline of graphene, and should be marketed by 2015 [8]. Consequently, research has examined the rapid synthesis of large-area, high-quality graphene based on chemical vapor deposition (CVD) [9–11], the development of etching and transfer processes to minimize mechanically and chemically induced damage of graphene [12–14], and post-processing of graphene after transfer to the desired substrate to enhance its electrical performance and environmental stability; i.e., its reliability [15–17]. To accelerate the commercialization of graphene electrodes, a straightforward,

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industry-compatible fabrication process that improves both the electrical performance and reliability of graphene electrodes should be developed.

Various doping methods have been used to enhance the electrical conductivity of graphene electrodes [18–20]. Adsorption-based doping has been the focus of intense research because of its non-destructive nature (the unique hexagonal structure of graphene is maintained after doping) [15,16]. To achieve such doping, graphene is initially transferred to the desired substrate and then doped with dopant in a post-doping step. However, the post-doping process inevitably complicates the device-fabrication, which is not favorable from a practical perspective. Recently, simultaneous transfer and doping technique has been suggested and allows fabrication of graphene electrode simple and less laborious [21,22].

The fabrication of graphene electrodes usually involves the transfer of graphene to desired flexible and transparent substrates, and successful transfer is realized by well-controlled adhesion between graphene and the substrate, which directly influences the mechanical and environmental reliability of the graphene electrodes [17,23,24]. In particular, if the roughness effect is excluded, the adhesion of graphene to a substrate is governed primarily by the surface energy of graphene and the substrate [25]. Although the surface energy of the substrate can be adjusted readily using surface-modification techniques, such as plasma treatment and covalent/non-covalent functionalization, the development of a simple method for varying the surface energy of graphene without interfering with its superb characteristics remains a challenge [26,27].

Here, we present a facile, highly industry-compatible copper (Cu) etching method that simultaneously enhances the electrical conductivity and reliability of CVD-graphene electrodes during the Cu etching process without any post-doping and surface modifications. This approach, in which Cu etching is conducted in imidazole-containing ammonium persulfate solution, allows the synergistic adsorption of imidazole and etched Cu ions to the graphene surface, enhancing the electrical conductivity of the graphene *via* p-type doping. Importantly, the improvement in the electrical properties is achieved without reducing the intrinsic transparency of graphene, and it remained stable after 30 days of storage under ambient conditions. Furthermore, increased adhesion of graphene was clearly observed after the etching process, due to the adsorption of imidazole onto the graphene surface, which further improves the reliability of the graphene electrodes. Along with dry transfer, which will enable the fabrication of large-area graphene-based devices, our method is readily scalable and should simplify the fabrication process.

2. Results and discussion

The graphene samples studied were prepared *via* the following steps: (1) graphene was grown on Cu foil by CVD; (2) then, the CVD-graphene grown on Cu was attached to a carrier film (CF), the graphene on one side was removed, and Cu etching was performed; and (3) the graphene attached to the CF (graphene/CF) was then transferred to the desired substrate *via* a dry-transfer process [7]. The Cu etching was performed with ammonium persulfate (APS) for several reasons. First, metal-free APS leaves almost no particle-like metallic residues on graphene after complete etching of Cu, whereas particle-like metallic residues are frequently seen after etching with iron-based Cu etchants [29]. Second, the mechanical properties of the graphene prepared by Cu etching with APS were similar to those of pristine graphene, whereas weakening of the intrinsic mechanical properties of graphene was observed when iron-based etchants were used [12].

To check the improvement of the electrical conductivity of graphene when using our etching methods, we assessed the changes in the electrical resistance of graphene. Fig. 1a illustrates how the electrical resistance of graphene/CF was measured before the transfer of graphene onto arbitrary substrates. Using this approach, the effect of etching on the electrical resistance of a graphene sheet can be separated from that of transfer-induced mechanical damage. After measuring the resistance of the graphene sheet, the measured resistance was converted into the sheet resistance directly by considering the two-dimensional geometry of a graphene sheet. Fig. 1b shows the effect of the imidazole added to the APS etchant on the sheet resistance of graphene/CF. Graphene/CF prepared by Cu etching in APS solution without adding imidazole (hereafter referred to as “graphene (APS)”) resulted in somewhat higher, more variable sheet resistance of graphene (2890 ± 510 Ω/sq).

However, when imidazole was added to the APS for etching Cu, the sheet resistance of the graphene/CF (hereafter referred to as “graphene/CF (IM–APS)”) was decreased substantially with less deviation (270 ± 10 Ω/sq). With IM–APS etching, continuous reduction in the sheet resistance of graphene (IM–APS) was observed until 5 mM imidazole was added to 0.1 M APS solution; the addition of more than 5 mM imidazole did not further reduce the sheet resistance of graphene (IM–APS). Note that we added sulfuric acid (H_2SO_4) to the IM–APS to ensure stabilization of the etching speed and to minimize the etching-induced damage to graphene possibly caused by an uneven etching speed, although we observed similar enhancement in the electrical conductivity of graphene in the absence of H_2SO_4 [30]. In terms of the stability of the enhanced electrical resistance, we observed a 10% increase in the sheet resistance after 30 days of storage, indicating that the decrease in the sheet resistance of graphene after Cu etching with IM–APS was stable under ambient conditions (Fig. 1c). Although we observed a slight decrease in the transmittance of graphene (IM–APS) compared with graphene (APS) at spectral ranges from 400 to 550 nm, both graphene samples had similar transmittances for given wavelength ranges (Fig. 1d). This indicated that the light absorption by adsorbed imidazole was negligible, and that the electrical properties of graphene were enhanced while maintaining the intrinsic transparency of graphene throughout the etching process. Fig. 1e shows the layer-dependent sheet resistance of graphene transferred to a polyethylene terephthalate (PET) substrate. Interestingly, transfer-induced mechanical damage of the graphene was clearly manifest by the increase in the sheet resistance of monolayer graphene after the transfer of graphene/CF to PET (from 280 to 365 Ω/sq). By stacking layers, a sheet resistance of 88 Ω/sq was reached with four layers of graphene transferred to PET.