The influence of the Ag nanoparticles concentration on the modulation of the graphene sensing behavior

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The potential of graphene in gaseous analytes detection is widely recognized [1], in particular, it is well known that the pristine graphene exhibits a specificity towards nitrogen dioxide [2,3], and that such specificity can be modulated towards other analytes by functionalizing the graphene surface [4,5]. In this framework the decoration with metal nanoparticles have already been proposed as effective means to turn the specificity of material, and in our recent work we have shown that the functionalization through Ag nanoparticles makes the graphene highly specific to ammonia [6]. The presence of nanoparticles on the surface of the material acts as a mediator in the interaction between the analyte and graphene determining different mechanisms of charge transfer that can be due to both chemical and electronic sensitization [7]. In this paper we show that the content of Ag on the surface of graphene is decisive to switch the specificity of material from NO_2 to NH_3, proving that the former analyte is mainly revealed by the free graphene surface, whereas the latter has a preferential interaction with the Ag. One suspension of pristine graphene (GR), prepared as described in ref [8] and two solutions of graphene/silver nanoparticles (GR/AgNPs) were prepared. Graphene suspension was mixed with ethylene glycol and $AgNO_3$ in aqueous solution at two molarity (0.1 M and 0.01 M) so obtaining suspensions with a different content of AgNPs. The suspensions were exposed to a microwave treatment, afterwards were centrifuged and washed. Chemiresistor devices were fabricated by drop-casting onto transducers. To investigate the effect of concentration of AgNPs on the graphene sensing properties, for each device, that is GR, GR/AgNPs-0.1M and GR/AgNPs-0.01M, the response to 240 ppb of NO_2 and 250 ppm of NH_3 gases was recorded (Figure 1). The sensor response, S, is defined as $S=G_{max}-G_0/G_0=\Delta G/G_0$ 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 noteworthy effect of Ag decoration was the strong enhancement of the device response towards ammonia respect to pristine graphene: an almost 20% decrease in the relative conductance was observed and shown in Fig.1 b and Fig.1 c respect to 2,5 % of GR. It was already observed that the presence of a native AgO layer onto the Ag NPs provides more effective adsorption sites for ammonia and stronger adsorption ability, which may be responsible for the significant sensing enhancement [9]. This series shows however another very interesting feature: the AgNPs concentration (Fig. 1 b and Fig. 2 c) switches the specificity of graphene versus NH_3. In fact, for lower AgNPs concentration, the free graphene surface is higher and so graphene is more strongly sensitive to NO_2 (Fig. 2 c). Further tests with other concentrations of silver nanoparticles, are currently ongoing with the aim to evaluate the minimum concentration of silver that ensures the specificity of GR/AgNPs device towards NH_3.

References

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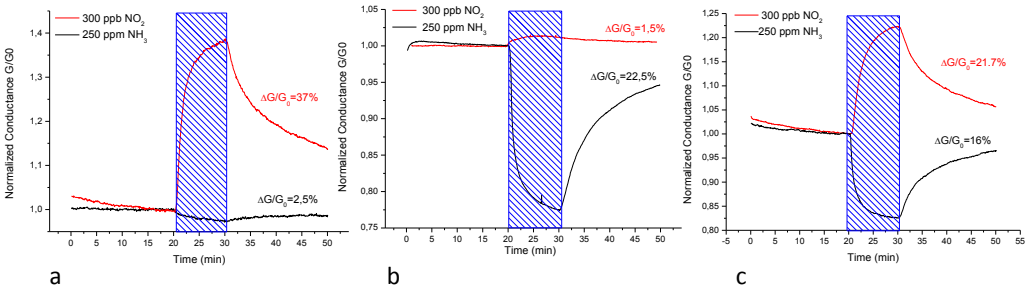

Figure 1: Dynamic responses of GR, GR/AgNPs-0.1M and GR/AgNPs-0.01M based devices towards NO_2 and NH_3. On the y-axis the normalized conductance is reported.

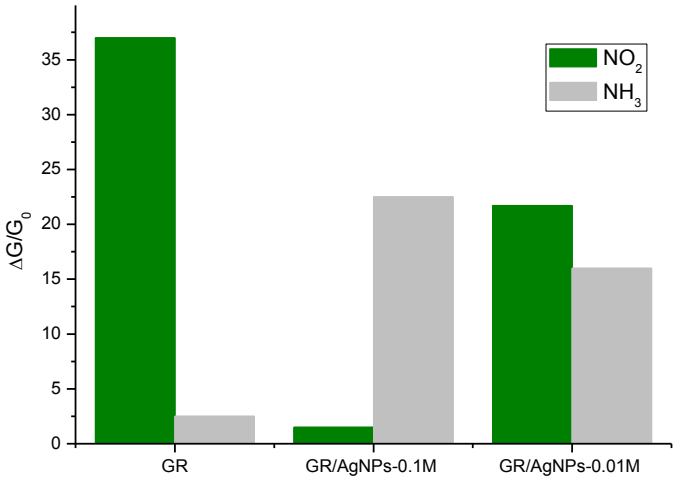

Figure 2: Summary of the sensing responses of GR, GR/AgNPs-0.1M and GR/AgNPs-0.01M based devices towards NO_2 and NH_3 For a better comparison, on the y-axis the absolute values of the device responses (|ΔG|/G0) are drawn.