Extended characterization methods for covalent functionalization of graphene on copper

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ABSTRACT

Graphene is a material of great potential in a broad range of applications, for each of which specific tuning of the material's properties is required. This can be achieved, for example, by covalent functionalization. We have exploited two protocols for surface grafting, either by diazonium salts or by nucleophilic exchange, to perform graphene covalent modification directly on a copper substrate, which is routinely used for the synthesis of the material, and investigated the difference in reactivity compared with other substrates. The successful functionalization was confirmed by Raman and surface-enhanced Raman spectroscopy, mass spectrometry, X-ray photoelectron spectroscopy and scanning electron microscopy with energy-dispersive X-ray spectroscopy. In addition, we have found that the copper substrate can serve as a plasmonic surface enhancing the Raman spectra. Furthermore, the covalent grafting was shown to tolerate the transfer process, thus allowing *ex post* transfer from copper to other substrates. This protocol avoids wet processing and enables an all-gas-phase transformation of functionalized graphene, which eliminates the main sources of contamination.

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1. Introduction

In the last decade, graphene has been identified as a unique material with remarkable properties [1,2]. Research groups around the globe have engaged themselves in the development of practical applications of graphene, one of which is sensor fabrication [3–7]. On the way to achieve this goal, two critical challenges arise: first, specific features for recognition and signalling have to be implemented in the material and second, accurate and unambiguous analysis of the material must be available to provide solid ground for drawing structure–functionality relationships.

Functionalization of graphene by covalent grafting represents a beneficial approach as it can simultaneously deliver signalling [5], due to the graphene bandgap modulation and doping, as well as recognition via complementarity of intermolecular interactions [8–10]. High-quality large-area monolayer graphene is prepared by the chemical vapour deposition (CVD) method [11–13] on copper foil and then typically transferred onto another substrate (e.g. Si/SiO₂ wafers) by copper etching/polymer-assisted techniques [14] to perform the functionalization and characterization. However, this procedure is the main source of surface contamination caused by etchant, polymer and reactant residuals and solvent impurities [14–16]. The contaminants are typically local and they thus prevent homogeneous functionalization of the surface or, when in high amounts, contaminants can even completely prevent the reaction at graphene. Therefore, performing the functionalization reactions directly on copper would be highly desirable as it allows bypassing the etching and polymer-assisted transfer and performing the whole synthesis and functionalization sequence in the gas phase. In this way, wet processing is avoided and the fabrication can be implemented into a continuous line processing. Nevertheless, so far most of the reactions of CVD-grown graphene were performed on Si/SiO₂ substrates [17–32] as graphene on this support can be easily identified optically and/or by Raman spectroscopy. It has been shown that the substrate plays a significant role in covalent

functionalization as it has an effect on the reactivity of the graphene monolayer [28,33–35], therefore to achieve successful functionalization for a given substrate specific reaction conditions must be found.

The development of the functionalization protocols on substrates different from Si/SiO₂ is complicated because characterization methods for graphene or functionalized graphene are limited in number, sensitivity and experimental conditions. Therefore, there is an urgent need for extended characterization methods for on-surface chemical transformations. Among others, surface-enhanced Raman spectroscopy (SERS) [30,36–39] is particularly promising as it reveals the characteristic vibrational bands of the grafted moieties. In this case, performing the functionalization directly on copper can be again of benefit because copper has been reported as a SERS-active substrate [40] that allows the measurement of enhanced spectra without additional metal film deposition, which in turn makes this technique non-destructive.

We have performed functionalization of CVD graphene directly on the copper substrate used for the graphene synthesis and compared it with functionalization of graphene on a Si/SiO₂ wafer. To achieve graphene functionalization we exploited the protocols using either diazonium salts (Meerwein arylation) [24,29,31,41–43] or nucleophilic substitution on fluorinated graphene [19,21,30,44,45]. Raman spectroscopy is routinely used to investigate graphene functionalization due to the emergence of the D mode attributed to creation of sp^3 'defects' in the 2-D sp^2 carbon lattice [46–48]. However, this feature is not indicative of the actual chemical nature of the functionalization product. In this vein, we have employed SERS [30,36–39], mass spectrometry (MS) [33,49,50], X-ray photoelectron spectroscopy (XPS) [51] and scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDX) [52,53] to study graphene functionalization directly on the copper substrate.

2. Results

Single-layer graphene was synthesized using the CVD method on copper foil according to the standard procedure [54]. This material was either directly subjected to chemical modification, or, for comparison, transferred onto a silicon wafer (Si/SiO₂, 300 nm oxide layer) using the polymer-assisted method with nitrocellulose [14] and then reacted (Fig. 1). For covalent chemical functionalization, we have selected two complementary approaches: direct Meerwein arylation with diazonium salts (method D) [29,31,41–43] or primary activation by fluorination followed by a nucleophilic exchange of fluorine atoms (method S) [21,30,45]. In brief, diazonium

salts were employed as approx. 5 mM solutions in deionized water (>18 MΩ cm^{-1}) and the solution was prepared either by dilution of commercial diazonia or by diazotization of aromatic amines by sodium nitrite in the presence of an acid (see SI for details). The fluorination was performed using XeF₂ in the gas phase as reported earlier [30,55]. The subsequent nucleophilic exchange by S-, N- and O-nucleophiles was performed either in the gas phase for volatile reagents or in solution. To show the general applicability of graphene functionalization on copper, we have performed a series of substitutions by altering the nucleophile for fluorine exchange using thioacetic acid, benzylthiol, octadecylthiol (S-nucleophiles), propylamine, 1-pyrenemethylamine (N-nucleophiles) and sodium ethoxide (O-nucleophile) or by employing various diazonium salts (4-nitrobenzenediazonium or 4-sulfonylbenzenediazonium). The corresponding experimental conditions are given in the SI.

As a benchmark reaction, we have taken the previously studied system of single-layer CVD-grown graphene, which after fluorination was treated by thiophenol in the gas phase to undergo nucleophilic substitution of fluorine atoms by sulfur [30]. In this vein, we have performed the reaction sequence, *i.e.* fluorination and substitution by thiophenol (g), in parallel on both substrates and investigated them by Raman spectroscopy (Fig. 2). Pristine graphene on Cu measured with 633 nm excitation laser shows the characteristic G and 2D bands at 1586 and 2658 cm^{-1}, respectively. Fluorination leads to the appearance of the D mode at 1343 cm^{-1}, which is accompanied by a dramatic decrease in the 2D mode intensity and shift of the G band to 1596 cm^{-1}. After the reaction with thiophenol in the gas phase, the 2D/D intensity ratio increases and the D′ band (1621 cm^{-1}) is resolved from the G mode, which shifts to lower wavenumber (1584 cm^{-1}). Interestingly, in the case of functionalization on copper, the characteristic phenylsulfanyl bands (476, 694, 1001, 1027 and 1083 cm^{-1}) have been observed in the spectrum due to the plasmonic enhancement by the substrate, while on Si/SiO₂ these bands appeared only after deposition of silver film and measuring using SERS (Fig. 2) [30].

The reactive nucleophile can be also prepared *in situ*, such as, for example, in the case of octadecylthiol, prepared from the corresponding isothiouronium salt. The Raman spectrum measured on graphene@Cu showed the typical graphene modes (1327, 1584, 2643 cm^{-1} for D, G and 2D, respectively) as well as characteristic vibrations of the octadecylsulfanyl moiety: 746 (C–S stretching), 524, 1062, 1102, 1130 (skeletal vibrations, CCCC trans and gauche), 1294 (twisting), 1440, 1461 (C–H deformation, scissoring), 2848 and 2884 cm^{-1} (C–H stretching), Fig. 3. Importantly, we have intentionally damaged the sample by bending the copper foil (this results in partial removal of graphene) and in the Raman spectra
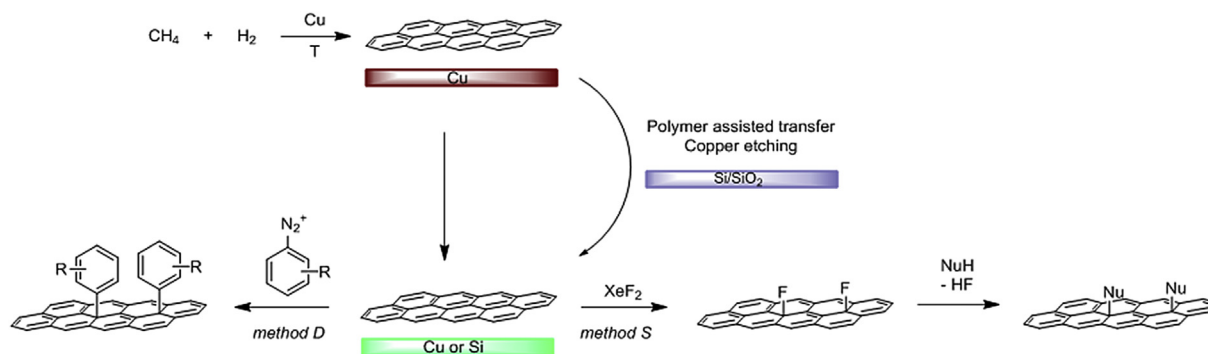

Fig. 1. Graphene was synthesized using the CVD method on copper foil, from which it can be transferred onto other substrates by polymer-assisted methods and copper etching. Graphene both on copper and Si/SiO₂ was covalently functionalized either by direct grafting of diazonium salts (method D) or activated by fluorination in the gas phase by XeF₂ followed by nucleophilic substitution (method S). Methods D and S are complementary in chemical compatibilities and in medium (solution or gas-phase processing). (A colour version of this figure can be viewed online.)