Letter to the editor

Vibrational fingerprints of residual polymer on transferred CVD-graphene

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The use of vibrational sum-frequency spectroscopy (VSFS) to study transferred graphene, produced by chemical vapour deposition, is presented. The VSF spectrum shows a clear C–H stretching mode at ~2924 cm^{-1}, which is attributed to residue of the polymer used for the transfer. This makes VSFS a powerful tool to identify adsorbates and contaminants affecting the properties of graphene.

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Due to its extraordinary physical, electronic and chemical properties, graphene has the potential to find use in many applications including coatings, electronics, and sensors to name a few [1]. In particular, large-area uniform polycrystalline graphene films grown by chemical vapour deposition (CVD) show promise for many applications [2]. However, the CVD process requires transfer from the copper support onto desirable substrates [3]. The transfer is usually done using polymers such as poly (methyl methacrylate) (PMMA) which need to be removed completely after the transfer to not affect the properties of graphene [3]. It is hence of paramount importance to be able to identify any polymer residues on CVD graphene.

Vibrational spectroscopy techniques are attractive for the characterization of graphene as they are fast, non-destructive and easily implemented. Raman spectroscopy is the most common technique for characterising graphene [4]. However, Raman spectroscopy is only sensitive to defects through the D peak [5], which is not activated by molecules physisorbed on its surface. Direct identification through the typical C–H vibrations of polymers is challenging because of the low Raman intensity of these modes [6]. Reflection-Absorption Infrared Spectroscopy (RAIRS), routinely performed on monolayers and thin films deposited on metallic substrates, has a relatively low sensitivity. Vibrational Sum-Frequency Spectroscopy (VSFS) is a technique in which two photons, one IR and one visible (VIS), are combined at a surface or interface to generate a photon at the sum-frequency of the two input frequencies if the IR frequency is resonant with vibrational modes of molecules at the interface [7]. [8] It is only allowed in non-centrosymmetric media, *i.e.* VSFS is surface or interface specific [8], [9] and has been shown to be an invaluable tool for the study of surfaces and interfaces [9].

We here report the characterization of commercial CVD graphene transferred onto gold using Raman, RAIR and VSF spectroscopy. Previous studies aimed at identifying the polymer residue

showed contrasting results: an earlier study employing VSFS attributed the residues to polyethylene-like impurities, not to PMMA [10]. However, recent work using secondary ion mass spectrometry (SIMS) and employing deuterated PMMA identified and located trace amounts of PMMA trapped on or below the transferred graphene film [11]. Such contrasting results warrant further investigation, and we show here that we can unambiguously (using the non-destructive and fast spectroscopic methods of RAIRS and VSFS) identify the polymer residues to be PMMA, in agreement with the recent study by Willson and co-workers [11].

Commercially available CVD graphene (purchased from 2-DTech Ltd) was transferred onto home-grown gold-coated silicon wafers (IDB Technologies Ltd) using PMMA in anisole (950 PMMA Series Resists, MicroChem Ltd). The same PMMA solution was spin-coated onto cleaned gold-coated silicon substrates. The samples were subsequently annealed at 220 °C for 1 hour. The film thickness of the PMMA sample was measured by using a Dektak stylus (Bruker) profiler (more details on sample preparation the SI). A broadband Mai-Tai Ti:Sapphire laser (Spectra-Physics) capable of producing ~120 fs with a centre wavelength of 803 nm was used as a seed laser for a Ti:Sapphire Legend Elite F-HE (Coherent) amplifier; its ~120 fs output pulses at 803 nm (repetition rate 1 kHz) were used as the visible (VIS) beam for the VSFS setup, and also pumped an OPerA Solo Optical Parametric Amplifier (OPA, Coherent) to produce the tuneable infrared (IR) beam. The bandwidths/average power of the VIS and IR beams were ~12 cm^{-1}/5 mW and ~200 cm^{-1}/9 mW, respectively. The SF beam was spatially and spectrally filtered and directed into a spectrograph (Shamrock 750, Andor Technology) combined with an intensified charge-couple device camera (iStar ICCD DH 374, Andor Technology), shown in more detail in Fig. S1 in the SI. Non-resonant background suppression was achieved by delaying the VIS pulse with respect to the IR beam by typically 1ps. This setup is generally applicable to all surfaces and interfaces which are sufficiently flat and reflective, and

hence ideally suited to the study of 2D-materials on metal substrates.

Fig. S2 in the SI shows the Raman spectrum of CVD graphene transferred onto gold. No D peak is visible, and the shape of the 2D peak confirms that the sample is graphene [4]. No peaks around 3000 cm^{-1}, typical of C–H vibrations, are visible in the Raman spectrum.

Fig. 1 (top panel) shows the RAIR spectrum of CVD graphene transferred onto gold. In this spectrum, an antisymmetric stretch ν_{as} due to a methoxy group, (O)CH$_3$, is observed at 2996 cm^{-1}, a symmetric stretch ν_s at 2927 cm^{-1}, and an aliphatic C–H stretch is observed at 2852 cm^{-1}. Comparing this spectrum to that of bare gold (Fig. 1, top panel) indicates the contamination is *not* coming from the gold substrate, but instead from PMMA. Comparison of the RAIR spectrum of CVD graphene with that of spin-coated PMMA (Fig. 1, bottom) shows a shift of the methoxy signatures by a few tens of cm^{-1}, most likely because of a different structural arrangement of the on-graphene compared to the spin-coated samples. The graphene was grown on copper and transferred onto gold using a graphene CVD growth procedure similar to those used elsewhere in the literature [2], [12] and transferred using a wet chemical approach utilising a PMMA support layer comparable to procedures used by others [13].

Fig. 2 shows the VSF spectrum of CVD graphene transferred onto gold (top panel). The VIS beam was delayed with respect to the IR beam by 1 ps to suppress non-resonant signals from the gold substrate, and the polarisation of the three beams (SF, VIS, IR) was *ppp*. A C–H stretch at ~2924 cm^{-1} was recorded, which was detected in all samples and is entirely reproducible (SI, Fig. S4). For comparison, the VSF spectrum of pure spin-coated PMMA (Fig. 2, bottom panel) shows a peak at ~2954 cm^{-1} which corresponds to a stretching mode of the methoxy group, and the position of this peak is consistent with literature values [14]. By comparing the spectra in Fig. 2, we attribute the peak observed in the VSF spectrum of transferred CVD graphene to the antisymmetric stretch (O)CH$_3$(ν_{as}) of PMMA. The possibility of C–H stretches from hydrogen directly bound to e.g. defect sites of the graphene lattice can be ruled out, as these appear between 2550 cm^{-1} and 2750 cm^{-1} [15].

However, the peak is red-shifted by ~30 cm^{-1} compared to the pure PMMA peak, the same trend as observed in the RAIRS data shown in Fig. 1. Since the PMMA is physisorbed onto the surface of the graphene [9], the shift in frequency between the transferred CVD graphene as compared to PMMA for both the RAIRS and VSFS measurements is likely due to intermolecular interactions between the graphene and residual PMMA. Furthermore, the VSF spectra of CVD graphene recorded with a polarisation combination of *ssp* (SF, VIS, IR) show no C–H stretches, despite the bare PMMA polymer showing a C–H stretch at ~2956 cm^{-1}, see Fig. S4 in the SI. This suggests that the residual (O)CH$_3$ of PMMA left on the surface of graphene is preferentially orientated parallel to the surface normal, whereas in the PMMA film, the (O)CH$_3$ groups are mainly orientated perpendicular to the surface normal.
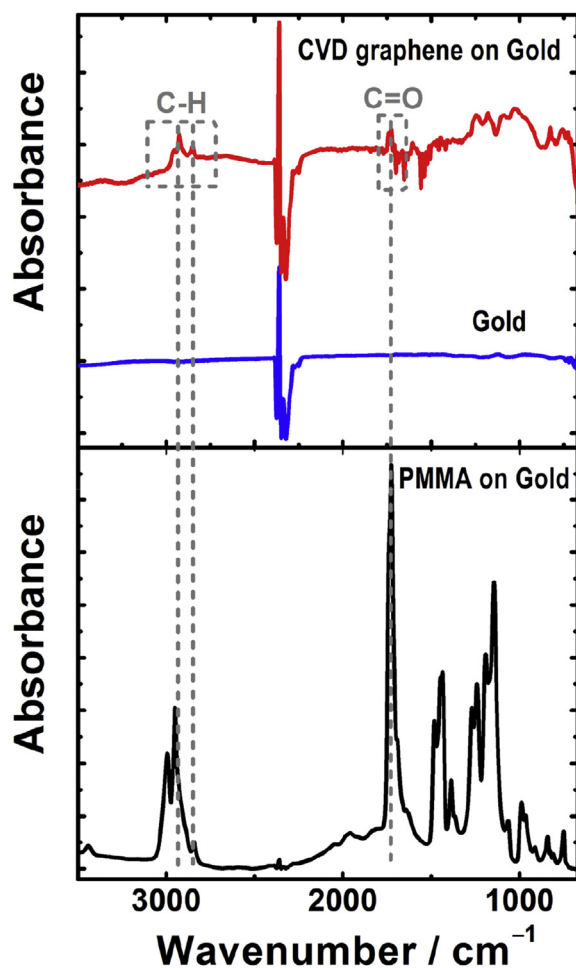

Fig. 1. RAIR spectra of CVD graphene transferred onto gold (red line, top panel), bare gold substrate (blue line, top panel), and PMMA on gold (bottom panel). (A colour version of this figure can be viewed online.)
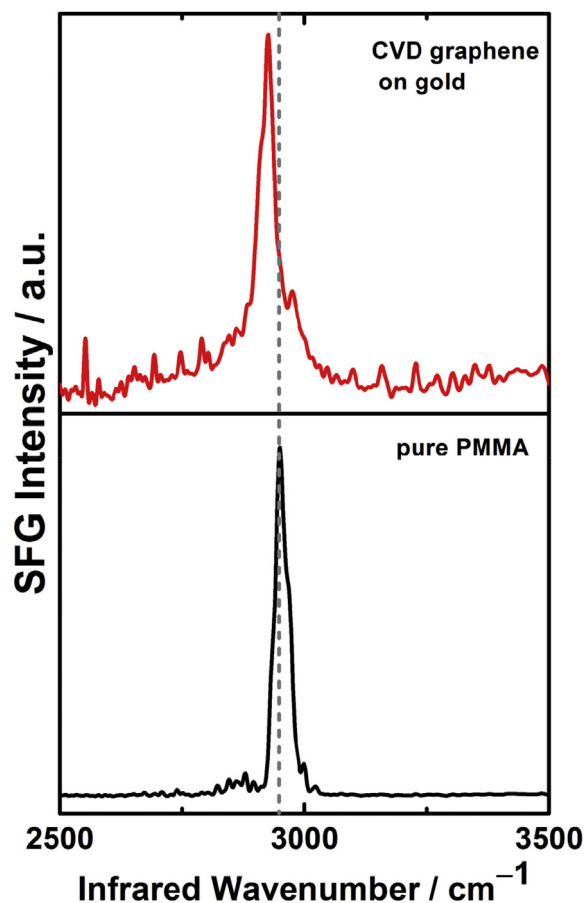

Fig. 2. VSF spectra taken using a polarisation combination of *ppp* of (top) CVD graphene transferred onto gold and (bottom) pure PMMA used for graphene transfer. (A colour version of this figure can be viewed online.)

Our results are in contrast to a recent VSFS study by Su et al. [10], which attributed the contamination from the transfer process to long alkane or polyethylene-like impurities in the polymer used for transfer, but are in agreement with a study by Willson and co-workers who employed secondary-ion mass spectrometry to detect PMMA residue on transferred graphene [11]. The only difference between our transfer process and the transfer process mentioned by Su et al. is that isopropyl alcohol, not chloroform, was used after acetone in our cleaning procedure. We note that chloroform may dissolve PE-like residues from plastic bottles unless it is kept in glass bottles, and may lead to the introduction of impurities. Therefore, more work is required to further clarify the true origin of contaminations in transferred CVD graphene. This is of great technological relevance as polymer residues are well known to affect the performance of graphene and heterostructure-based devices [16].

In order to establish whether or not the residual PMMA was physisorbed or chemisorbed onto the graphene, we looked specifically at the full-width at half-maximum of the 2D peak, FWHM(2D), which is ~40 cm^{-1}, see SI Fig. S2, *i.e.* close to the FWHM(2D) of CVD graphene transferred on gold (~30 cm^{-1}). This small difference can be attributed to a slightly increased strain on the graphene sheet, possibly caused by the roughness of the gold substrate. The small FWHM(2D) and lack of D peak indicate that PMMA is physisorbed. While weaker interaction forces are responsible for physisorption as compared to chemisorption, the PMMA nonetheless is difficult to remove thermally even at 600 °C under ultra-high vacuum conditions [11].

In conclusion, different yet complementary vibrational spectroscopic techniques have been used to investigate the origin of possible contamination on high quality transferred CVD graphene on gold. Raman spectroscopy is not sensitive enough to identify any polymer-based contamination, but both RAIRS and VSFS have successfully identified PMMA residues on transferred CVD graphene samples. In contrast to RAIRS, however, VSFS is selective to interfaces, yields a superior signal-to-noise ratio, and can provide information about the orientation of molecular groups at the surface. In addition, as an optical method, it is non-destructive, quantitative, and can be employed without the need for high-vacuum equipment; this makes VSFS a powerful tool to identify contaminants on graphene and other 2D-materials, and to characterise non-covalent and covalent functionalised graphene.

Acknowledgments

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.carbon.2017.03.008.

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