Graphene-based textured surface by pulsed laser deposition as a highly efficient SERS platform for pesticides detection

T. Tite[a], A.-S. Loir[a], C. Donnet[a], S. Reynaud[a], J. -Y. Michalon[a], F. Vocanson[a], V. Barnier[b] and F. Garrelie[a]

[a] Université de Lyon, CNRS UMR 5516, Laboratoire Hubert Curien, Université de Saint-Étienne, 42023 Saint Étienne, France

[b] École Nationale Supérieure des Mines de Saint-Étienne, Laboratoire Georges Friedel UMR 5307, 158 cours Fauriel, 42023 Saint-Etienne, France

teddy.tite@univ-st-etienne.fr, florence.garrelie@univ-st-etienne.fr

Abstract

The design of new graphene architectures has become a stake for the fabrication of advanced materials with various functionalities. Despite its outstanding properties, pristine graphene has many shortcomings, and for practical applications it is needed to alter its surface and electronic properties. New routes are envisaged such as strain, patterning/texturing and chemical functionalization [1]. Of our particular interest, graphene sheets decorated with nanoparticles (NPs) are new hybrids materials that can be used as catalysts, supercapacitors and biosensors. It was reported that graphene decorated Au or Ag NPs can effectively enhance Raman signals of absorbed organic molecules that makes it a useful surface-enhanced Raman scattering (SERS) substrate [2]. Nowadays, reduced graphene oxide (r-GO) is one of the most used burgeoning supports to disperse and stabilize metallic NPs because of its rich surface chemistry. Nevertheless, although news approaches have been reported to provide a better surface control synthesis and coverage of NPs on r-GO, alternative graphene platforms are still needed to be developed for simplest preparation method, large scale and sensitive detection of molecular fingerprints. Recently, it was proposed to convert through thermal treatment and with a metal catalyst, various solid carbon sources such as amorphous carbon (a-C) into graphene [3]. However, to date the applications remain largely unexplored.

Recently, we have synthesized few-layer (fl) graphene by pulsed laser deposition (PLD) and have shown its applications as an efficient SERS platform [4]. However, at this time, the growth mechanism of graphene using energetic carbon species from PLD is not fully understood and the full potential of this method not totally used. PLD has the advantages to be simple, cost-effective, fast and versatile technique to fabricate amorphous carbon such as Diamond-Like-Carbon (DLC). Moreover, by providing energetic carbon species, PLD is an emerging technique to growth graphene at low temperature.

Herein, we report the synthesis of fl-graphene by PLD for different stacking configurations of a-C thin film and investigate its performance to detect various insecticides in solution by SERS. Thin DLC films were obtained under high vacuum condition by ablating a graphite target (99.997% purity) with an excimer laser in a deposition chamber evacuated to a base pressure of about 10^{-4} Pa. A KrF laser with a wavelength of 248 nm, a pulse duration of 20 ns, a repetition rate of 10Hz and an energy density of 15 J cm^{-2} was used for the ablation. A nickel thin film was deposited by evaporation either on top of a DLC thin film (system I) or as an intermediate layer between the DLC film and the substrate (system II). We observed that although homogeneous large scale *fl*-graphene could be obtained with a standard SiO_2 substrate, the use of Si substrate induced textured graphene surface. Figures 1a and b show the SEM images of a-C(5nm)/Ni/Si sample after been thermal annealed at 780°C during 45 min. Distinct surface morphologies were observed (A-II, B-II, and B*-II), indicative of a texturing of the surface. Figure 1c shows some typical Raman spectra recorded at 442 nm excitation in the three aforementioned regions. The presence of a well-defined symmetric 2D mode (~2750 cm^{-1}) in the Raman spectra indicates without ambiguity the formation of fl-graphene. The texturing of the fl-graphene is explained through a diffusion of Ni atoms into the Si substrate during the heating and the concomitant formation of Ni_3Si_2 silicides compounds as confirmed by Raman spectroscopy and Auger analyses. Texturing of surface with nanoscale roughness could be particularly attractive for SERS. Au NPs, prepared by chemical reduction, were deposited on the fl-graphene to investigate its SERS activity (see Figure 2). Rhodamine 6G used as a probe molecule was detected for both aforementioned systems with high sensitivity (10^{-6}M). Lastly, deltamethrin and Methyl Parathion (MP), which are active molecules of commercial insecticides have been chosen to further evaluate the SERS performance of our devices. MP is one of

the most toxic organophosphate pesticides. Recently, Yazdi et al. have detected MP with high sensitivity (5 ppm) using an original method [5]. Figures 3a and b show typical Raman spectra of MP at different concentrations (10^{-5}M and 10^{-4}M) obtained on the fl-graphene. Distinct Raman features at around 859, 1110, and 1344 cm^{-1} that are characteristic peaks of MP are clearly observed for a MP concentration as low as 10^{-5}M (3 ppm). The method developed is simple, fast and cost effective.

References

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Figures

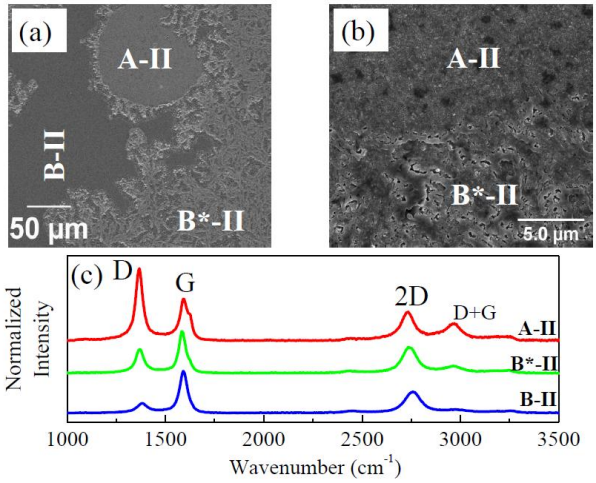

Figure 1. SEM images of a-C(5nm)/Ni/Si after thermal processing at a) 500× and b) 6000× magnifications. (c) typical Raman spectra at 442 nm laser excitation recorded in the regions A-I, B-I and C-I.

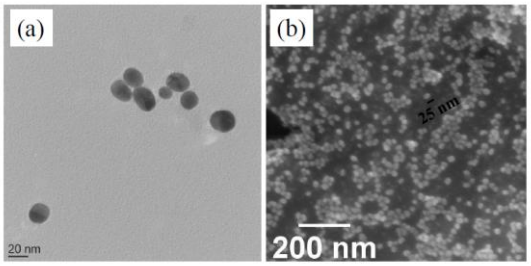

Figure 2. a) TEM image of Au nanoparticles; b) typical SEM image of Au NPs decorated few-layer graphene.

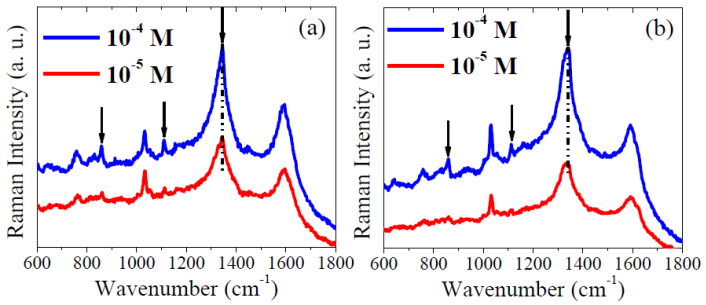

Figure 3. Raman spectra at 633 nm of aqueous methyl parathion deposited on a) AuNPs/fl-G (system I, Ni/a-C(5nm)/Si) and b) (system II, a-C(5nm)/Ni/Si) at concentrations 10^{-5}M and 10^{-4}M. The arrows indicate the peaks signature of methyl parathion.