Sensors and Actuators B 202 (2014) 523–526

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Nanochemical fabrication of a graphene oxide-based nanohybrid for label-free optical sensing with fiber optics

Lucia Sansone[a], Viera Malachovska[a], Pietro La Manna[a], Pellegrino Musto[a], Anna Borriello[a,*], Giovanna De Luca[a,b,*], Michele Giordano[a]

[a] IPCB-CNR, Istituto per i Polimeri Compositi e Biomateriali, Napoli, Italy
[b] Dipartimento SCIFAR, University of Messina, Messina, Italy

ARTICLE INFO

Article history:
Received 12 February 2014
Received in revised form 14 May 2014
Accepted 14 May 2014
Available online 4 June 2014

Keywords:
Graphene oxide
Optical fiber
Sensor

ABSTRACT

In this article, we report our latest research results concerning the possibility to develop a chemical probe sensor based on reduced graphene oxide. In particular, a layered nanohybrid consisting of a nanostructured Ag surface and of reduced graphene oxide has been fabricated on an optical fiber, and used as a model device aiming to label-free optical gas sensing. A semitransparent, conductive Ag coating has been fabricated on the optical fiber via wet chemistry, and used as electrode for the electrophoretic deposition of an ultrathin layer of graphene oxide. After in situ reduction, the reduced graphene oxide layer has been used as functional organic coating for label-free optical sensing of water and ammonia vapors.

1. Introduction

To combine nano- and supramolecular chemistry concepts has become a simple but powerful approach to the bottom-up fabrication of complex functional architectures [1,2]. Nanostructured materials with applications spanning from organic electronics to nano medicine are often obtained via a careful control of hierarchical interactions among molecular or nano sized building blocks in solution [3–5]. Among these, graphene, the solution-processable graphene oxide (GO) and its reduced form (rGO) have attracted scientists' attention due to their applicability as 2D nanomaterials in many different fields [6–8]. Several examples can be found in the literature investigating the behavior of these species as active layers in sensing devices based on different transduction principles [9–13].

Here we report on the nanochemical approach to the fabrication of a bilayered Ag/rGO nanohybrid right at the tip of a standard single mode optical fiber, as a model label-free optical sensor working in reflection mode. A fiber optics transduction solution offers many sought-after advantages, allowing to work in harsh (or difficult to be reached) environments, enabling remote sensing and multiplexing, and coupling real-time detection capability with low costs and broad applicability [14]. As well, optical sensors are compatible with a label-free detection protocol in which the analytes are detected in their pristine, unlabeled forms, e.g. monitoring changes in the refractive index as the sensing transduction signal [15,16].

2. Results and discussion

Our experimental design exploits the sensitivity of the optical signal, which is reflected by the internal interface of a suitably cleaved optical fiber, to the changes in the refraction index occurring at its external interface. This setup also allows the construction of the active nanoarchitecture to be monitored in real time, building the functional layers with a great control over the various fabrication stages. The basic steps carried out to fabricate the active nanohybrid can be summarized as follows: (i) electroless deposition of a conductive, semitransparent silver nanolayer [17]; (ii) electrophoretic deposition of a GO nanolayer onto the Ag-coated surface [18]; (iii) in situ chemical reduction of GO to rGO [19].

The deposition of a semitransparent, nano-structured Ag layer at the fiber end is carried out *via* electroless plating: the tip of a cleaved, single mode optical fiber is immersed in an aqueous solution containing diamine silver (I) ions (Tollens' reagent) and D-glucose, right after mixing the reagents [17]. The reflectance signal from the fiber tip increases as the electroless plating proceeds, and this observable can be used to monitor the formation kinetics of the Ag layer (Fig. 1a). Its growth can be controlled by influencing the reaction rate of $[Ag(NH_3)_2]^+$ reduction to Ag, which can, in fact, be slowed down by an increase of NH_3 concentration in

---

* Corresponding authors at: National Research Coucil, Istituto per i Polimeri Compositi e Biomateriali, p.le Fermi, 1, 80055 Portici Napoli, Italy. Tel.: +39 0817758814.

E-mail addresses: borriell@unina.it (A. Borriello), delucag@unime.it (G. De Luca).

http://dx.doi.org/10.1016/j.snb.2014.05.067
0925-4005/

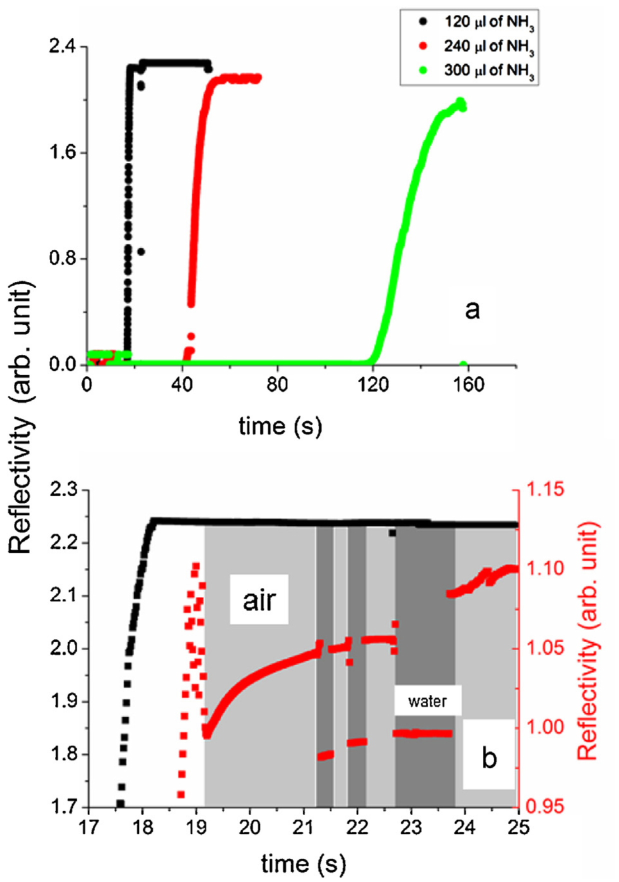

Fig. 1. (a) Change in reflectivity signal, as detected through the optical fiber setup, during the kinetics of formation of the silver film at the fiber tip, as a function of ammonia concentration. (b) Sensitivity to changes in the index of refraction by the fiber tip (air/water) for completely (black) or partially (red) metalized fibers, showing that a clear response can be obtained by the optical setup in the second case. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

solution (Fig. 1a). The experimental evidence indicates an inverse proportionality between ammonia concentration and the global rate of tip metallization, with an increase in the nucleation time (Fig. 1a, black arrows) and a decrease in the rate at the growth regime (Fig. 1a, green arrows) as [NH_3] increases. This allows to finely tune the transparency of the metallic layer, and to couple the formation of a conductive layer to the ability of the device to sense the changes in the external index of refraction, e.g. like those occurring when the tip goes from air to water (Fig. 1b; *n* value at $\lambda = 589.3$ nm: 1.0003 and 1.333, respectively. As well, an amplification of the variation in the reflectivity signal is obtained after tip metallization ($\Delta refl_{\text{Ag-coated}}/\Delta refl_{\text{bare}}$: ~25, see Fig. S1), technically allowing a greater sensitivity to changes in the environmental refraction index[1]. SEM and EDS analyses confirm that a nanostructured Ag layer now covers the fiber tip surface (Fig. 2a), the film conductivity having been verified by using it as electrode against a Pt counter electrode ($V = 3$ V) in a NaCl solution.

The metalized tip can be then used as anode in the second step of the fabrication process, where it is immersed in a NMP suspension of GO (100 ng/mL) together with a Pt cathode, to obtain the electrophoretic deposition of the negatively charged nanoflakes [18] onto the Ag surface. As soon as a 3 V bias is applied, a small current starts flowing in the circuit thanks to the presence of the GO nanosheets (~15 or 0.1 μA, in the presence or absence of GO, respectively). Again, this process can be observed in real time by monitoring the reflectance signal from the semitransparent tip, which varies as GO is depositing onto the fiber optics surface (Fig. 3a). This step is carried out for few minutes during which the current intensity decreases in time as the deposition proceeds.

The process is stopped when both the current and the optical signal intensities reach a plateau (Fig. 3a), GO coverage being finally checked after thoroughly washing the tip in clean solvent and drying it. SEM analysis confirms that an ultrathin film of GO has been deposited on the optical fiber end through this method (Fig. 2b–d), obtaining a very smooth and uniform surface once the deposition parameters, e.g. voltage or GO concentration, have been optimized (see Experimental details in Supporting information). High concentrations (~1 mg/mL) of suspended GO nanosheets seem to work against the deposition of a good quality film, as a non-uniform surface coverage and the presence of lumps across the surface is observed (Supporting information Fig. S2a), probably due to a poorer dispersion of the material in the starting suspension in NMP. As well, when a higher bias is used (10 V), the anisotropy of the electric field at the tip causes a preferential deposition of GO at the edges of the fiber optics end (Supporting information Fig. S2b). A qualitative evidence of the small thickness and uniformity of the deposited films is given by SEM images recorded by using different beam energies: going from 5 to 20 kV, the morphological details in the images go from those of the very smooth GO surface to those of the grainy Ag coating lying beneath it (Fig. 2 b–d).

Once a GO film has been formed on the tip of the metalized optical fiber, it can be subjected to reduction by hydrazine vapors (room temp., 30 min). During this step, the reflectance signal is not stable due to the changing density of the reducing vapors by the fiber tip, and the progress of GO reduction cannot be followed in real time. SEM analysis show that after reduction the film surface appear more rugged and flaky (Fig. 3b, inset), but no statistically relevant change in its chemical composition has been detected. So, Raman spectroscopy has been used as a more reliable way to provide evidence on the efficiency of the reduction of the films.

Raman spectra of GO and reduced GO are reported in Fig. 3b, the bands associated at ~1350 and ~1610 cm^{-1} correspond to D and G modes, respectively, the first corresponding to the destruction of sp^2 network by the sp^3-bonded C atoms, and the second to the bond stretching of all pairs of sp^2 atoms in both rings and chains [20,21].

The reduction of GO restores the G band to 1581 cm^{-1} and corresponds to the recovery of the hexagonal network of carbon atoms going from GO to rGO. The increase in the intensity ratio of the G to D bands (Fig. 3b and Fig. S3) can be attributed to the decrease in the defect concentration, i.e. an increase in the size of the sp^2 domains, as the reduction proceeds.

After the fabrication of the layered nanohybrid architecture have been attained as described above, we have carried out some preliminary investigations to test its behavior as model label-free sensor for the detection of species in the vapor phase, such as H_2O or NH_3 (Fig. 4). Going from air to H_2O or NH_3 vapors, no change in reflectance is observed if the optical fiber coated with pristine GO is used as sensor (black lines).Contrarily, a strong response is detected through the same optical setup after GO is reduced by hydrazine vapors (red lines). This same behavior has been observed in conductance-based sensors, where a chemically reduction step restores sensibly the conductivity of the insulating GO layer due to oxygen removal and recovery of aromatic double-bonded carbons [8]. In our case the detection is based on a change in the optical signal, as a feasible consequence of a change in the refractive index of GO and of rGO upon interaction with the gas molecules. Interestingly, the change in reflectance is in opposite directions for the two vapors, with an approximate 20% output

---

[1] The complex, non-reversible increase of reflectivity observed with time for the red line is probably due to the solubilisation of D-glucose residues on the Ag surface.