

Electrochemical Modification of Graphene**

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The recent discovery of graphene has triggered enormous interest both in fundamental and applied science communities.^[1–3] So far, the studies have focused on the physical properties of graphene, in particular its electronic transport behavior under applied electric and magnetic fields.^[4,5] This has resulted in first prototype devices such as field-effect transistors^[6] and chemical sensors of extraordinary sensitivity,^[7] which demonstrate the high application potential of graphene. However, in contrast to its physical characterization, the chemical modification of graphene remains largely unexplored, despite the intriguing properties anticipated for functionalized graphene. Specifically, chemical functionalization of the edges of graphene is predicted to enable tailoring its electronic properties.^[8] Moreover, according to theory, metal-doping enhances the binding capability of graphene for environmentally relevant compounds like dioxin.^[9]

The chemical modification protocols that are currently available in the field of graphene have been developed as alternative synthetic routes enabling its large-scale production. This task is important as the most established fabrication method, namely micromechanical cleavage, delivers quite a low yield of pristine monolayers of graphene.^[10] An alternative epitaxial approach involves annealing of SiC substrates.^[3,11] However, it requires high temperatures exceeding 1 100 °C and provides non-uniform graphene films. The chemical routes comprise the removal of functional groups in exfoliated graphite–fluoride^[12] and –oxide.^[13–15] It has recently been shown that the reduction of graphene oxide monolayers gives convenient access to graphene,^[16,17] albeit further improvements are required in order to completely eliminate oxygen-containing groups and heal remaining vacancies in the carbon lattice. Microscopic and electrical studies suggest a structure in which intact, nanometer-sized graphene islands are separated by defect-rich regions.^[16] The latter regions are small enough that the electrical characteristics of graphene are largely

preserved, rendering these sheets useful for electronic applications.

Here, we present the controlled modification of individual chemically derived graphene layers by electrodeposition of palladium nanoparticles as a first step toward an emerging chemistry of graphene. Functionalization through electrochemistry offers several advantages for the modification of carbon-based nanostructures, as has been demonstrated by the attachment of organic functional groups^[18] or metallic nanoparticles^[19] to carbon nanotubes. The obtained palladium-decorated graphene layers are promising as components of nanoscale sensors. As in the case of carbon nanotubes, the attached metal particles are expected to impart sensitivity toward certain analytes whose direct interaction with the unmodified material is too weak to cause a significant response.^[20,21] In the present work, we investigate the hydrogen sensitivity of the Pd-modified graphene and evaluate the electronic properties of this novel hybrid system.

Individual monolayers of graphene, obtained through reduction of graphene oxide by H₂ plasma,^[16] with sizes on the order of several hundreds of nanometers, were electrically contacted by Ti/Au electrodes on Si/SiO₂ substrates (Fig. 1a). Palladium electrodeposition was then performed by reduction of Na₂PdCl₄ with LiClO₄ as supporting electrolyte. AFM images of a graphene layer modified successively using two different deposition voltages for a fixed duration (15 s) are displayed in Figure 1b and 1c. It is apparent that a more negative potential (–0.85 V vs. Pt) resulted in a denser Pd particle decoration, as compared to a lower voltage (–0.70 V vs. Pt). Contrary to the particle density, the mean size of the particles is found to increase only slightly from 7 to 9 nm with a more negative potential (Fig. 1d and 1e). A reasonable explanation for the largely unchanged particle size is the preferred nucleation of the palladium at vacancies along the edges of the intact, nanometer-sized graphene islands (Fig. 1f). In fact, enhanced metal nucleation at the edge of graphitic planes is well-documented for other carbon-based electrodes such as highly oriented pyrolytic graphite (HOPG) and multi-wall carbon nanotubes.^[22,23] Due to the likely differences in their local chemical environment, the range of accessible edge sites should expand upon application of increasingly negative voltages. In addition, one observes continued growth of the pre-formed nanoparticles, explaining the broader distribution toward higher particle sizes as in Figure 1e.

Further support for the above scenario stems from the electrical characterization of the Pd-modified samples. To this

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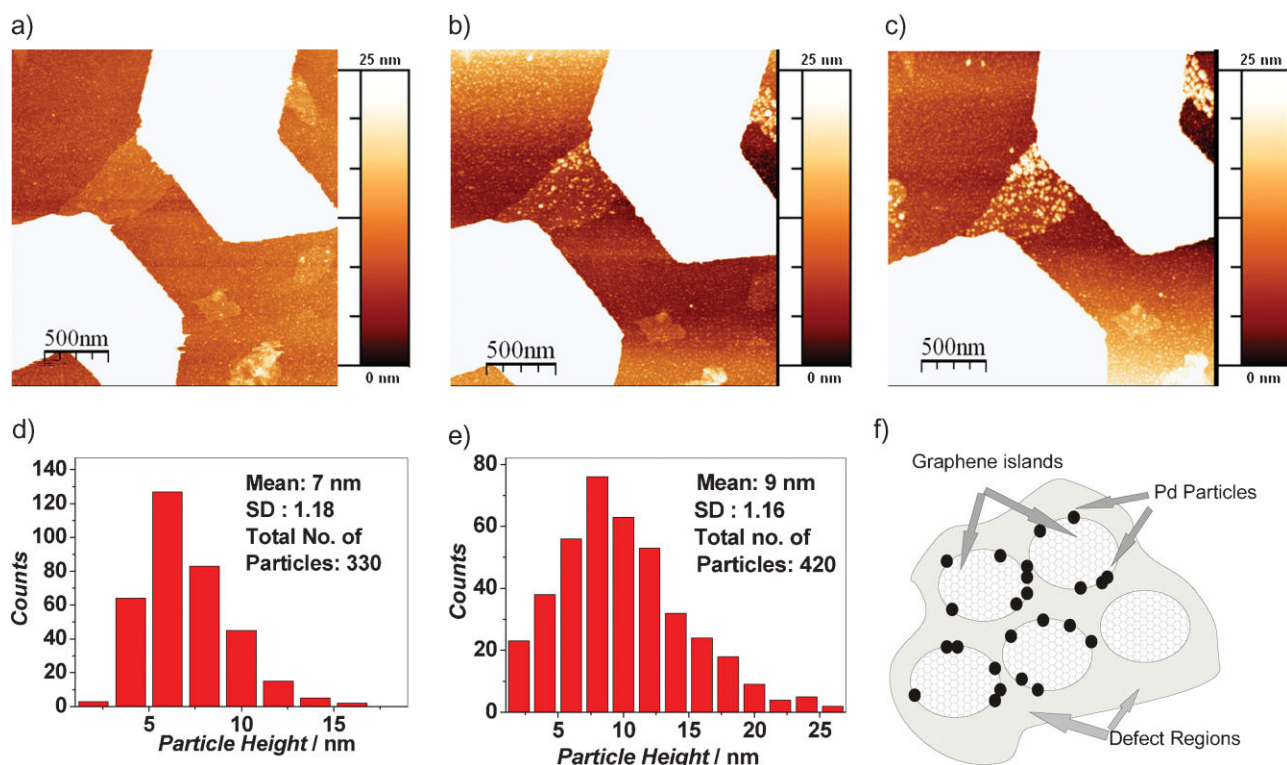


Figure 1. AFM images of an individual graphene sheet contacted by two electrodes at various stages: a) initial bare unmodified layer; b,c) after electrodeposition of Pd at -0.70 V and -0.85 V versus Pt, respectively. d,e) Histograms showing the size distribution of particles for the case of (b) and (c), respectively. f) Scheme illustrating possible nucleation sites for Pd at defects at the edges of the intact graphene islands.

end, the electrical resistance of the sheets was measured under ambient conditions as a function of voltage applied to the Si substrate (back gate). The resistance of the bare graphene displays a maximum at a gate voltage of approximately $+40$ V (Fig. 2), a finding attributable to p-type doping upon contact with the ambient, which causes a shift of the charge neutrality-point toward positive gate voltages. A similar

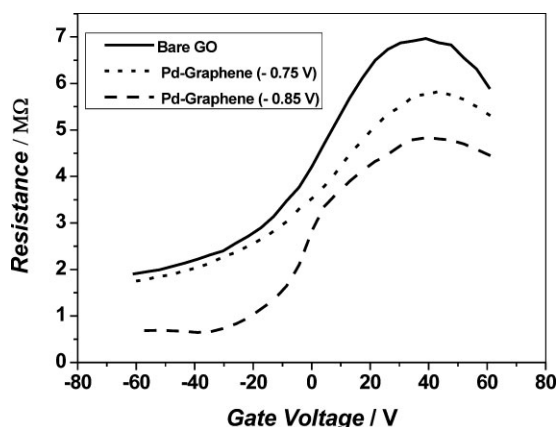


Figure 2. Dependence of electrical resistance (bias: ± 0.2 V) on the back-gate voltage (in ambient) for a graphene sheet before modification (continuous curve) and after consecutive electrodeposition at -0.75 V (dotted curve) and -0.85 V (dashed curve) versus Pt. The electrodeposition was performed in a solution of ethanol with Na_2PdCl_4 (0.1 mM) and LiClO_4 (0.1 M).

behavior has been observed with pristine graphene monolayers.^[1] In the Pd-modified samples, the position of the resistance maximum remains at the same gate voltage, whereas its magnitude is clearly decreased. This decrease is more pronounced for samples with higher particle densities. The persistence of gate dependence indicates that the Pd particles do not form continuous conduction pathways that connect the two electrodes. Nonetheless, they obviously introduce some connections between the graphitic regions, thus reducing the barrier for charge transport due to the defective regions. These metallic bridges are sufficient to decrease the resistance by a factor of 2–3. Temperature dependent electrical measurements (performed from room temperature down to 4 K) revealed that the overall charge transport is dominated by carrier hopping through defective regions as in the non-decorated graphene sheets (see Supporting Information).^[16]

In order to evaluate their applicability as chemical sensors, the resistances of the bare and Pd-modified graphene sheets were measured under different gas atmospheres. Upon exposure of the bare graphene samples to hydrogen, the resistance maximum in the gate dependence curve remained almost unaffected, as can be seen from Figure 3a (see short dashed and long dashed curves). The behavior of the Pd-modified samples was significantly changed against hydrogen. In this case, the resistance maximum is strongly shifted toward negative gate voltages (Fig. 3b). This shift can be attributed to the dissolution and partial dissociation of

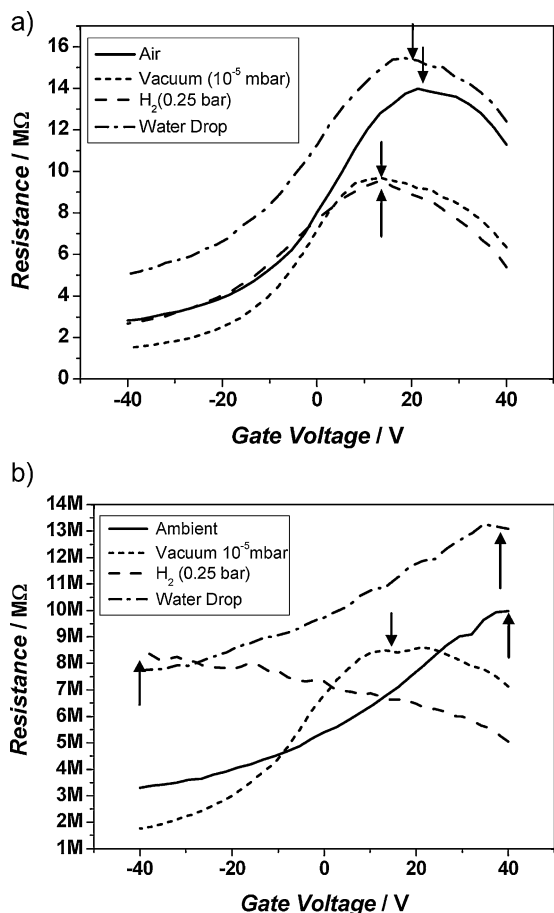


Figure 3. Influence of the chemical environment on the gate dependence of electrical resistance for the a) bare and b) Pd-decorated graphene sheets. For the device in (b), Pd was electrodeposited at -0.85 V versus Pt. All transport measurements were carried out at room temperature (bias voltage: ± 0.2 V). Arrows drawn at the resistance maximum signify the charge-neutrality point. In both cases, the device was first measured in ambient and then brought to vacuum. Subsequently the sample was purged in hydrogen. Finally, after removing the device from the chamber, the resistance was measured after placing a drop of water on the sample and drying with N_2 flow.

hydrogen at the Pd particles, whereupon the particle's work function is decreased such that electrons are transferred onto the graphene sheet.^[20,24,25]

When the hydrogen-exposed Pd-graphene samples were brought back to ambient conditions, the original resistance was restored, although the recovery required several hours (continuous curve in Fig. 3b). In analogy to the behavior of hydrogen sensors based on palladium-modified carbon nanotubes, the resistance recovery of the present samples is expected mainly to arise from the reaction of the dissolved hydrogen with oxygen contained in air.^[26] However, we have observed that the humidity of the ambient plays a dominant role in restoring the electrical response. In particular, when placing a drop of water onto the sample surface (and drying it using N_2 flow), the resistance maximum shifted back to positive

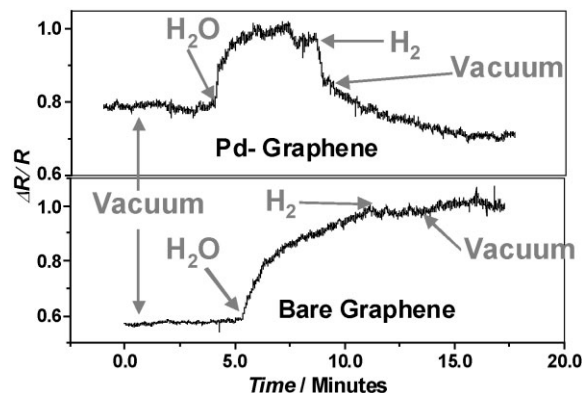


Figure 4. Room-temperature dynamic response of a bare (lower panel) and a Pd-modified graphene sheet (upper panel) toward changes in the gas atmosphere (bias: $+0.2$ V and gate voltage: 0 V). In the latter sample, palladium was electrodeposited at -0.85 V versus Pt. The relative change in resistance normalized to the resistance is plotted as the ordinate.

gate voltages (dash-dotted curve in Fig. 3b). This shift indicates a high p-type doping of the graphene through adsorbed water molecules. The notion of water behaving as electron acceptor when adsorbed on graphene is in accordance with recent theoretical studies.^[27] An alternative mechanism that also appears plausible involves water adsorption on the residual oxygen containing groups that reduces the p-type doping.^[28] However, our observations suggest that such a mechanism only plays a minor role, most likely due to the high concentration of water used here. Furthermore, a similar shift is observed upon exposure of the bare graphene samples to water (dash-dotted curve in Fig. 3a). Hence, the major effect of water originates from an interaction with the uncovered regions of the sheet, rather than being mediated through palladium.

Temporal responses of the bare and Pd-modified graphene layers to changes in the chemical environment are compared in Figure 4. Starting from vacuum, the Pd-modified sample displays a pronounced increase in relative resistance ($\Delta R/R$) upon introduction of water (N_2 bubbled through distilled water), followed by a decrease upon exposure to H_2 , with both changes occurring on the scale of a few minutes. Subsequent evacuation restores the original state, albeit over a much longer time span. The bare graphene shows a similar response upon exposure to water, but it does not respond toward hydrogen.

In conclusion, we have demonstrated electrochemical modification to be a valuable approach to chemically functionalize individual graphene monolayers. It enables covering these fascinating ultrathin sheets with a controllable density of metal particles. The electrodeposition of palladium was found to impart hydrogen sensitivity to the chemically derived graphene layers. Electrochemical functionalization emerges as a valuable tool to expand the application spectrum of graphene and related two-dimensional materials. As one possibility, it could be extended to modify graphene with ferromagnetic metal particles. Moreover, the decoration with

an array of metal particles might enable tailoring quantum interference phenomena in the electrical transport through graphene sheets.

Experimental

Graphite oxide was prepared via the Hummers and Offeman method [29], starting from graphite flakes of 20 μm size (Sigma-Aldrich). The resulting oxidized material was dispersed in water with the aid of soft ultrasonication and then deposited onto degenerately doped silicon substrates with a thermally grown SiO_2 layer (200 nm thickness). The substrates were treated with 3-(aminopropyl)triethoxysilane (APTES) prior to deposition. Reduction was carried out under hydrogen plasma at a pressure of 0.8 mbar at 30 W for 5 s. Standard electron beam lithography was used to contact the graphene sheets using Ti/Au electrodes. The electrochemical modification was carried out in ethanol containing Na_2PdCl_4 (0.1 mM) and LiClO_4 (0.1 M) as supporting electrolyte, with Pt pseudoreference and counter-electrodes. The applied potential was controlled using a Solartron 1285 potentiostat. AFM images were acquired with a Digital Instruments Nanoscope IIIA microscope operated in tapping mode using standard silicon cantilevers (Nanosensors). Statistical analysis was performed using WSxM [30]. Gas sensing measurements were carried out in a custom-made vacuum chamber.

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