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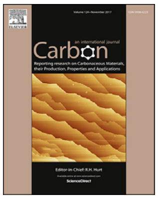

Surface enhanced infrared absorption spectroscopy for graphene functionalization on copper

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ABSTRACT

The monolayer form of CVD graphene is imposing crucial challenges in characterization of the targeted covalent functionalization due to the low amount of grafting moieties on the surface, which in turn hampers drawing conclusions about reactivity-properties relationships. Due to the growing interest in chemically modified graphene new, reliable and non-destructive methods for its characterization are critically required. Herein we demonstrate the use of surface-enhanced infrared absorption spectroscopy for detection of characteristic vibration modes of species being grafted to the material either via radical (Meerwein arylation) or nucleophilic substitution pathway on copper foil. The phenomenon is allowed by the appropriate metal surface morphology and no signal could have been obtained neither on Si/SiO_2 substrate, nor on bare copper. The surface of copper foil exhibit partial corrosion during the reaction which leads to the creation of active substrate for SEIRA. The measurements were performed using reflection-absorption and attenuated total reflection modes with almost identical results, thus making this analytical approach feasible, practical, non-destructive and easy to use for routine characterization of graphene functionalization.

1. Introduction

Controlled on-demand functionalization of 2D materials is a very important milestone on the way seeking potential applications across all fields [1–8]. The strict monolayer and flat character of these materials, which is in large part responsible for their fascinating features [9–11], also represents a critical challenge in development of appropriate characterization methods for clear, fast and unambiguous analysis of the prepared materials. The usual surface-selective techniques used in the field such as X-ray photoelectron spectroscopy [12–14] or Raman scattering [15–17] provide only limited insight into the chemical transformation taking place on the surface and typically cannot distinguish in between covalent grafting and surface contamination, which is almost inevitable due to the polymer-assisted transfer and in-solution chemical functionalization. It is thus of high importance to strive after new opportunities to obtain characteristic structural information about species being introduced to the monolayer in a non-invasive and non-destructive fashion [18].

Recently, surface-enhanced versions of Raman spectroscopy (SERS) [19,20] and mass spectrometry (SELDI) [18] have been demonstrated to provide dramatic signal enhancement of species being covalently attached to graphene. Yet, these techniques rely on laser irradiation of small sample areas, which in some cases may lead to degradation of the sensitive samples. In addition the use of Raman spectroscopy is limited to functional groups which obey Raman selection rules.

A traditional complementary method to the Raman spectroscopy is infrared spectroscopy (IR). In addition IR is an absorption technique minimizing the risk of eventual damage by working with very low energy of electromagnetic radiation and have been used in characterization of graphitic materials in bulk [21–23]. Therefore, the application of IR spectroscopy for characterization of functionalized graphene will be extremely beneficial. However, IR often faces low sensitivity and signal-to-background ratio problems [24] which are even more troublesome in the case of monolayer materials functionalization deposited on a substrate. This obstacle can be actually turned into an advantage if the substrate is made of a material, which is capable to induce surface-enhanced infrared

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absorption (SEIRA) [25]. In general, the SEIRA can be induced by transition metals including Au, Ag or Cu [26–29]. Copper is particularly interesting in the context of graphene functionalization because Cu foils are routinely used for the chemical vapor deposition (CVD) synthesis of graphene. It has been shown recently that various protocols for graphene functionalization yield also roughened metal surface to induce SERS hotspots for detection of the functionalizing species [18]. Similarly, in the case of SEIRA the roughened metal surface can enhance vibrational modes of molecules with a change in dipole moment perpendicular to the surface by a factor of up to 10^4 on Au or Ag films [25–27]. Although there are obvious benefits of the SEIRA, this method was not applied to study functional groups on graphene yet.

Herein we succeed for the first time to obtain SEIRA of functionalized graphene samples using Attenuated Total Reflection (ATR) and Reflection-Absorption IR Spectroscopy (RAIRS) techniques. The method was tested for different functional groups attached on graphene using different mechanisms, where the successful functionalization was previously confirmed by other techniques [18,19,30]. The measured spectra allowed to resolve IR absorption bands characteristic for functional groups of each particular reagent used.

2. Experimental part

2.1. Graphene synthesis and functionalization

Graphene was grown on copper using CVD, as described previously [31,32]. In brief, a polycrystalline copper foil was annealed for 20 min at 1000 °C in hydrogen atmosphere. Graphene was then grown in the flow of 1 standard cubic centimeter per minute (sccm) CH_4 for 45 min and then annealed for another 5 min in H_2 atmosphere. The sample was then cooled to room temperature. For the experiments on Si/SiO_2 substrate the transfer was performed using the nitrocellulose-based technique [33].

The graphene fluorination was performed in a home-made apparatus. The sample on a substrate was placed in a vacuum chamber containing blank Si/SiO_2 wafer, evacuated to $\approx 2 \times 10^{-4}$ mbar, then isolated from the pump and connected to the solid XeF_2 (Aldrich, 99.99%) reservoir. When the pressure reached 8 mbar (about 60 s), the valve to the reservoir was closed and the system was evacuated to remove residual XeF_2 vapors and then slowly ventilated to the ambient atmosphere.

Gaseous nucleophilic exchange: The fluorinated graphene sample (about 1 cm^2 on a substrate) was placed in a vial ($\approx$40 mL). The chamber was then evacuated with a membrane pump and refilled with argon (>99.95%) three times to remove oxygen. The nucleophile was then introduced via a Hamilton syringe through a septum on the bottom of the chamber without direct contact with the fluorinated graphene. The reaction thus proceeds only with the nucleophiles in the gas phase. After exposure for 2 h at r.t., the excess of the reagent was removed using a membrane pump and the samples were further exposed to vacuum (10^{-5} mbar) for 15 min.

Diazonium grafting: Grafting was performed according to the published protocols [6,22,34]. Diazonium salts were diluted in deionized water (>18 MΩ cm^{-1}) or mixture of deionized water and acetonitrile (7:3) to help the solubility to give 5 mM solution. Graphene on a substrate was immersed into the solution for 2 h, then removed and thoroughly washed with water and spectroscopy grade methanol.

Diazonium synthesis: Commercial diazonia were used if available. Otherwise, they were synthesized according to the following protocol: an aromatic amine (75 μmol) was diluted or suspended in 5 mL of the mixture of deionized water/acetonitrile 7:3 and 1.1 eq. of $NaNO_2$ was added. The reaction mixture was then acidified by 1 M HCl to reach pH of ~3–4 when graphene on a substrate was immersed in. Reaction was carried out for 120 min at r.t., then the sample was removed and thoroughly washed with deionized water and methanol (spectroscopy grade).

The successful functionalization of graphene was confirmed by Raman spectroscopy, surface-enhanced Raman spectroscopy, X-ray photoelectron spectroscopy and laser-desorption ionization mass spectrometry and the obtained results are in agreement with the previously reported data [18].

2.2. Infrared spectroscopy

The FTIR spectra of the functionalized graphene samples deposited on the coper foil surface were recorded using ATR (Ge-crystal) and RAIRS techniques on a ThermoScientific Nicolet iN10 FTIR Microscope with a resolution of 4 cm^{-1} and Norton-Beer strong apodization function in the 675–4000 cm^{-1} spectral region, average spot size 150 × 150 μm (RAIRS) or 100 × 100 μm (ATR).

2.3. Light and scanning electron microscopy

Surface of copper substrates with functionalized graphene was visualized by light microscopy (LM; microscope DM6000 M; Leica, Austria) and scanning electron microscopy (SEM; microscope Quanta 200 FEG; FEI, Czech Republic). In the light microscope, the samples were observed “as received” using reflected light (episcopic illumination, LM/EPI). In the scanning electron microscope, the samples were fixed with double adhesive carbon tape on a conductive support and observed at accelerating voltage 30 kV using secondary electron imaging (SEM/SE).

3. Results and discussion

CVD-grown graphene is typically grown on copper and then transferred onto silicon wafer with silicon dioxide layers (Si/SiO_2) which offer superb flatness, good optical contrast and stronger Raman signal than on the original copper foil due to interference and reflection of light from the substrate. However, the transfer procedure introduces contamination to the monolayer from etchant or polymer residuals and brings another variable into the discussion of on-surface covalent chemistry as it has been shown that reactivity of graphene on substrates differs to large extent [30]. Moreover, the Si/SiO_2 wafer has its own spectroscopic features which are often overlapping with or even completely jeopardizing all the signal of the grafted species. We have therefore exploited the currently published methodology for covalent functionalization and characterization of CVD graphene [5,18,19,22,35–37] (see Fig.1) and investigated the potential of infrared spectroscopy to determine the characteristic vibrations of the grafted species. The strict monolayer character of the material is naturally imposing critical challenges on the sensitivity and thus two techniques inherently designed for 2D samples have been used: Attenuated Total Reflection (ATR) and Reflection-Absorption IR Spectroscopy (RAIRS).

Graphene has been grown, functionalized and characterized on copper as described earlier [18] and in the Experimental part. Reaction with diazonia is among the most frequently used functionalization procedures and we have thus taken the 4-nitrophenyldiazonium as benchmark grafting agent for IR investigations, because the strongly electron-withdrawing character of the nitro group prevents cascade azo-coupling reactions leading to polymeric species [38]. Indeed, when graphene on copper was reacted in aqueous diazonium solution, washed and dried,