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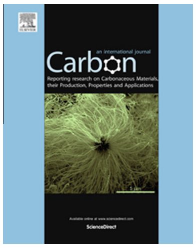

Graphene oxide coupled with gold nanoparticles for localized surface plasmon resonance based gas sensor

Michela Cittadini [a], Marco Bersani [a], Francesco Perrozzi [b], Luca Ottaviano [b,c], Wojtek Wlodarski [d], Alessandro Martucci [a,*]

[a] Dipartimento di Ingegneria Industriale, Università di Padova, Padova, Italy
[b] Dipartimento di Scienze Fisiche e Chimiche, Università dell'Aquila Via Vetoio 10, 67100 L'Aquila, Italy
[c] CNR-SPIN Uos L'Aquila, Via Vetoio 10, 67100 L'Aquila, Italy
[d] School of Electrical and Computer Engineering, RMIT University, Melbourne, Australia

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ABSTRACT

An optical gas sensor was prepared by depositing graphene oxide flakes over a monolayer of gold nanoparticles, chemically attached to a functionalized fused silica substrate. The coupling between flakes and nanoparticles lead to optical changes upon exposure to different gases: in particular, we observed a shift of the surface plasmon resonance band in presence of both reducing and oxidizing gases. This effect can be explained in terms of a strong gold–graphene interaction and specifically of electron transfer between the gold nanoparticles and the two-dimensional sheet of the sp^2-hybridized carbons of graphene oxide.

1. Introduction

In recent years, graphene has been attracting considerable attention due to its unique morphological and electronic properties [1,2]. Despite its interesting features some of the attention has diverted towards its partially oxidized form, graphene oxide (GO), that has emerged as an alternative to graphene for selected applications, thanks to its low cost, production scalability, ease of processing and good compatibility both with aqueous and organic solvents [1,3].

GO consists in atomically-thin graphene sheets that are covalently decorated with oxygen-containing functional groups, either on the basal plane or at the edges, so that it contains a mixture of sp^2- and sp^3-hybridized carbon atoms. In particular, tailoring of the size, shape and relative fraction of the sp^2-hybridized domains of GO by chemical or thermal reduction provides opportunities for tailoring its optoelectronic properties. For example, as-synthesized GO is insulating but just by varying the oxidation level, with a controlled de-oxidation, a partially reduced GO can act as a semiconductor [4].

It has been shown that GO can act as a photocatalyst for the production of H_2 from a 20 vol.% solution of methanol in water [5]; other studies [6] have explained this behavior by ab-initio modeling, suggesting that GO is particularly effective thanks to its clean band gap and providing criteria for the determination of the ideal oxidation state for a given application. Furthermore, its highly 2-dimensional nature, which determines huge surface-to-volume ratio, and efficient UV absorption make it a very promising material for photocatalysis [7] and suggest potential applications wherever its peculiar optoelectronic properties can be exploited.

In this work we used partially reduced GO coupled with Au nanoparticles (NPs) for optical gas sensing with the aim of combining the semiconducting and photocatalytic activity behavior of the partially reduced GO with the Localized

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* *Corresponding author.*
E-mail address: alex.martucci@unipd.it (A. Martucci).

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Surface Plasmon Resonance (LSPR) of gold NPs. The synergistic interplay between these materials resulted in an enhancement of the photocatalytic properties of GO [8], extending them to the visible range where the LSPR of Au NPs can be used as an optical probe. The LSPR is known to be extremely sensitive to the changes in the dielectric properties of the surrounding medium, a characteristic that has been widely exploited for the preparation of sensing devices [9,10]. Here we expect an even larger enhancement of this effect induced by the electronic coupling of Au NPs and GO and the interactions of GO with reducing and oxidizing gases. While the use of GO for gas sensing has been covered in multiple reports [11–13], with the GO–Au NPs system already employed as a resistive gas sensor [14], only very recently GO has been used in an optical fiber array for the detection of vapors [15] and to the best of our knowledge this is the first time that GO is used as sensing material in an optical sensor for the detection of reducing and oxidizing gases. Moreover Au NPs exhibit a well-established, wavelength-dependent optical response, which can be exploited as a means to improve the selectivity of the sensor using wavelength modulation.

2. Experimental

2.1. Synthesis of Au NPs

Gold colloids, were prepared according to the Turkevich method [16] by reducing $HAuCl_4$ with trisodium citrate in water, and were successively capped with poly (vinyl pyrrolidone) (PVP, MW = 10,000) according to the method described by Della Gaspera et al. [17], resulting in a final concentration of 30 mM in ethanol.

2.2. Preparation of Au monolayers

Au monolayers have been prepared on fused silica slides or silicon. The substrate was first functionalized with (3-aminopropyl) trimethoxysilane (APTMS) as described in [18]. To deposit the monolayer, we used Au NPs PVP capped using the procedure reported in [18]. The monolayers were formed by spin-coating at 3000 rpm for 30 s the liquid suspensions of gold NPs directly onto the APTMS.

In this study, we prepared Au monolayers with 2 different extents of surface coverage, hereafter indicated as low (L), and high (H). L and H samples have been obtained by spinning 15 and 30 mM Au NPs solution, respectively. The as-deposited monolayer samples were thermally treated at 150 °C for 30 min in air. Following this stabilizing treatment, the samples were used as substrates for the GO deposition.

2.3. GO deposition

Commercial (Graphene Supermarket [19]) GO solution with a concentration of 0.5 mg/mL has been spin coated on the Au monolayers in two successive depositions, the first at 3000 rpm and the second at 2000 rpm in order to increase the flakes density, and the resulting samples were annealed at 150 °C for 1 h in air. As the annealed GO samples resulted to be partially reduced (see Section 3), such samples have been labeled rGO.

2.4. Sample characterizations

Atomic Force Microscopy (AFM) images have been acquired in air using a Veeco Digital D5000 system equipped with silicon tip.

Scanning Electron Microscopy (SEM) images have been acquired with a Zeiss-Gemini LEO 1530 system.

X-ray photoemission spectroscopy (XPS) spectra have been acquired with a PHI 1257 spectrometer equipped with a monochromatic Al Kα source ($h\nu = 1486.6$ eV) with a pass energy of 11.75 eV, corresponding to an overall experimental resolution of 0.25 eV. The acquired XPS spectra have been fitted with Voigt line shapes and Shirley backgrounds.

2.5. Gas sensing measurements

Optical gas sensing tests were performed by conducting optical absorption measurements in the 200–900 nm wavelength range on films deposited on SiO_2 substrates using a Harrick gas flow cell (with 5.5 cm path length) coupled with a Jasco V-650 spectrophotometer. The operating temperature (OT) was set at 150 °C and the sensor was tested for both reducing and oxidant gases, (H_2, CO, NO_2) all balanced with synthetic air, with a flow rate of 0.4 L/min. In particular, the concentration of H_2 was set at 10,000 and 100 ppm; the concentration of CO was set at 10,000 ppm; the concentration of NO_2 was set at 1 ppm in order to minimize the effects related to its optical absorption in the analytical range.

The substrate size was approximately 1×2 cm and the incident spectrophotometer beam was normal to the film surface and covered a 9×1.5 mm area of the film.

The time spent by the sensor on achieving 90% of the total absorbance change is defined as the response time in the case of gas adsorption or as the recovery time in the case of gas desorption.

For the UV irradiation it has been used a Hamamatsu LC6 lamp with an intensity of 460 mW cm^2 at 365 nm. The samples were illuminated at a distance of 2 cm for 60 s.

3. Results and discussion

3.1. Structural and optical properties

The UV–Vis spectra of the gold monolayer are reported in Fig. 1. In accordance with previous publications, an increase of the surface coverage results in both an increase of intensity and a red shift of the Au NPs LSPR peak [20,21]. The increase in absorbance with higher surface coverage is simply related to the larger cross-section of the NPs interacting with the incoming beam, while the red shift of the plasmon absorption can be ascribed to the decrease in the interparticle distance: the stronger coupling of the localized plasmon on neighboring Au NPs results in the red-shift of the plasmon resonance [22].

SEM images of the metal NP monolayers are reported in Fig. 2, from which it is possible to note that the Au NPs are