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Graphene decoration with metal nanoparticles: Towards easy integration for sensing applications

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A simple and versatile method for the decoration of CVD grown graphene with metal nanoparticles is presented. The mechanism of nanoparticle formation is galvanic displacement resulting in physically adsorbed clusters. The single layer graphene obtained by this method can be easily transferred. Integration onto a gas sensing transducer is presented as proof of concept.
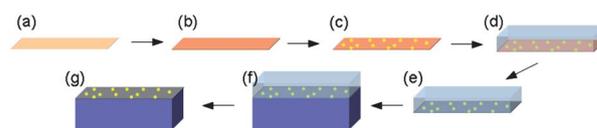
Graphene has become a promising material for many different applications, such as nanoelectronic devices,[1] physical, chemical and biochemical sensors,[2,3] transparent conductive films,[4,5] clean energy devices,[6] or nanocomposite formulation.[7] Sensing applications using graphene sheets as transducers have experienced a surge in the last few years, especially for gas sensing platforms,[8] or electrochemical sensors,[9] because of the high electrical conductivity of graphene. In many cases graphene is initially decorated with metal nanoparticles to increase the sensitivity, selectivity, limit of detection, or a combination of these properties. In most cases the decoration process is performed by electrochemical reduction of metal salts with the help of external power sources for the reduction of the metal ions using graphene flakes obtained from graphene oxide,[10,11] or by using other external reducing agents such as light,[12] or microwaves.[13] In other cases the formation of metal nanoparticles is achieved by chemical reduction of the metal salts by the addition of a reducing agent and graphene is decorated by adsorption of the formed nanoparticles in solution.[14,15] The transfer process is then performed by drop-casting of the dispersed graphene flakes on top of the transducer platform, a method that does not allow control over the complete coverage of the surface, homogeneous layer formation or reproducibility of the coverage from sensor to sensor.

Here we present a simple and easy-to-implement method to decorate graphene, grown *via* chemical vapor deposition (CVD) on a copper substrate,[16] by electroless deposition of the metal using the

copper as the reducing agent. Considering the reduction potentials of the substrate and those of the different noble metals that present useful catalytic activities, one may conclude that at least gold, platinum, palladium and silver can be deposited on Cu-catalyzed graphene by this method. The only requirement for the process to happen spontaneously is that the reduction potential of the metal to be deposited needs to be higher than that of copper (+0.34V). The parameters that tune the formation, diameter and density of the metallic nanoparticles on the graphene sheets are in our case the concentration of the noble metal salt dissolution and the time in which the copper-graphene sheet is in contact with the noble metal dissolution. More elaborate baths involving surfactants or different temperature conditions would be possible, but are not considered here. After the electroless deposition, the decorated graphene is transferred by spin coating with polymethylmethacrylate (PMMA) and copper etching process similar to the one described previously by Reina *et al.*[17] Fig. 1 shows the complete process reported in this paper, including the graphene growth, decoration, and transfer.

Fig. 2 shows SEM images of graphene on a Cu substrate before (a) and after the electroless deposition of gold (b), platinum (c) and palladium (d). The particular conditions for the three depositions were in all cases a 1mM dissolution of the corresponding metal salts (KAuCl$_4$, K$_2$PtCl$_4$ and K$_2$PdCl$_4$ respectively, Sigma Aldrich) and an immersion time of 60 s.

It can be observed that under the same experimental conditions, the three metals behave differently. Platinum forms smaller nanoparticles with a lower density while gold and palladium tend to present similar reactivities with higher nanoparticle densities and diameters when compared to platinum. Raman spectroscopy was used to determine the possible interaction of the metal nanoparticles

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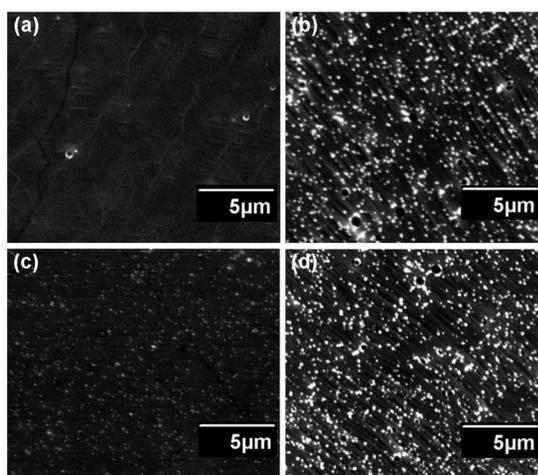

Fig. 1 Schematic diagram of the graphene growth, decoration and transfer processes. Starting with a copper foil (a) graphene is grown by CVD (b). Electroless deposition of a noble metal is performed (c) and PMMA is applied by spin-coating (d). Copper is etched by a FeCl3 dissolution (e) and after rinsing PMMA/graphene is transferred onto the sensing transducer (f) with a final PMMA dissolution in acetone (g).

Fig. 2 SEM images of graphene on copper before (a) and after a 60 s immersion time in a 1mM dissolution of KAuCl$_4$ (b), K$_2$PtCl$_4$ (c) and K$_2$PdCl$_4$ (d). Lines along the surfaces correspond to copper substrate flattening process during manufacturing.

and graphene. Fig. 3a shows the XPS spectrum of an Au decorated graphene substrate after 60 s immersion time in a 1mM dissolution. The obtained spectrum reveals pure metallic Au formation suggesting an adsorption mechanism of the Au on graphene. Sonication of the sample confirmed this fact as the nanoparticles were no longer on the graphene surface. Fig. 3b shows Raman spectra of graphene on copper before the electroless deposition of gold (black line) and after an immersion of 60 s in a 1mM of KAuCl$_4$ (red line). As can be observed the G to D peak ratio decreases substantially, pointing out increased defects in the graphene structure during the metal deposition, caused by the interaction of the metal with the graphene lattice.

We have employed this simple functionalization scheme to fabricate a gas sensor. A 5×5 mm Au decorated graphene sheet was transferred using the PMMA stamping method onto a transducer consisting of two opposing gold comb-shaped electrodes of 25 μm width, separated by a 25 μm gap. Fig. 4a shows the schematic fabrication of the sensing platform while Fig. 4B shows the SEM image of the obtained electrodes. Raman spectroscopy was performed after the transfer to ensure the complete removal of PMMA and to verify the quality of the transferred graphene. Because of the known interaction of gold with hydrogen sulfide, this gas was used as test molecule.
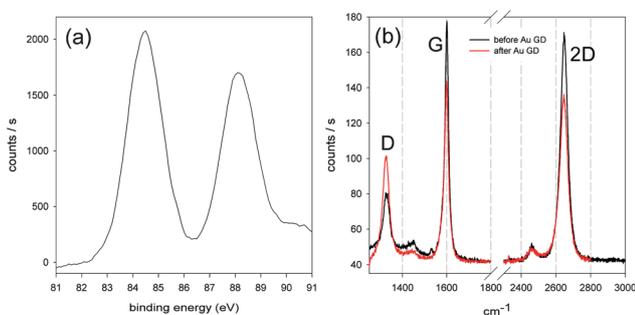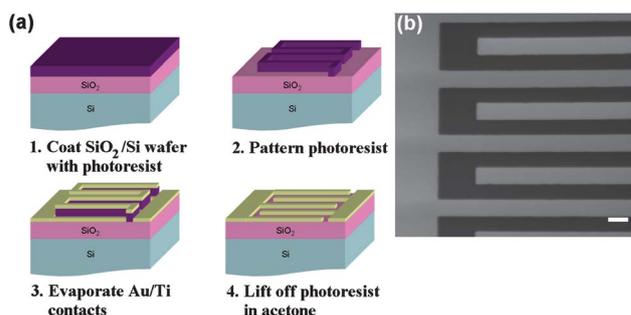
Fig. 4 (a) schematic fabrication of the Au-comb electrode. (b) SEM image of the fabricated device. Scale bar corresponds to 25 microns.

Hydrogen sulfide (H$_2$S) was delivered to the metal-decorated graphene device using mass flow controlled dilution of a 500-ppm cylinder of H$_2$S with clean, dry air. The sensor was exposed to varying concentrations of H$_2$S for 60 s every 30 min. The metal-decorated graphene device was measured using a Keithley 2602 source-measure unit by applying a 50 mV source–drain bias while measuring the electrical current. A chemiluminescence sensor (Teledyne API 101E) was used as a H$_2$S reference sensor. The gas dilution, reference sensor, and graphene device data were collected using the open-source computer control software, Zephyr.[18] Fig. 5 shows the sensor response (in red) in terms of change in conductance obtained during introduction of varied H$_2$S concentrations (in black) into the flow cell. As can be observed, the response of the developed sensor is relatively fast but presents irreversible slow recovery due to the formation of strong S–Au bonds.

Even though the response of the developed sensor is not optimal, it demonstrates the possibility of using a simple approach to develop new transducing materials for sensing applications. In this particular case, for the determination of H$_2$S, the sample heating is deemed necessary to facilitate the desorption of the bonded H$_2$S-dervied species and help in the recovery of the sensor's baseline. Because of the simplicity in the decoration process we believe that the proposed method could be easily integrated into the already existing roll-to-roll fabrication methods,[19] allowing the mass production of sensing devices. Future works will combine the developed substrates with biomolecules and biomarkers towards the development of electrochemical biosensors.
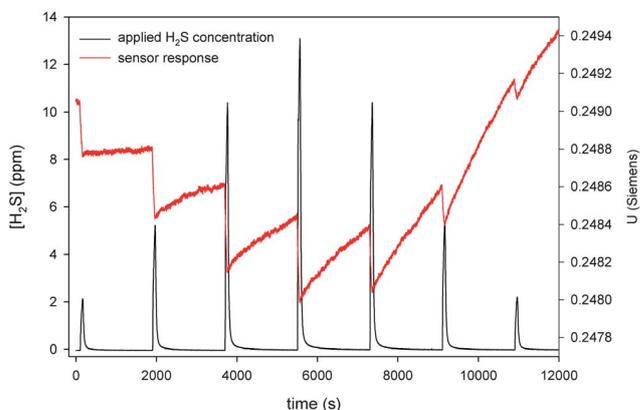

Fig. 3 (a) XPS spectrum of the Au nanoparticles on graphene in the Au 4f region. (b) Raman spectra obtained on graphene on Cu before (black line) and after an immersion in a 1mM KAuCl$_4$ dissolution for 60 s.

Fig. 5 Au-decorated graphene sensor response (red line) during an H$_2$S exposure profile (black line).

Acknowledgements

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