Photoluminescence of Graphene Oxide Infiltrated into Mesoporous Silicon

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ABSTRACT: Graphene oxide (GO) is a photoluminescent material whose application in optoelectronics has been strongly limited due to its poor emission intensity. In this work, a GO–porous silicon (GO–PSi) hybrid structure is realized in order to investigate the emission properties of GO infiltrated into a porous matrix. GO–PSi is characterized by Fourier transform infrared spectroscopy, spectroscopic reflectometry, and steady-state photoluminescence. A photoluminescence enhancement by a factor of 2.5 with respect to GO deposited on a flat silicon surface is demonstrated. Photoluminescence measurements also show a modulation of the emitted signal; this effect is attributed to the interference phenomena occurring inside the PSi monolayer.

1. INTRODUCTION

Graphene oxide (GO) is composed of graphene sheets modified with oxygen functional groups in the form of epoxy and hydroxyl groups on both the basal plane and edges.1,2 In recent years, GO has received great interest because of its superior dispersion ability in water and a finite electronic band gap different with respect to graphene.3 Because of these properties, several applications ranging from electronic to biomedical field have been proposed.4–6 Innovative biosensors based on GO surface functionalization with small molecules or polymers through activation and amidation/esterification of either the carboxyls or hydroxyls have been demonstrated.7 In addition, new perspectives in optoelectronics have been opened by the discovery of the steady-state photoluminescence (PL) properties of GO. A broad PL emission from 500 to 800 nm has been reported.8 Unfortunately, GO PL is very weak due to the presence of oxygen functionalities (e.g., hydroxyl and epoxy groups) producing nonradiative recombination as a result of transfer of their electrons to the holes present in sp² clusters.9 Many approaches based on oxidation or reduction treatments have been followed to get higher PL emission from GO.10,11 A new approach could be to infiltrate GO into large specific surface area substrates, and porous silicon (PSi), realized by electrochemical dissolution of crystalline silicon in a hydrofluoridric-based solution, is a perfect candidate for this task. PSi is characterized by a sponge-like morphology with a specific surface area up to hundreds of m² cm⁻³. This property makes PSi an ideal support for sensing of different substances such as gases, liquids, and biological molecules.12–14 Changes of several physical properties (e.g., dielectric constant and electrical conductivity) can be observed after infiltration of an analyte inside nanometric pores. Moreover, the PSi refractive index can be widely tuned between that of Si and air (approximately). This is achieved by varying the porosity of PSi during the electrochemical fabrication process. Owing to these characteristics, a lot of photonic structures, such as Fabry–Perot interferometers, Bragg mirrors, and microcavities, have been proposed.12,15,16

In this work, we investigated enhancement and wavelength modulation of photoluminescence signal of GO sheets infiltrated by spin-coating technique into silanized mesoporous silicon. GO-modified PSi layer was characterized by spectroscopic reflectometry, Fourier transform infrared spectroscopy, and steady-state photoluminescence. This hybrid structure showed an intense and wavelength-modulated photoluminescence signal on a broad range of optical frequencies.

2. MATERIALS AND METHODS

2.1. Preparation of Graphene Oxide. The graphene oxide (GO) was purchased from Cheap Tubes, Inc. (USA). The GO was synthesized from purified natural graphite by the modified Hummers method.15–19 Ten milligrams of GO powder was suspended in 5 mL of distilled water (D.I. was purchased from Aldrich Chemical Co.) and sonicated by means...
of an ultrasonic processor (Misonix Incorporated Ultrasound liquid Processors, U.S.A.) for 4 h at room temperature so as to produce a stable yellow–brown colloidal suspension of GO sheets. Solution was then filtered with pore size of 0.22 μm (Millipore).

2.2. Porous Silicon Layer Fabrication. PSi was fabricated by electrochemical etching of p⁺ crystalline silicon (0.001 Ω cm resistivity, ⟨100⟩ oriented, 500 μm thick) in hydrofluoric acid (HF; 50% in weight)/ethanol = 1:1 solution, in dark and at room temperature. Before the anodization process, the silicon substrate was immersed in HF solution for 2 min to remove the native oxide layer. A current density of 200 mA/cm² was applied for 15 s to produce a single layer of PSi with a porosity of 72% (n = 1.54) and a thickness of 2 μm. Porosity and thickness of PSi layer were estimated by spectroscopic ellipsometry (data not shown here). After the electrochemical process, pore dimension was increased to favor the infiltration of graphene oxide by rinsing the “as-etched” PSi layer in a KOH−ethanol solution (1.5 mM) for 15 min.20

PSi sample was immersed in Piranha solution, a 4:1 mixture of concentrated sulfuric acid (H₂SO₄; was purchased from Aldrich Chemical Co.) and 30% hydrogen peroxide (H₂O₂; 30% w/w was purchased from Aldrich Chemical Co.), for 40 min in order to ensure the formation of Si−OH bonds on its surface. After Piranha treatment, sample was rinsed with deionized water and dried in a nitrogen stream. Afterward, the PSi surface was silanized (i.e., functionalized by aminosilane) by incubating the chip in a 5% v/v solution of 3-aminopropyltriethoxysilane (APTES was purchased from Aldrich Chemical Co.) and anhydrous toluene (anhydrous 99.8% was purchased from Aldrich Chemical Co.) for 30 min at room temperature.21−23 After the reaction time, we washed three times the sample in toluene so as to remove any physisorbed APTES and baked it at 100 °C for 10 min.

2.3. Graphene Oxide Infiltration into Porous Silicon Layer. GO solution was infiltrated into aminosilane-modified PSi layer by spin-coating processing (Karl Suss Microtec Delta 80T) with a defined delay time, prior to spinning, necessary for GO infiltration. PSi substrate was completely covered with sufficient amount of the GO solution, allowed to stand for 60 s, after which the sample was allowed to spin at 600 rpm for 60 s to cause uniform spreading of the solution on the substrate, then at 800 rpm for 60 s to thin the solution layer, and finally at 1600 rpm for 60 s to dry the film. After spin coating, the sample was dried in desiccator overnight at room temperature.

2.4. Dynamic Light Scattering. Size distribution of GO sheets dispersed in water (pH = 7) was investigated by dynamic light scattering (DLS) using a Zetasizer Nano ZS (Malvern Instruments, U.K.) equipped with a He−Ne laser (633 nm, fixed scattering angle of 173°, 25 °C).

2.5. Atomic Force Microscopy. A XE-100 AFM (Park Systems) was used for the imaging of GO sheets deposited on silicon substrate. Surface imaging was obtained in noncontact mode using silicon/aluminum coated cantilevers (PPP-NCHR 10M; Park Systems) 125 μm long with resonance frequency of 200 to 400 kHz and nominal force constant of 42 N/m. The scan frequency was typically 1 Hz per line.

2.6. Scanning Electron Microscopy. The morphology of GO infiltrated PSi layer was investigated by scanning electron microscopy (SEM) using a field emission instrument (Zeiss-Supra 35). Sample was mounted on a double-faced conductive adhesive tape. Images were acquired at 5 kV accelerating voltage and 30 μm wide aperture.

2.7. Fourier Transform Infrared Spectroscopy. Chemical composition of PSi layer before and after GO infiltration was analyzed by Fourier transform infrared (FTIR) spectroscopy. Spectra were recorded by a Thermo-Nicolet NEXUS Continuum XL (Thermo Scientific) equipped with a microscope, at 2 cm⁻¹ resolution.

2.8. Spectroscopic Reflectometry. The reflectivity spectra of PSi samples were measured at normal incidence by means of a Y optical reflection probe (Avantes), connected to a white light source and to an optical spectrum analyzer (Ando, Figure 1. Size distribution of graphene oxide in water, analyzed by DLS (A). AFM image of graphene oxide deposited on silicon and corresponding height measurement (B).
AQ6315B). The spectra were collected over the range 600−1200 nm with a resolution of 0.2 nm.

2.9. Steady-State Photoluminescence. Steady-state photoluminescence (PL) spectra were excited by a continuous wave He–Cd laser at 442 nm (KIMMON Laser System). PL was collected at normal incidence to the surface of samples through a fiber, dispersed in a spectrometer (Princeton Instruments, SpectraPro 300i), and detected using a Peltier cooled charge coupled device (CCD) camera (PIXIS 100F). A long pass filter with a nominal cut-on wavelength of 458 nm was used to remove the laser line at monochromator inlet.

3. RESULTS AND DISCUSSION

Even if GO sheets are nanometric in size, their infiltration in a porous material, such as a PSi layer, requires a careful characterization of both the GO size distribution and the PSi pores average dimension. Size distribution of GO nanosheets dispersed in water (pH = 7) at a concentration of 2 mg/mL was investigated by DLS analysis. Results, reported in Figure 1A, highlight the presence of two peaks corresponding to 30 ± 5 and 110 ± 40 nm size populations (poly dispersion index; PdI = 0.211). It is worth noting that the heights of two peaks shown in Figure 1A are related to the scattering intensities and not to the amount of small and big GO particles. The low value of PdI indicates that GO sample is constituted by only two populations, but we cannot say which is the most abundant. AFM image of GO deposited on flat crystalline Si and corresponding height profile of GO sheets are reported in Figure 1B. Nanosheets with different sizes ranging from few tens of nanometers to hundreds of nanometers can be observed. Height measurement demonstrates the presence of sheets up to 4 nm thick. Since a single-layered sheet is known to be as high as 1 nm,24 the measured thickness is compatible with a multilayered morphology.

The chemical nature of graphene oxide was confirmed by Raman spectroscopy. Raman spectrum of GO deposited on
crystalline silicon is reported in Figure S1, Supporting Information: the broad G and D peaks and the low intensity 2D and D + G bands characteristic of GO \(^2\) are clearly visible.

In our experience, GO cannot be simply deposited in the PSi sponge-like matrix by drop casting and spin coating: without a proper chemical modification of the PSi surface, we did not obtain any infiltration of GO into the PSi. On the contrary, GO strongly interacts with a silanized surface. For this reason, GO solution was spin-coated on PSi layer modified by APTES. Silanization procedure is crucial to guarantee interaction between GO and PSi surface: carboxyl and epoxy groups of GO can interact with positively charged amine group of APTES forming a stable GO−PSi hybrid structure.\(^2\) Figure 2 shows SEM top view images of an aminosilane-modified GO layer deposited on the chip surface. The thickness of this layer highlights GO in the PSi structure, reported in Figure 2C. The image highlights GO infiltrated along nanometric PSi pores as well as GO layer deposited on the chip surface. The thickness of this GO layer is just of few nanometers, much smaller than the overall PSi thickness (approximately 2 μm).

Chemical composition of the hybrid structure was investigated by FTIR analysis. Figure 3 shows FTIR spectra of aminosilane-modified PSi (A), GO deposited on flat crystalline silicon support (B), and GO infiltrated in aminosilane-modified PSi (C). FTIR spectrum of bare silanized PSi is characterized by the peak at 1100 cm\(^{-1}\), corresponding to Si−O−Si bond, and the peak at 955 cm\(^{-1}\), corresponding to Si−OH group, both due to Piranha treatment in strong acid. Surface aminosilane modification is demonstrated by the presence of peaks at 1475 and 785 cm\(^{-1}\), indicating amine and SiOCH\(_2\)CH\(_3\) groups, respectively.\(^2\) In the spectrum of GO deposited on crystalline silicon, a peak at 1740 cm\(^{-1}\) corresponding to C＝O carbonyl stretching of −COOH can be observed; other peaks are present at 1640 cm\(^{-1}\) for C＝C and at 1460 cm\(^{-1}\) for CH\(_2\) deformation vibrations. The broad band located at about 970 cm\(^{-1}\) can be assigned to epoxy group.\(^2\) FTIR spectrum of GO infiltrated aminosilane-modified PSi shows peaks characteristic of both silanized PSi and GO, demonstrating the formation of the hybrid structure.

The optical spectrum of a PSi layer consists of a fringe pattern due to interference occurring at air/PSi and PSi/bulk crystalline silicon interfaces. In other words, the PSi layer optically acts as a Fabry−Perot interferometer whose reflectance can be written as

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R(\lambda) = \frac{\left( r_1 + r_2 \right) + 2r_1r_2 \cos\left(\frac{4\pi n_{\text{PSi}}L}{\lambda}\right)}{\left( r_1 + r_2 \right) - 2r_1r_2 \cos\left(\frac{4\pi n_{\text{PSi}}L}{\lambda}\right)}
\]

where \(r_1 = \left( \frac{n_{\text{Air}} - n_{\text{PSi}}}{n_{\text{Air}} + n_{\text{PSi}}} \right)\) is the Fresnel reflection coefficient at air/PSi interface, \(r_2 = \left( \frac{n_{\text{PSi}} - n_{\text{Si}}}{n_{\text{PSi}} + n_{\text{Si}}} \right)\) is the Fresnel reflection coefficient at PSi/crystalline silicon interface, \(L\) is the thickness of the PSi layer, \(\lambda\) is the wavelength, and \(n_{\text{Air}}, n_{\text{PSi}},\) and \(n_{\text{Si}}\) are the refractive indices of air, porous silicon layer, and bulk silicon, respectively. The optical path (\(n_{\text{PSi}}L\)) of the PSi layer can be calculated from the reflectivity spectrum just counting fringe maxima, which satisfy the relationship \(m\lambda = 2n_{\text{PSi}}L\), where \(m\) is an integer and \(\lambda\) is the wavelength of the incident light.\(^3\) A faster method for calculating the optical path is based on the fast Fourier transform (FFT) of PSi reflectivity spectrum. FFT of the spectrum displays a peak whose position along the x-axis corresponds to two times the optical path (2\(n_{\text{PSi}}L\)) of the layer.

In Figure 4A, normal incidence reflectivity spectra are shown for aminosilane-modified PSi layer before and after GO infiltration. The corresponding Fourier transforms, reported in Figure 4B, show two peaks centered at 5800 and 6000 nm, before and after GO infiltration, respectively. Since the thickness \(L\) of the layer is fixed, the peak shift of about 200 nm is ascribed to the increase of the PSi layer average refractive index. The GO solution penetrates into the porous silicon matrix, and some nanosheets bind the silanized porous silicon surface, partially filling the pores. Since air is displaced by GO into the pores, the layer density increases, and as consequence, the average refractive index increases, too. Considering a PSi thickness of 2000 nm, a refractive index increase of 0.05 after GO infiltration can be calculated.

Since SEM characterization showed the presence of a thin GO layer on the top of PSi surface that could clog pores, we investigated their accessibility exposing GO−PSi hybrid device to ethanol vapors. It is well-known that vapors of volatile substances can condensate into nanometric pores by capillary condensation inducing an increase of the average refractive index of the PSi layer and a consequent red shift of its optical spectrum. Figure 5 reports the reflectivity spectra (A) of bare
PSi in air and on exposure to ethanol vapors together with corresponding FFTs (B). We observed a FFT shift of 50 nm due to ethanol condensation inside pores of the PSi device.\textsuperscript{29} The experiment was repeated in the case of GO−PSi device. Spectra are shown in Figure 5C, together with corresponding FFTs (Figure 5D): a FFT peak shift of 100 nm was measured. The larger shift is due to the presence of GO nanosheets that, coating the pores wall of the hybrid device, reduce their diameter making the structure more sensitive, according to the Clausius−Kelvin equation, which rules the condensation.\textsuperscript{31}

This experimental result demonstrates that, even if GO nanosheets are deposited onto and inside the PSi, the pores are still accessible to organic vapors, probably due to both the presence of voids between the GO sheets and the partial permeability of these extremely thin (just few nanometers) layers, whereas thicker and more compact GO coatings have been found to be quite impermeable.\textsuperscript{32}

The PL signal emitted from GO nanosheets infiltrated in PSi in air and on exposure to ethanol vapors together with corresponding FFTs (B). We observed a FFT shift of 50 nm due to ethanol condensation inside pores of the PSi device.\textsuperscript{29} The experiment was repeated in the case of GO−PSi device. Spectra are shown in Figure 5C, together with corresponding FFTs (Figure 5D): a FFT peak shift of 100 nm was measured. The larger shift is due to the presence of GO nanosheets that, coating the pores wall of the hybrid device, reduce their diameter making the structure more sensitive, according to the Clausius−Kelvin equation, which rules the condensation.\textsuperscript{31}
silanized PSi and of GO spin-coated on silanized crystalline silicon, for comparison. As it is well-known, any PL signal cannot be detected in the case of p+ PSi. A weak and broad photoluminescence was measured in the case of GO spinned on silanized Si in the wavelength range between 500 and 800 nm. This very low signal is due to the presence of a thin GO layer, with an average height of about 3 nm (see AFM characterization reported in Figure 1). After infiltration in PSi, a strong enhancement of the PL emitted from GO by a factor of almost 2.5 with respect to GO on crystalline silicon was experimentally measured. This strong enhancement in PL emission was attributed to the high GO concentration inside the sponge-like PSi structure. Moreover, a modulation of the photoluminescence signal can be observed, too. PL intensity modulation can be explained by considering the theory of the Fabry–Perot interferometer. Among all the wavelengths, \( \lambda_{\text{em}} \) emitted by GO infiltrated in PSi, only those fulfilling the relationship \( L = m(\lambda_{\text{em}}/2n_{\text{PSi}}) \), with \( L \) thickness of the PSi layer and \( m \) integer, can constructively interfere forming maxima in the photoluminescence spectrum of hybrid structure. As it can be seen in Figure 6B, the distance between two consecutive maxima/minima in the reflectivity/transmittivity spectrum of an interferometer) of the GO–PSi hybrid structure. In order to exclude the possibility that the interference fringes present in photoluminescence spectrum of GO–PSi device could be due to the thin GO layer deposited on the PSi interferometer surface and not to the material infiltrated inside pores, GO was spinned on a layer of aminosilane-modified amorphous silicon (aSi), 800 nm thick. The homogeneous layer (not porous) of aSi acts as an interferometer with a free spectral range (i.e., distance between two consecutive maxima/minima in the reflectivity/transmittivity spectrum of an interferometer) of 0.05. In addition, a strong enhancement of the PL emitted from GO by a factor of almost 2.5 with respect to GO on crystalline silicon has been experimentally measured. Wavelength modulation of GO photoluminescence emission is very attractive and opens new perspectives for GO exploitation in innovative optoelectronic devices and high sensitive fluorescent sensors.

4. CONCLUSIONS

This work demonstrates the enhancement and the modulation of the photoluminescence signal emitted by GO nanosheets infiltrated in silanized mesoporous silicon matrix. The formation of GO–PSi hybrid structure is confirmed by several spectroscopic techniques, such as FTIR spectroscopic reflectometry and steady-state photoluminescence. FFT analysis reveals a refractive index increase, due to the infiltration of GO inside the PSi layer, of 0.05. In addition, a strong enhancement of the PL emitted from GO by a factor of almost 2.5 with respect to GO on crystalline silicon has been experimentally measured. Wavelength modulation of GO photoluminescence emission is very attractive and opens new perspectives for GO exploitation in innovative optoelectronic devices and high sensitive fluorescent sensors.

ASSOCIATED CONTENT

Supporting Information
Raman analysis, aSi optical characterization, and confocal microscopy imaging. This material is available free of charge via the Internet at http://pubs.acs.org.

Figure 6. Photoluminescence spectra of aminosilane-modified PSi (solid line), GO on silanized Si (dashed line), and GO infiltrated in silanized porous Si layer (short dashed line) at an excitation wavelength of 442 nm (A). Comparison between photoluminescence spectrum (upper graph) and reflectivity spectrum (lower graph) of GO-infiltrated PSi layer (B).
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Notes
The authors declare no competing financial interest.

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