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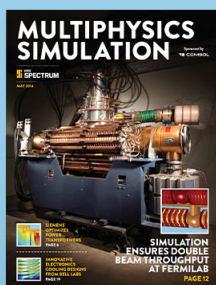The ripple's enhancement in graphene sheets by spark plasma sintering
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Dry-cleaning of graphene

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Studies of the structural and electronic properties of graphene in its pristine state are hindered by hydrocarbon contamination on the surfaces. Also, in many applications, contamination reduces the performance of graphene. Contamination is introduced during sample preparation and is adsorbed also directly from air. Here, we report on the development of a simple dry-cleaning method for producing large atomically clean areas in free-standing graphene. The cleanness of graphene is proven using aberration-corrected high-resolution transmission electron microscopy and electron spectroscopy. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4871997]

Contamination build up on the surfaces of materials is a prevalent problem in any application, where the surface properties of the material are important. The consequences of contamination are especially dire in the case of graphene and other 2D-materials, which consist essentially only of surfaces. The exceptional transport properties of graphene are strongly influenced by residual impurities,[1] the wettability of graphene changes dramatically with adsorption of contamination,[2] and the performance of graphene based vapor detectors depends on the cleanness of the surface,[3] to name only a few examples. Atomic-scale structural characterization of graphene with aberration-corrected high-resolution transmission electron microscopy (HRTEM) is strongly hindered by contamination, as clean patches of only few to tens of nanometers can be located in typical samples. Consequently, the success of graphene as "the ultimate" supporting film for studies of inorganic, organic, and biological nano-objects is directly linked to the prerequisite of finding efficient methods to clean it.[4,5]

Contamination is introduced on the surface of graphene during sample preparation where, for example, the use of organic solvents and other liquids cannot typically be avoided. Airborne pollutants landing on surfaces in ambient air is the other main source of contamination. A measurable consequence of the latter is the gradual increase of the mass of the international standard kilogram.[6] The surface contaminants are typically composed of hydrocarbons with wide variation in their stoichiometry ($C=O$, $C–OH$, or $H–C$) and chain lengths.[7] Such contamination can be cross-linked and/or graphitized under the electron beam of a transmission electron microscope (TEM)[8] or at high temperatures.[9,10]

Heating treatment is a common practice for removing hydrocarbon contamination from surfaces. Although annealing of graphene in vacuum or inert atmosphere reduces the amount of contamination,[11,12] it has been shown that residuals are still present after such treatment.[13,14]

Recently, a different approach for cleaning graphene was developed: The use of a metal catalyst to aid in the removal of surface contamination[15] on graphene. Longchamp *et al.* demonstrated that a metal-catalyst, i.e., Pt or Pd, removes efficiently all contamination from graphene over large areas ($\approx 0.2\,\mu m^2$) at moderate temperatures ($300\,°C$) and under atmospheric conditions. However, depositing metals on the sample surface is not always desirable, for instance if graphene is to be used in electronic applications.

Here, we present a different graphene-cleaning method—dry-cleaning with adsorbents—which is very simple and effective. By embedding free-standing single-layer graphene supported on Quantifoil TEM grids in commonly used adsorbents, such as activated carbon (Merck, "charcoal activated for analysis"), and annealing the samples in moderate temperatures, we observe surface cleanness of ~95% in single layer graphene, where cleanness is defined by the ratio of contamination-free surface area to the total sample area. For analyzing the cleanness of the samples, we employ HRTEM using an aberration corrected FEI 80–300 TITAN operated at $80\,kV$, and Auger electron spectroscopy (AES) using a scanning electron microscope equipped with an electron energy analyzer (Multiscan Lab, Omicron). Further on, we characterize the residual contamination after dry-cleaning using electron energy-loss spectroscopy (EELS) in the TEM (GIF Quantum energy filter). Where the typical contamination on non-cleaned samples consists mainly of hydrocarbons, the residual contamination after the dry-cleaning procedure has a distinctly different character, namely, aggregates with Si constitution.

The samples used were made of commercially available graphene grown on Cu foil by chemical vapour deposition (Graphenea S.A.) transferred to gold Quantifoil TEM-grids ($1.2\,\mu m$ hole diameter) with a variation of the transfer method reported by Pantelic *et al.*[16] That is, in order to avoid the use of polymethyl methacrylate, we transferred graphene directly from the copper foil by contacting the TEM-grid to graphene with isopropyl alcohol and afterwards etching away the copper foil with ammonium peroxodisulfate. In the case of dry-cleaning with activated carbon, the TEM-grid with the transferred graphene was embedded in a powder of activated carbon inside a glass vial. The vial was then placed on a heating plate, which was heated from room temperature

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to ∼210 °C at a rate of 5 °C/min. The sample was held at this temperature for 30 min. Afterwards, the sample was let to cool to room temperature and inserted in the TEM. To test the dry-cleaning effect with two other adsorbents, i.e., activated alumina (Edwards) and molecular sieve 5A (Sigma Aldrich), the adsorbents were first crushed in a mortar and regenerated at a temperature of 300° for 30 min and cooled down to ∼200 °C. Then the samples were embedded in the adsorbent and allowed to clean for another 30 min. All the samples were blown gently with air before inserting them in the TEM to remove remaining adsorbent granules from the surface of the sample.

The cleaning effect of the dry-cleaning treatment with activated carbon is exemplified in Figure 1. Panels (a) and (b) show low and medium magnification HRTEM images of a non-cleaned graphene sample. Here, the sample surface, covered with contamination, has only small patches of clean graphene with sizes ranging from nanometers to some tens of nanometers and with only ∼6% of the sample surface free of contamination. Such contamination coverage is typical of non-cleaned graphene samples. It is worth noting that the non-cleaned samples were produced no more than a week before the experiment and stored in standard grid boxes. The cleanness after dry-cleaning with activated carbon is considerably improved, as shown in Figure 1, panels (c) and (d), where the graphene cleanness rises to ∼95%, which can be

explained by the fact that activated carbon is a good adsorbent for a broad range of organic impurities.[17] The HRTEM image in Figure 1(e) obtained from the boxed area in (d) confirms that dry-cleaned graphene is, in fact, atomically clean. Importantly, the graphene layer survives this treatment even when it is free-standing over the holes of the Quantifoil grid.

The effect of dry-cleaning with activated carbon was characterized by AES with spatial resolution better than 100 nm using a primary electron beam at 3 keV and EELS in the low energy-loss region. The AES data (Figure 2(a)) of dry-cleaned graphene (blue line) and non-cleaned graphene (red line) on Quantifoil grids were acquired under the same experimental conditions, which allow their quantitative comparison. From these data, the intensity of the C_{KVV} peak for the non-cleaned graphene is observed to be ∼50% higher in comparison to that for dry-cleaned graphene. Moreover, the full-width at half maximum (FWHM) of the peak is also higher for the non-cleaned sample (FWHM = 35 eV) in comparison to the dry-cleaned sample (FWHM = 27 eV). In Figure 2(a), the AES spectrum for the Quantifoil film
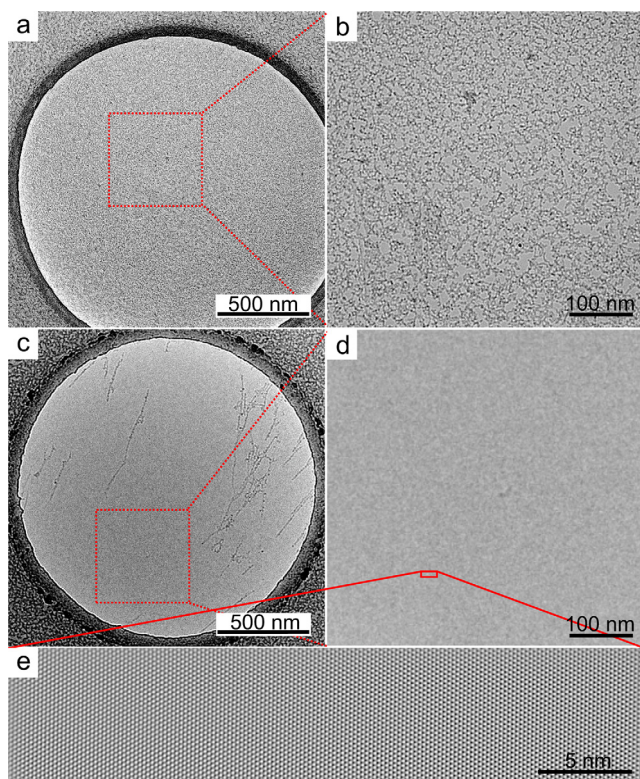

FIG. 1. HRTEM images showing the effect of dry-cleaning of graphene with activated carbon. (a) Low and (b) medium magnification images of non-treated graphene. The sample surface is completely covered in contamination, with only small clean patches from one nanometer to tens of nanometers in diameter. (c) Low and (d) medium magnification images of graphene which has been dry-cleaned with activated carbon. The cleanness of graphene obtained using activated carbon reaches 95%. (e) At high magnification, the surface of graphene is observed to be atomically clean (average image over 10 frames).
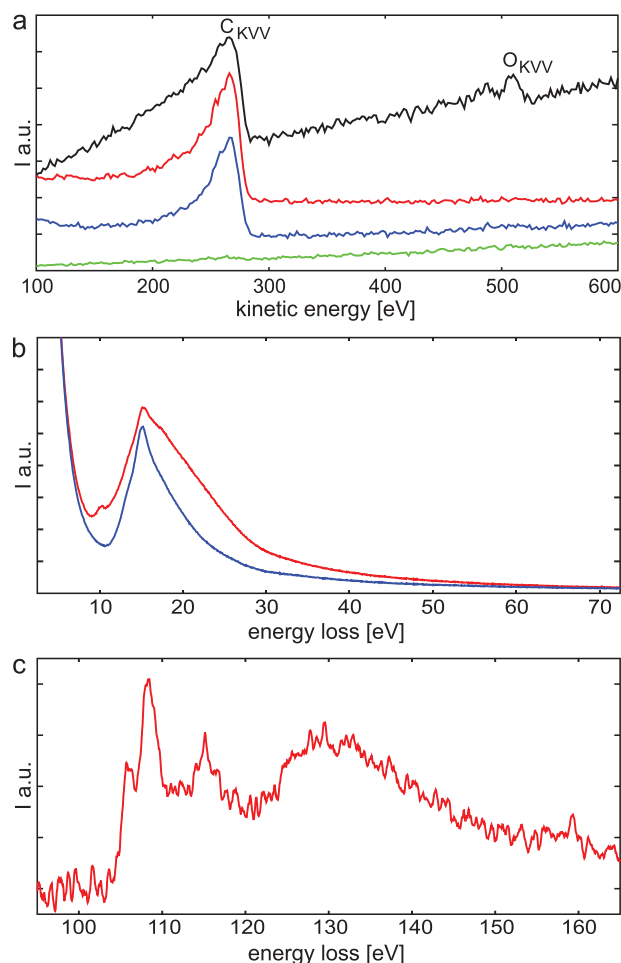

FIG. 2. Characterization of the dry-cleaning effect and residual contamination. (a) AES spectra from Quantifoil film (black), free-standing non-cleaned graphene (red), free-standing dry-cleaned graphene (blue), and vacuum reference (green). (b) Electron energy-loss spectrum of non-cleaned (red) and dry-cleaned graphene (blue) in the low-loss region showing the intensity and shape difference of the carbon $\pi + \sigma$ excitation peak (∼15 eV). (c) Background subtracted (2nd order log polynomial) EEL spectrum (95–165 eV) of residual contamination on dry-cleaned graphene. The shape and position of the peaks are correlated to the $Si-L_{2,3}$ ionization edge.[21,22]

consisting of ~10–20 nm, of amorphous carbon is shown as reference (black line). The intensity of the C_{KVV} peak is 260% higher than that of dry-cleaned graphene with the FWHM value of 48 eV. The lower intensity and the narrow FWHM value of C_{KVV} signal for the dry-cleaned graphene clearly show the lower amount of carbon and its narrow chemical variation. In the studied energy range, no other Auger signals than the C_{KVV} were identified in the graphene samples. Carbonaceous contamination on graphene is known[18,19] to change the features of the plasmon $\pi + \sigma$ (~15 eV) peak in EELS. The removal of carbonaceous contamination is corroborated by the stark difference in the intensity and shape of the plasmon peaks (Figure 2(b)) in our EELS measurements (under same conditions) on non-cleaned and dry-cleaned graphene (red line and blue line, respectively). The intensity difference of the peaks is related to the amount of carbon material which has been removed by the cleaning method. Moreover, excitations at ~10 eV and 20 eV in the non-cleaned graphene sample demonstrate the presence of additional carbon species.[20] This result is in good agreement with the AES and HRTEM characterizations. Together, all these results unambiguously show the efficient removal of carbonaceous contamination from graphene by activated carbon.

Nevertheless, some residual contamination is present on the surface of graphene after the dry-cleaning treatment, seen as dark long stripes in Figure 1(c), which qualitatively differs from the typical carbonaceous contamination observed in a non-cleaned sample. Therefore, the elemental composition of this residual contamination was investigated by EELS (convergence angle ~1 mrad and collection angle 3.3 mrad). An area of a dry-cleaned sample with residual contamination was studied by scanning over an energy-loss range between 0 eV and 600 eV. During scanning, we found a set of energy-loss peaks between 95 eV and 165 eV, Figure 2(c). The prominent peaks with energies around 105 eV and 108 eV energy-loss are distinctive for the Si-$L_{2,3}$ ionization edge of Si-containing compounds.[21,22] We speculate that the Si originates from the TEM grid as X-ray photoelectron spectra of bare TEM grids have shown that they contain traces of Si.

In addition to using activated carbon as the adsorbent, we explored the use of other adsorbents, i.e., activated alumina and molecular sieve 5A for cleaning graphene. A cleaning effect was observed also with these adsorbents,
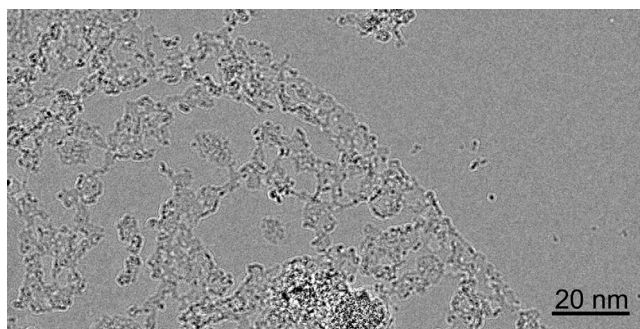
FIG. 4. Image of an area of a dry-cleaned graphene sample with single and bi-layer graphene showing that the bi-layer (left-hand side) is not cleaned by the dry-cleaning process.

albeit not as impressive as in the case of activated carbon (see Figure 3). The activated alumina treatment resulted in cleanness of ~15%–40% with clean areas of up to ~0.24 μm^2 (Figure 3(a)), and the molecular sieve 5A treatment resulted in cleanness of ~10%–30% with clean areas up to ~0.06 μm^2 (Figure 3(b)). We would like to point out that these results most of all indicate the cleaning potential of other adsorbents, as no optimization of the procedure with these adsorbents was conducted.

A curious feature which was also observed in our experiments is that only single-layer graphene gets cleaned, while multilayer graphene remains contaminated (Figure 4). At this point, we do not have a clear explanation for this behaviour. However, one could speculate that the adhesion energy of contamination in multilayer graphene is higher, as compared to single-layer graphene;[23–25] and therefore, a higher temperature would be required for desorption and/or migration of the contamination.

In summary, we have presented a simple and efficient cleaning method—dry-cleaning with adsorbents—for removing surface contamination from graphene. The most effective adsorbent is activated carbon while using the activated alumina and molecular sieve 5A resulted in significant but less efficient cleaning. The dry-cleaning treatment produced atomically clean areas in the micrometer range. The cleaning effect was observed only in single-layer graphene, whereas bi- and multilayer graphene remained contaminated. A major advantage of the dry-cleaning treatment is its simplicity and non-invasive nature, as compared to, for example, deposition of Pt or Pd catalysts on sample surfaces. Therefore, dry-cleaning has the potential to enable graphene as the ultimate substrate for characterization of, e.g., nano-objects and biological samples by TEM. Although the experiments, here, were conducted only on graphene, one can speculate that such a treatment could have wider use whenever clean sample surfaces are required.
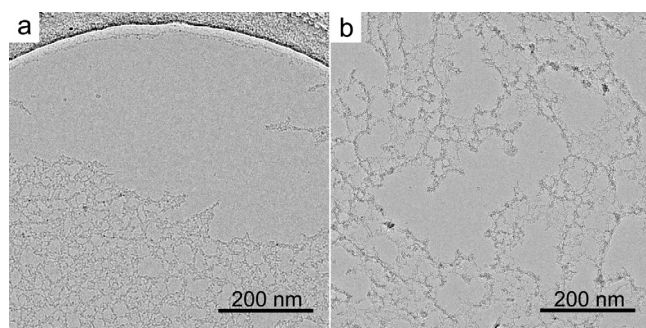
FIG. 3. HRTEM images of graphene dry-cleaned with activated alumina and molecular sieve 5A ((a) and (b), respectively). Graphene cleaned with activated alumina has a cleanness of 15%–40%, while with molecular sieve 5A the cleanness is 10%–30%.

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