## Fabrication of a 2D Nanohybrid Structure in Graphene Oxide for Fluorescent Sensing

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A layered nanohybrid consisting of Graphene Oxide (GO) has been fabricated on silanized Porous silicon (PSi) matrix. An enhancement of the photoluminescence (PL) emitted from GO nanohybrid by a factor of 2.5 with respect to GO on crystalline silicon was successfully demonstrated. Moreover, a wavelength modulation of GO PL emission was observed. This modulation takes on attractive aspect for research in innovative optoelectronic devices and high sensible fluorescent sensors.

Materials with high efficiency and stable luminescent are of technological importance in optoelectronic devices, biological labeling and sensing. Intensive efforts have been made in the research of new efficient emitters such as semiconductor quantum dots, silicon nanoparticles, gold nanodots, and carbon-based nanomaterials including carbon nanotubes, nano-diamond and carbon dots (C-dots). Among those materials, the fluorescent carbon-based nanomaterials have been attracted much more attention because they show more stable emissions and lower cytotoxicity. The origin of photoluminescence (PL) in these carbon-based nanomaterials is tentatively proposed to be from isolated polyaromatic structures or passivated surface defects. However, the preparation of these carbon nanomaterials usually shows a very low yield and is carried out under extreme conditions, e.g. laser ablation, high temperature and high pressure [1-4].

A GO nanosheet, a two-dimensional material, contains isolated polyaromatic clusters and can be easily exfoliated from graphite with a high yield under simple oxidizing conditions. While it has been widely studied in regard to electrical conductivity, drug delivery, self-assembly, and surface functionalization [5], the PL properties of GO have rarely been explored due to its low emission efficiency [6].

In this work, a new approach has been investigated in order to enhance and wavelength modulate the photoluminescence signal of GO, based on the infiltration of GO sheets into silanized mesoporous silicon by spin-coating technique. This hybrid structure showed an intense and wavelength-modulated photoluminescence signal on a broad range of optical frequencies opening new perspectives for GO exploitation in innovative optoelectronic devices and high sensible fluorescent sensors.

PSi was prepared by electrochemical etching of highly doped p-type crystalline silicon (0.001  $\Omega$  cm resistivity, <100> oriented, 500 µm thick) in HF solution (25%) in dark at room temperature. After electrochemical process, pores dimension was increased to favor the infiltration of GO by rinsing the fresh-made PSi devices in a KOH ethanol solution (1.5 mM) for 15 min. The PSi structure was then thermally oxidized against uncontrolled environmental aging. PSi sample was immersed in Piranha solution (H<sub>2</sub>O<sub>2</sub>:H<sub>2</sub>SO<sub>4</sub> 1:4) for 30 min at room temperature so as to generate Si-OH groups on the PSi surface and extensively washed in distilled water flow and dried with nitrogen gas. The structure was silanized by immersion in 5% aminosilane APTES/dry toluene solution for 30 min at room temperature, in order to facilitate the formation of hybrid GO-PSi interface via ionic interactions [7].

GO was purchased from Cheap Tubes, Inc (USA); GO powder (10 mg) was suspended in 5 mL of distilled water and sonicated by an ultrasonic processor for 4 hours at room temperature, producing a stable yellow-brown colloidal suspensions of GO sheets. Solution was then filtered with pore size

of 0.22 µm and infiltrated into aminosilane-modified PSi layer by spin-coating processing (Karl Suss Microtec Delta 80T). PSi substrate was completely covered with sufficient amount of the GO solution, after which the sample was spun. After spin coating, the sample was dried.

Figure 1 shows SEM top view images of an aminosilane-modified PSi layer before (see, Figure 1a) with a pores dimension included between 20 and 80 nm with an average value of 40 nm. Figure 2b shows GO nanosheets (size $\approx$ 30 nm), while larger particles (size $\approx$ 110 nm). These sheets are accumulated on PSi surface (see, Figure 1c). The result is also evident from cross-sectional SEM image of GO–PSi structure, reported in Figure 1d.



Figure 1: a) SEM image of bare aminosilane-modified porous silicon; b) GO nanosheets; c) SEM image of aminosilane-modified PSi after GO infiltration; d) cross-section of SEM image of aminosilane-modified PSi after GO infiltration.

An enhancement of the PL emitted after infiltration in PSi from GO of almost 2.5 with respect to GO on crystalline silicon has been experimentally measured (see Figure 2). This effect has been attributed to the high GO concentration inside the sponge-like PSi structure.



Figure 2: PL 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.

This work demonstrates the enhancement and the modulation of the PL emitted by GO nanosheets infiltrated in aminosilane-modified PSi matrix. This very attractive wavelength modulation of GO photoluminescence emission opens new perspectives for GO exploitation in innovative optoelectronic devices and high sensitive fluorescent sensors.

## References

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