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Highly-controlled thiol-functionalization as a route to versatile graphene-based platforms for robust nano-bio-hybrid devices

Although pristine graphene is one of the most relevant materials this decade, several important shortcomings must be overcome before it can step from fundamental physics to applied technology.[1] In particular, its extreme chemical inertness and the absence of an electronic band-gap present important limitations to its use as an active element in electronic devices and hybrid structures. Thus, technologically useful and robust graphene-based interfaces for nano-bio-hybrid devices require highly selective, stable and covalently bonded functionalities on the graphene surface, but in order to be effective and competitive they must essentially retain the electronic properties of the pristine graphene surface. There have been many attempts to modify graphene via non-destructive methodologies that aim to preserve its extraordinary properties and incorporate added value.[2] The most common covalent functionalization methods are via chemical routes, mainly by reacting free radicals or dienophiles with the C=C bonds of pristine graphene,[3] and although well-developed wet chemistry may succeed in linking diverse groups to the surface, the resulting graphene platforms are usually poor performers either due to low functionalization yield or to the nature of the reaction conditions that disrupt the graphene layer with an unacceptable amount of defects.

In this work [4], we describe a relatively straightforward route to the covalent chemical functionalization of graphene sheets with a robust thiol-terminated moiety. We employ a recently reported and patented strategy [5] for the selective functionalization of graphene through the controlled formation of atomic vacancies (Fig. 1a), obtaining a graphene surface uniformly covered with a covalently bound spacer molecule that is formed from the spontaneous bonding of *p*-aminothiophenol (pATP) molecules at the vacancies. The result is a controlled decoration of the graphene surface with active thiol moieties, which can subsequently be directly used to bind diverse nanoarchitectures to graphene. We have used this strategy to covalently couple two systems of broad interest: gold nanoparticles (Au-NPs) and thiol-modified nucleic acid aptamers (Fig. 1b).

The highly-controlled covalent functionalization protocol is undertaken under UHV conditions and the properties of pristine graphene are largely preserved, as shown by a large number of experimental techniques including XPS, Raman microspectroscopy, UV-vis spectroscopy, AFM and TEM, and confirmed by theoretical methods.

Two types of Au nanoparticles of different origin were used; citrate capped Au-NPs produced in a salt solution and NPs made using a multiple ion cluster source in UHV conditions.[6] A nucleic acid aptamer, in this case a single-stranded DNA (ssDNA) oligonucleotide that binds with high affinity and specificity to a target protein molecule that mediates relevant biological processes, PCBP-2, was used. Both systems studied, which were also characterized using multiple techniques, remain firmly anchored to the graphene surface even after several washing and annealing cycles, thus demonstrating the highly robust nature of the nanostructures. Further, atomic force microscopy images show that, when coupled to the graphene surface, the conjugated aptamer retains the functionality required to recognize its target protein.

We believe that this functionalization mechanism paves the way to the integration of high-quality graphene layers into technological platforms for plasmonics, biosensing or advanced field-effect transistor devices. As an example we assess its applicability for graphene solution gated field-effect transistors (gSFET).

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Figures

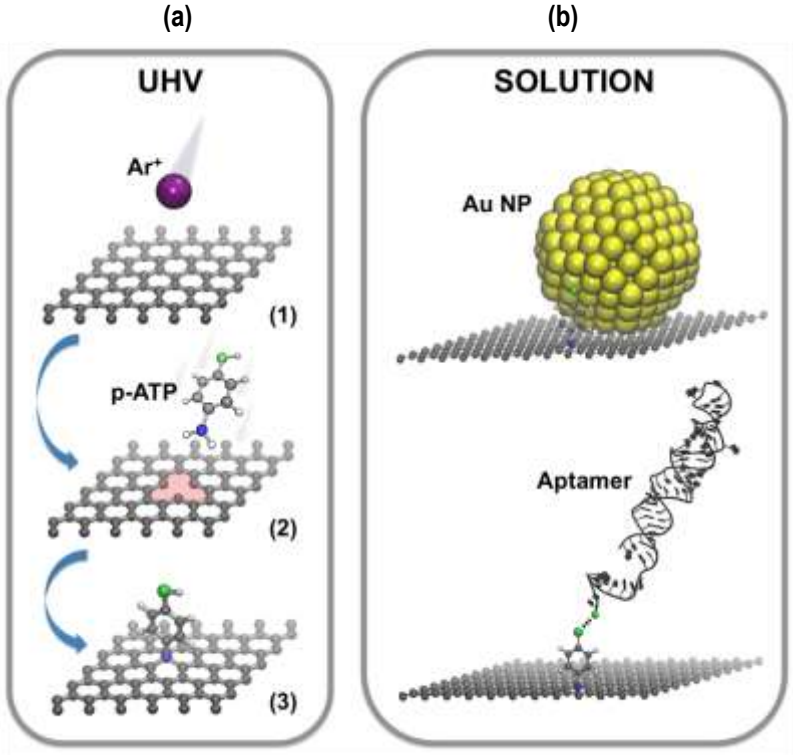

Figure 1: (a) Schematic illustration of the functionalization process: (1) 140 Ar+ irradiation of the graphene surface; (2) exposure of the graphene surface with ion-beam induced vacancies to pATP molecules; (3) covalent bonding of the N terminal of pATP to the carbon network at the induced vacancy in the carbon network, leaving the thiol group exposed to the medium. (b) *top:* scheme of the thiol linkage to gold nanoparticles; *bottom:* conjugation of a thiol-modified DNA aptamer to the graphene-anchored thiol group through the formation of a disulfide bond.