

Palladium nanoparticles graphene hybrids for hydrogen detection

B. Alfano^{1,2*}, M. L. Miglietta¹, T. Polichetti¹, E. Massera¹, F. Ricciardella¹, and G. Di Francia¹

¹ ENEA C.R. Portici P.le E. Fermi 1, I-80055 Portici (Naples), Italy

² Department of Physical Sciences University of Naples Federico II Via Cinthia, I-80126, Naples, Italy

* brigida.alfano@enea.it

As described in many literature works, graphene functionalization with metal nanoparticles (GR/M-NP) could help in improving the material sensitivity and selectivity towards different gases [1-4].

In this frame, we demonstrate controllable fabrication of Pd nanoparticles (NPs) decorated graphene (GR/PdNPs) hybrids and its application for fast and selective detection of hydrogen at room temperature. The synthesis of graphene/metal nanoparticles hybrids started from a pristine graphene obtained by Liquid Phase Exfoliation (LPE) of natural graphite in a hydroalcoholic solution [5]. The graphene colloidal suspension was then directly added to the metallic salt together with a reducing agent in water-solution (palladium acetate and sodium dodecyl sulfate respectively). By application of a microwave treatment, Pd NPs were synthesized in situ and directly attached to the graphene surfaces so attaining a straightforward and eco-friendly chemical process. Scanning Electron Microscopy (SEM) was used to characterize the morphology and composition of the nanohybrid material (Fig. 1 a and Fig. 1 b) while the Raman spectroscopy was used to understand the type of interactions occurred between graphene and metal nanoparticles (Fig. 2).

A drop-casted film of this hybrid material was used as receptor for the fabrication of conductometric gas sensors. The sensing performances of the GR-PdNPs and GR were compared to demonstrate the enhancement of the sensing response versus hydrogen (Fig. 3 a). The real-time sensor electric conductance change during replicated test measurement shows the good stability of the sensor device (Fig. 3 b). The device was also probed to different gas concentrations as shown in Fig. 3 c and Fig. 3 d. The response increased from 2 to 12 % with increasing H₂ concentrations from 0.25 to 2.5 %.

In conclusion, herein the effective modulation of the sensing properties of graphene by means of an eco-friendly and straightforward preparation method was proved. The deposition of palladium nanoparticles onto graphene surface completely modified the device behaviour making the graphene responsive towards the H₂. Further tests, involving other metal nanoparticles, are currently ongoing with the aim to modulate sensor response towards other analytes.

References

- [1] M. Gautam et al., *Solid-State Electron.* 78 (2012) 159.
- [2] B. Hwan Chu et. al., *Sensor. Actuat. B* 157 (2011) 500.
- [3] S. Cui et al., *Analyst* 138 (2013) 2877.
- [4] M. Ding et al., *J. Am. Chem. Soc.* 134 (2012) 3472.
- [5] F. Fedi et al., *Mat. Res. Exp.* 2 (2015) 035601.

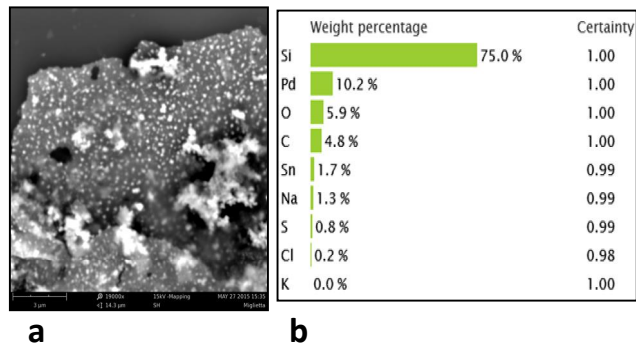


Figure 1: (a) SEM image of GR/Pd-NPs; (b) Elemental analysis spectrum by energy dispersive x-ray spectroscopy (EDX) of GR/Pd-NPs performed focusing on the Pd nanoparticles.

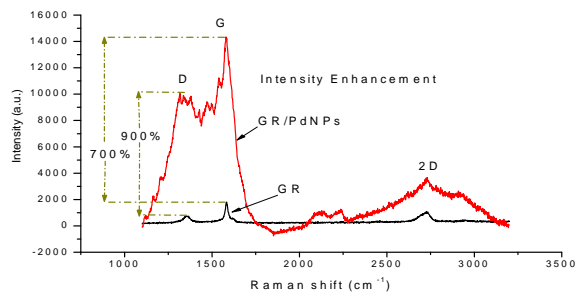


Figure 2: Raman spectra of GR/Pd-NPs graphene deposited on Si/SiO₂ substrates. The spectrum was acquired in the region covered by the metal NPs (red solid line) and compared to the one recorded in the area not covered by the NPs (black solid line). The comparison between the spectra highlights an intensity enhancement of the bands by 700%.

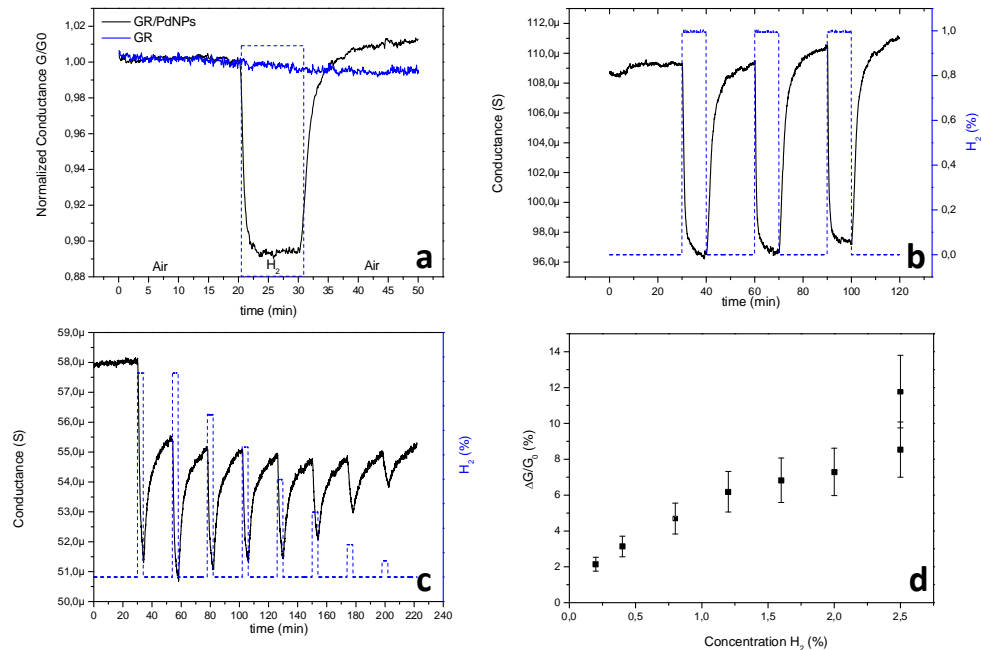


Figure 2: a) dynamic sensing responses of graphene to H₂ before and after Pd NPs deposition; b) three cycles sensing behavior of GR/PdNPs; c) dynamic sensing responses of GR/PdNPs versus different H₂ concentrations; d) correlation between sensor response and H₂ concentration. Here, the sensor response is defined as $S = (G_{\max} - G_0) / G_0 = \hat{e} G / G_0$ where G_0 is the electric conductance in the initial, unperturbed, state and G_{\max} is the maximum of the conductance value during analyte exposure. The device, biased at 1 Volt DC was tested relative humidity (RH) set at 50 % and at room temperature.