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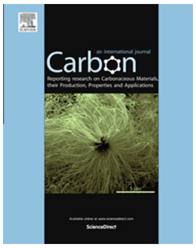

Low cost, rapid synthesis of graphene on Ni: An efficient barrier for corrosion and thermal oxidation

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ABSTRACT

Graphene because of its inert and impermeable nature holds a great promise as a protective coating against corrosion and oxidation. It is envisioned that graphene coated metals will be increasingly used in metal and electronic industries. To date, mainly expensive chemical vapor deposition methods are being employed for its synthesis over large area involving hydrogen at high reaction temperatures. Here we report, a simple and rapid method of Joule heating a Ni foil coated with naphthalene in rotary vacuum to produce graphene without hydrogen gas. The graphene thus grown protects the Ni surface against corrosion and oxidation even at elevated temperatures. This synthetic approach has a great potential for widespread use as it is low cost and adaptable to metal surfaces of complex curvatures.

1. Introduction

Graphene, a one atom thick sp^2 carbon lattice, is a well celebrated material ever since it was experimentally realized, a decade ago [1]. It exhibits a fascinating range of properties such as high mobilities for charge carriers, high transparency in the visible range as well as high degree of flexibility and mechanical strength [2]. Exploiting these properties, devices such as field effect transistors [3,4], sensors [5], photodetectors [6–9], supercapacitors [10] as well as transparent conducting electrodes [11] have been fabricated in recent years.

Graphene being a 2D material, its effective usage depends on the ability to synthesize over extended areas, with assured monodispersity in terms of number of layers. The latter is an important parameter in device fabrication as the nature of graphene varies sensitively with the number of layers [12]. There have been several methods for growing graphene employing top-down, bottom-up or hybrid methods. Graphene obtained from micro-mechanical cleavage of graphite crystals [1–2] does possess high quality but is produced in low yield. To obtain in large quantities, chemical [13,14] and liquid-phase exfoliation [15] methods have been developed. In practice, chemical vapor deposition [16] (CVD) over catalytic Ni and Cu substrates has gained importance. As carbon feedstock, solid [17–18], liquid [19] or gaseous hydrocarbon sources [20] are being used in flowing hydrogen. Natural

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carbon sources [21] as well as amorphous carbon [22,23], have also been used. However, the conventional thermal CVD processes can be energy intensive and time consuming [24]. Recently, there have been reports of modified CVD methods such as radio frequency magnetic inductive heating (RFCVD) which enabled rapid production of high quality graphene over few cm^2 area [25]. Using halogen lamps as heating unit, a rapid thermal CVD (RTCVD) process has been developed for roll to roll graphene production [24]. As hydrogen is a safety concern, particularly at high process temperatures (~1000 °C), some modified methods [26,27] have been reported recently without hydrogen usage. Here, we report a rapid method of graphene synthesis by Joule heating a Ni foil coated with naphthalene in an ordinary vacuum, avoiding gaseous hydrocarbon sources including hydrogen.

Recently, graphene coating has gained importance as a protective barrier for metal surfaces as it is chemically inert and stable [28–32]. It is perhaps the thinnest coating ever possible. There are several efforts in recent literature for decreasing the corrosion rates of metals such as Cu and Ni using graphene, as graphene can be easily grown on these metals [33–37]. Preventing corrosion and oxidation of metal electrodes is a major challenge in device physics [28,38], in spintronic devices for example, involving spin active ferromagnetic metals. Recently, Dlubak et al. reported the novelty of graphene passivation for Ni electrodes in spin devices [39]. Graphene has also been demonstrated as a barrier for thermal oxidation, as it poses a high energy barrier to oxygen diffusion [29] and unlike conventional coating such as of polymers, it does not alter the intrinsic properties of the metal surface underneath [40]. Here we have examined the corrosion and thermal oxidation resistance behavior of graphene on Ni grown by the developed method.

2. Experimental section

Ni foils (4 × 0.8 cm, thickness ~50 μm, Alfa Aesar) were cut to fit into the slots for passing current in a vacuum chamber (~4×10^{-3} Torr) pumped by rotary pump. Typically, 10 μL of 1 mM chloroform solution of naphthalene was drop casted onto the Ni foil and allowed to dry. Currents of 20–25 A were passed at different primary voltage sources of 12–40 V (secondary voltages of 1–2 V) for 15 min. Temperature of the foil was measured using infrared thermometer MIKRON M90-R1. Raman spectra were recorded at different stages in the backscattering geometry using a 532 nm excitation from a diode pumped frequency doubled Nd:YAG solid state laser (model GDLM-5015L, Photop Suwtech, China) and a custom-built Raman spectrometer equipped with a SPEX TRIAX 550 monochromator and a liquid nitrogen cooled CCD detector (Spectrum One with CCD3000 controller, ISA Jobin Yvon). The morphology of the grown graphene on Ni was examined using a field emission SEM (Nova Nano SEM 600, FEI Company). AFM imaging was done on a diInnova SPM (Veeco, USA) using Si_3N_4 probes (model, DNP-20, spring constant 0.1 N/m) in contact mode at a scanning force of 5 nN. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) analysis were performed using a JEOL-3010 instrument operating at 300 kV. Graphene on Ni was transferred onto the holey carbon film of the Cu TEM grid by an electrochemical delamination method followed by lift off PMMA using acetone.

Electrochemical investigations were performed in order to evaluate the corrosion resistance property of graphene on Ni using CH instruments (Model: CH660E, Austin, USA) in three electrode configuration. In a conventional 3-electrode configuration, Ni or graphene coated Ni were employed as working electrodes, Pt as counter electrode and standard Ag/AgCl as reference electrode. The area of the working electrode is 0.64 cm^2 in a 0.1 M NaCl electrolyte at room temperature (25 °C). The open circuit potential (OCP) was monitored continuously till the steady state potential reached. After the OCP measurements, the polarization curves were measured for the samples in 0.1 M NaCl solution. The cathodic and anodic polarization measurements were performed at a scan rate of 10 mV/s. The corrosion potential (E_{corr}) and corrosion current (I_{corr}) were derived through extrapolation from Tafel polarization curve.

The corrosion rate was calculated using equation [41]:

$$CR = (I_{corr} \times K \times EW)/(\rho A)$$

where, K, corrosion rate constant = 3272 mm/year, EW = equivalent weight, 29 g for Ni, ρ, material density = 8.90 g/cm^3 for Ni and the sample area A = 0.8 × 0.8 cm^2.

For thermal oxidation study, Ni and graphene/Ni foils were heated in a heating furnace in O_2 atmosphere. Initially, X-ray diffraction (XRD) (Bruker D8 Discover diffractometer, Cu Kα, (1.5419 Å)) was recorded on bare Ni and graphene/Ni foils. The same foils were heated to 500 °C for 15 min and then again for 30 min under same conditions and XRD were recorded.

3. Results and discussion

A polycrystalline Ni foil (50 μm, Alfa Aesar, 0.7 Ω) was cut into a 4 × 0.8 cm^2 strip to fit into the electrode slot for passing current, (see Section 2). Typically, 10 μL of 1 mM chloroform solution of naphthalene was drop casted onto the Ni foil and allowed to dry (Fig. 1a). After reaching a rotary vacuum of ~4 mTorr, the Ni foil was Joule heated to red hot (~1050 °C as read using a pyrometer) by passing ~25 A of direct current, in a time span of 2 min (Fig. 1b) and after 15 min, the current was turned off and the foil was allowed to cool for a few minutes before taking out of the vacuum chamber. The formation of graphene is seen from the brown coloration in the middle of the foil (Fig. 1c). The nature of graphene obtained varied with the Joule heating temperature. A naphthalene coated foil Joule heated with 18 A current to reach 700 °C in the given instance, did not show any graphitic features in the Raman spectrum. The foil heated to 770 °C (current, 20 A), exhibited the characteristic G (position, 1586 cm^{-1}; FWHM, 21 cm^{-1}) and symmetric 2D (2712 cm^{-1}, 30 cm^{-1}) bands with the I_{2D}/I_G ratio of 2.1 which clearly indicates the formation of single layer graphene [42] (Fig. 1d, red curve). With the foil temperature of 850 °C (current, 22 A), mostly bilayer graphene (I_{2D}/I_G, 1.8) was produced along with a small intensity defect related D band (1350 cm^{-1}) (Fig. 1d, blue curve). At even higher temperature of 1050 °C (current, 25 A), multilayer graphene (I_{2D}/I_G, 0.5) was obtained on the Ni foil with a prominent D