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Surface enhanced Raman spectroscopy platform based on graphene with one-year stability

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We report the synthesis, characterization and use of a robust surface enhanced Raman spectroscopy platform with a stable detection for up to one year of Rhodamine R6G at a concentration of 10^{-6} M. The detection of aminothiophenol and methyl parathion, as active molecules of commercial insecticides, is further demonstrated at concentrations down to 10^{-5} – 10^{-6} M. This platform is based on large scale textured few-layer (fl) graphene obtained without any need of graphene transfer. The synthesis route is based on diamond-like carbon films grown by pulsed laser deposition, deposited onto silicon substrates covered by a Ni layer prior to diamond-like carbon deposition. The formation of fl-graphene film, confirmed by Raman spectroscopy and mapping, is obtained by thermal annealing inducing the diffusion of Ni atoms and the concomitant formation of nickel silicide compounds, as identified by Raman and Auger electron spectroscopies. The textured fl-graphene films were decorated with gold nanoparticles to optimize the efficiency of the SERS device to detect organic molecules at low concentrations.

1. Introduction

The design of graphene architectures has become a stake for the fabrication of advanced materials with various functionalities. Despite its outstanding properties [1–4], 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 patterning/texturing [5–7] and chemical functionalization through impurities or defects [8–10]. Of our particular interest, graphene sheets decorated with nanoparticles (NPs) are new hybrid materials that can be used as catalysts, supercapacitors and biosensors [8,11]. Graphene functionalized with metallic nanoparticles has been considered as a promising surface-enhanced Raman scattering (SERS) sensor for the detection of molecules at low concentration [8,11–12]. It should be pointed out that although the enhancement of Raman signal is usually less for gold than for silver nanoparticles, gold benefit of a better environmental stability. Higher enhancement factors are expected for silver-based substrates compared with other metals due to the dielectric function of silver, which restricts interband transitions to the ultraviolet (UV) region, minimizing plasmon resonance damping [13]. The new field of graphene-mediated enhanced Raman scattering has been done in concert with the expanding effort on the synthesis methods. 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 [12]. Nevertheless, although new approaches have been reported to provide a better surface control synthesis and coverage of NPs on r-GO [14–15], alternative graphene platforms are still needed to be developed for the 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 precursors such as amorphous carbon (a-C) into large scale graphene thin films. Although Co and Ni are generally preferred metal catalysts because of a higher carbon solubility [16–18], Ji et al. have recently demonstrated the possibility to also use Cu at the condition that hydrogen gas was present [19]. Orofeo et al. indicated that the use of a-C as solid source could provide an original approach to have a better control of the surface properties of graphene [16]. However, although the synthesis of graphene from a-C source has become an attractive research activity, to date the applications remain largely unexplored.

By providing energetic carbon species, pulsed laser deposition (PLD) is a typical emerging technique to grow graphene at low temperature [20–21]. In a recent paper, we have obtained the conversion of 20 nm diamond-like carbon (DLC), deposited by PLD and covered by a thin film of nickel, into few-layers (fl) of graphene [22].

In this manuscript, we introduce a new sensitive and stable SERS substrate for environmental applications. We extend the ability of PLD to growth graphene directly from the deposition of DLC onto a nickel catalyst to obtain 3D substrates as promising SERS platforms as they

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yield much greater surface area for particle coverage compared to traditional flat 2D substrate. The easy formation of 3D porous and textured graphene is explained by the diffusion of nickel into the silicon at the interface and the formation of silicides. This new system has been used as a highly stable SERS platform, using gold nanoparticles (Au NPs) deposited on the fl-graphene. Commercial insecticides, aminothiophenol and methyl parathion, have been detected with a sensitivity which has never been observed before, with high stability confirmed after one year under ambient conditions.

2. Experimental

A nickel (Neyco, 99.99% purity) thin film of ~150 nm thick was first deposited by thermal evaporation on n-doped Si substrate (1.5 cm × 1.5 cm) as support. Prior the transfer into the deposition chamber, the substrates were cleaned with acetone, ethanol and ultrapure water under ultrasonic baths successively, and finally dried with nitrogen gas. A thin amorphous carbon (a-C) film of about 5 nm has been deposited onto the Si/Ni substrate 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 10 Hz and an energy per pulse of 400 mJ was used for the ablation. The energy density of the pulsed laser was set to $15 \text{ J} \cdot \text{cm}^{-2}$ and the deposition rate of carbon was $2 \text{ nm} \cdot \text{min}^{-1}$. After in situ thermal annealing in vacuum (780 °C, 45 min), the a-C/Ni/Si film was cooled down naturally to room temperature. Au NPs were prepared by the reduction of gold salt in the presence of sodium citrate as reducer and stabilizer according the method developed in the literature [23].

Raman spectroscopy is a current tool to check the formation as well as the quality of graphene thin film [24–25]. Unpolarized micro-Raman experiments were carried out in backscattering configuration at room temperature with He-Cd laser wavelength at 442 nm. The spectral resolution was about 2 cm^{-1} . The laser beam was focused on the sample with an objective ×40 in UV and ×100 in visible range. The laser power on the sample was set below 3 mW to avoid any deterioration of the materials. For SERS detection, the laser power was set below 0.2 mW and acquisition time was typically 10 s. The scattered Raman signal was then measured with an Aramis Jobin Yvon confocal spectrometer equipped with a charge-coupled device (CCD) camera. Scanning electron microscopy (SEM) equipped with a field emission gun (FEI, NovaNanoSEM) operating at 15 kV, and atomic force microscopy (Agilent 5500) operating in tapping mode have been also used to characterize the films. UV-Vis absorption spectra of Au NPs were recorded at room temperature on a Perkin Elmer Lambda 900 UV/visible/near Infra-Red spectrophotometer for measuring the absorption band of nanoparticles in the 300–800 nm range. A Malvern Zetasizer 1000 HSA laser granulometer has been used for detection of aggregation of colloids. Transmission electron microscopy (TEM) images were obtained with a Phillips CM120 electron microscope (CMEABG, University of Claude Bernard Lyon I-France). One drop of highly diluted nanoparticles dispersion was placed onto a copper grid (mesh 200 and covered with formvar-carbon) and dried at room temperature before TEM analysis. The images were registered at 100 kV. Auger electron spectroscopy depth profile was performed on a Thermo VG Theta probe instrument using combined steps of Ar^+ sputtering and AES analysis. Sputtering sequences were carried out using 3 keV argon ions onto a 1 mm^2 rastered area with a $19 \mu\text{A} \text{ cm}^{-2}$ current density and an incidence angle of 45° . Auger analysis was carried out using a field emission gun with 150 nm spot size operating at 10 kV accelerating voltage and 5 nA beam current. AES spectra were recorded on a hemispherical analyzer in fixed retardation mode. Quantitative analysis was performed after derivation of AES spectra measuring peak to peak height of Si L_{3VV} at 92 eV and Ni $M_{2,3VV}$ at 61 eV corrected by their respective sensitivity factor measured on pure Si and Ni reference sample.

3. Results and discussions

3.1. Formation of large areas of textured fl-graphene

Fig. 1a shows the SEM image of a-C (5 nm)/Ni/Si after thermal annealing. Two distinct surface morphologies were observed (labelled A and B) and highlighted in Fig. 1b and c respectively. Such morphologies are indicative of a surface texturation and will be further discussed in terms of growth mechanism. Fig. 1d shows some typical Raman spectra recorded at 442 nm excitation in the two aforementioned regions.

The bands at ~ 1370 and 1590 cm^{-1} were attributed to D and G peaks, respectively. The presence of a well-defined symmetric 2D mode ($\sim 2750 \text{ cm}^{-1}$) in the Raman spectra indicates without ambiguity the formation of large graphitic domains after thermal annealing. The 2D/G intensity ratio of ~ 0.6 – 1.2 indicates the formation of few-layer (fl) graphene in both A and B regions [18,21,26]. No shoulder was observed on the low frequency side of the 2D peak, suggesting that the stacking between the layers in not AB stacking, and the interlayer coupling is rather weak [27]. Raman mapping of D/G and 2D/G (Fig. 1e and f respectively) of regions A and B supports that the Raman intensity of both modes from the region A is enhanced in comparison to the region B. On the other hand, the intensity ratio of D/G is slightly smaller in the region B, which indicates a reduction of the structural disorder or defects compared to the region A. By referring to the cartography of 2D/G, the formation of fl-graphene layer is obvious in both regions, but with a significant higher intensity in region A.

Compared to the Ni/a-C/Si system, the D/G intensity ratio in the present system reveals a higher defective structure compared to the previously published system [22]. Interestingly, the 2D/G intensity ratio could be found higher than unity in region A (Fig. 1f). This is clearly indicative of a high degree of crystallization in sp^2 carbon structure. It is important to notice that the results obtained by using a n-doped Si as substrate are found to be improved from those published by Koh et al. [21] and the intensity ratio of 2D/G is comparable with those obtained by other methods [18,28–30].

3.2. Growth mechanism of textured graphene on Ni/Si substrates

The mechanism of formation of graphene on nickel generally involves (i) dissociation of solid carbon thin film, (ii) dissolution and diffusion of carbon in the metal during heating, and (iii) segregation and/or precipitation of C atoms at the surface of the metal either at the growth temperature when the solid solution has been saturated, or during cooling because of the decrease of carbon solubility in the metal [31–32]. It is well known that the quality and thickness of a graphene film depends on crucial parameters such as the quantity of the carbon source deposited, the thickness and the type of the metal catalyst used, the heating temperature and duration, cooling rate and environment [20–21,33–34]. Our results deduced from Raman spectra were found comparable with those obtained by filtered cathodic vacuum arc technique [18] and reduced graphene oxide [28–30].

In the present study, the texturing of the fl-graphene is explained through a diffusion of Ni atoms into the Si substrate during the heating. This is clear evidenced by the presence of vibrational bands at low frequencies in the regions A (Fig. 2a), which was attributed to the formation of silicon-rich nickel silicides compounds [35–36]. The sharpness of the Raman peaks suggests that the silicides formed are well crystallized. No vibrational modes at low frequency were observed in the regions B where nickel is only partially consumed to form nickel silicides (Fig. 2a). The nickel silicides growth involves the consumption of Si atoms of the substrate. Fig. 2b shows the atomic concentration ratio profile of Ni/Si extracted from the AES depth profile measured in the region where the diffusion of Ni atoms into Si substrate occurs. The depth profile is built up by the measurement of the intensity of recorded peaks versus etching time. During the acquisition steps, AES analysis were carried out on two different areas corresponding to the regions A and B as

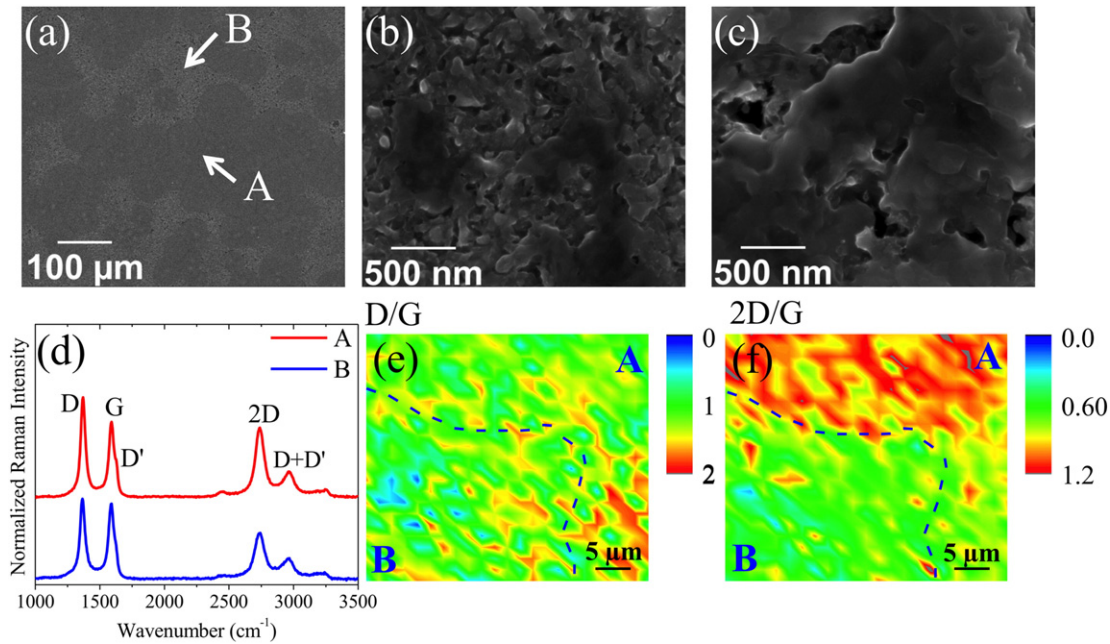


Fig. 1. SEM images of a-C (5 nm)/Ni/Si after thermal processing at (a) 500 \times and 12,000 \times magnifications for the areas A (b) and B (c) showing a 3D porous structure; (d) typical Raman spectra at 442 nm taken in the regions A and B. Raman mappings at 442 nm of the intensity ratio on 40 $\mu\text{m} \times 40 \mu\text{m}$ of (e) D/G and (f) 2D/G, respectively. The dash lines are guides delimiting the region A and B.

described previously. The spot size of the electron beam was 150 nm and a secondary electron picture was recorded periodically in order to unambiguously localize the two AES analysis areas in the region A and B. The Fig. 2b corresponds to ratio of atomic concentration of Si and Ni for the AES analysis in the region A. The first 1500 s of corresponds to the graphene top surface. At higher etching time, the Ni/Si ratio increases to reach 1.5 from about 5000 s to 25,000 s of etching, which is consistent with the stoichiometry of the stable orthorhombic Ni_3Si_2 phase. From thickness measurements performed after etching, 25,000 s corresponds to about 150 nm, consistent with the initial thickness of the nickel film and also with the position of the interface between the Ni film and the Si substrate found for the AES analysis in the region B where no silicides were detected. One can conclude that in the region A all the Ni film reacted to form silicides however this is only valid if we assume similar sputtering rate in pure Ni and silicide. It is believed that the formation of nickel silicides takes place through a sequence of stoichiometric transformations during heating [37–39]. At $\sim 200^\circ\text{C}$, Ni_2Si is the first phase to be formed and grow up until the Ni thin film is totally consumed; this is followed by the formation of NiSi from the reaction of Ni_2Si and Si at $\sim 350^\circ\text{C}$. The kinetic of Ni_2Si and NiSi is driven by a Fick diffusion law. The Ni_3Si_2 phase is formed at higher temperature ($\sim 500^\circ\text{C}$) and comes from the reactions of

Ni_2Si with NiSi [37–38]. Although internal stress and the presence of carbon may also affect the kinetics of the phases, such formation processes are found in good agreement with our results. Interestingly, Gas et al. indicated that the formation of Ni_3Si_2 is controlled by a nucleation process followed by a lateral propagation of elements, which gives rise to the emergence of ring topographic patterns similar to those observed from different SEM images [37], as observed in Fig. 1a. It is worth noting that nickel silicides are currently employed for many crucial applications including metal gate electrode in Complementary Metal Oxide Semiconductor devices, photovoltaics, thermoelectrics and catalysts [40–41]. Recently, Vilkov et al. have highlighted the importance to combine graphene and silicides compounds [41]. On the other hand, this present work shows that our method may enable the integration of large scale fl-graphene directly into the well-established nickel-silicides technology.

The formation of large scale textured graphene on Si substrate is a competition of two dynamical reactions during thermal heating involving different interfacial reactions (Kirkendall planes): a diffusion and precipitation of carbon on the surface of unreacted Ni film according to the aforementioned mechanism and a precipitation of carbon from silicides compounds supersaturated with carbon [31–32]. During cooling, the solubility of carbon into unreacted Ni or nickel silicides

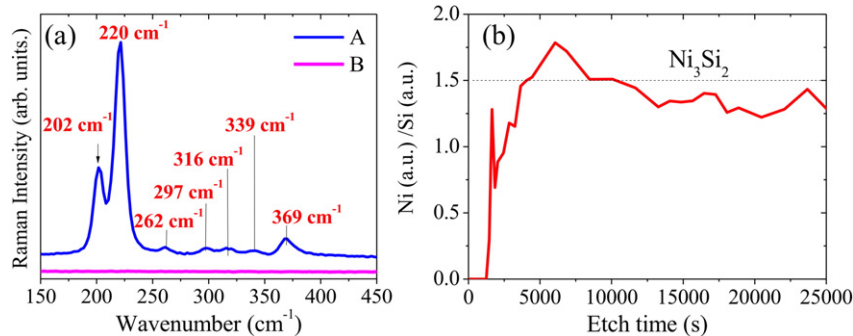


Fig. 2. (a) Raman spectra at 633 nm taken in the regions A and in the region B where nickel was not consumed; (b) Depth profile of the atomic concentration ratio between Ni and Si derived from Auger spectroscopy.

reduces and the resulting saturated carbon domains are released to form few-layer graphene on the surface. Since the solubility of carbon in Ni is lower than in nickel silicides, nickel layer is better and easier saturated during its partial consumption when heated [32]. This could explain why the 2D/G ratio was found in average higher for fl-graphene grown on silicides. Moreover, the diffusion of Ni atoms and the concomitant formation of nickel silicides are taken as responsible of a higher defective, porous and rough fl-graphene structure. Defects and roughness are usually seen as imperfections in materials that could significantly degrade their performance. However, at the nanoscale, defects and corrugated surface could be extremely useful since they could be exploited to generate new advanced materials [8–9]. In particular, it is worthwhile noting that defects as chemically active sites and roughness/porosity as higher specific area surface promote the adsorption and the detection of molecules. Recently, Xu et al. have fabricated a mechanically exfoliated graphene-veiled substrate, and have shown that both Au NPs and graphene topography should influence the SERS activity [42]. In this context, the specific surface architecture of our material with large scale textured fl-graphene on silicon substrate could be particularly attractive for the SERS which requires rough metallic surface for higher detection sensitivity.

3.3. SERS activity of textured fl-graphene grown by PLD

SERS enhancement typically comes from a change in Raman polarizability which refers to the chemical mechanism (CM) and a change in local field which corresponds to the electromagnetic mechanism (EM) [43–44]. CM is a short-range effect based on a charge transfer between the molecule and the substrate. On the other hand, the EM is a long-range effect which results from the large increase of the local electric field caused by surface plasmon resonances of nanosized metals deposited onto the graphene surface. Albeit, these two mechanisms contribute simultaneously to the overall Raman enhancement, EM is more effective (10^8 or more) than CM (usually 10 to 10^2) [43].

In this work, the Au NP size has been estimated by TEM analysis at ca. 23 nm (Fig. 3a). The NP size was also confirmed by laser granulometer which indicates a typical diameter of 25 nm with a standard deviation of 5 nm. By referring to UV–VIS–NIR absorption analysis, the surface plasmon resonance band was found at 525 nm (not shown). The as-grown fl-graphene has been decorated with Au NPs by simply depositing a small droplet of Au NPs in colloidal solution onto the surface of the sample, which has been hereafter generally rinsed twice in ultrapure water and dried in air. A typical SEM image of the fl-graphene surface decorated with Au NPs is shown in Fig. 3b. It is worth noting that these images have been taken after the sample has been unreasonably rinsed five times in ultrapure water. The Au NPs are obviously seen which indicates their good anchoring on the surface of the sample via electrostatic, Van der Waals and elastic interactions

(Fig. 3b). In particular, surface roughness, topography and wettability may play a predominant role in the adhesion.

To investigate whether the as-fabricated Au NPs on fl-graphene (AuNPs/fl-G) substrates can be used as an effective SERS platform, we employed it for insecticides detection. Pollutants even at very low concentration could be extremely harmful for environment and living beings. Therefore, efficient techniques are currently needed for their detections in trace amounts and their removal for environmental remediation. Among all challenging methods developed for detection of contaminants, graphene is becoming a promising electrochemical sensor due to its high adsorption efficiency [45–46]. In this context, we propose to evaluate the SERS performance of the as-fabricated samples to detect methyl parathion and para-aminothiophenol at low concentrations. The stability of the samples over a long time will be addressed on a standard probe molecule, namely Rhodamine 6G (R6G).

Methyl parathion (MP) is one of the most toxic organophosphate compounds. It is a potent insecticide and acaricide, highly toxic to non-target organisms including humans, with its use banned or restricted in many countries, and proposals to ban it from all use. Therefore, fast and robust detection of such highly toxic compound is of major interest and has been chosen to evaluate the SERS performance of our devices. Under ordinary sampling conditions, the SERS detection of MP is very poor [47–48]. Although sophisticated approaches have been developed to enhance the detection sensitivity of MP, the preparation procedures remain generally complicated [48–49]. Recently, Yazdi et al. have developed a simple and portable optofluidic SERS device for multiplex fungicides detection and have detected MP with high sensitivity (5 ppm) [50]. Fig. 4 shows the Raman spectra of MP at a concentration of 10^{-5} M at liquid and dry states obtained on the AuNPs/fl-G platform. We stress that direct detection was performed by simply depositing a droplet of diluted commercial insecticide on the surface of Au-fl-graphene sample. Distinct Raman features at around 859, 1110, and 1344 cm^{-1} that are characteristic peaks of MP [47] are clearly observed for this MP concentration as low as 10^{-5} M (3 ppm).

Para-aminothiophenol (p-ATP) is a well known molecule for surface-enhanced Raman spectroscopy (SERS) which strongly interacts with metallic SERS substrates and produce very intense SERS signals. It is a molecule that has often been used for mechanistic studies of the SERS mechanism and will be investigated here to address the robustness and highlight the detection stability of our SERS platform over large scale.

Fig. 5a compares the Raman spectra obtained at 633 nm for p-ATP (10^{-5} M) on Si, p-ATP (10^{-5} M) on AuNPs directly deposited on Si, and p-ATP on the AuNPs/fl-G platform at different p-ATP concentrations (10^{-6} M, 10^{-5} M, 10^{-4} M, 10^{-3} M). The reference spectra of fl-graphene without NPs, and of the platform (AuNPs/fl-G) are also added for comparison. The SERS spectrum of p-ATP on AuNPs/fl-G shows without any doubt the enhancement of SERS signal due to the presence of graphene layer associated with metallic NPs.

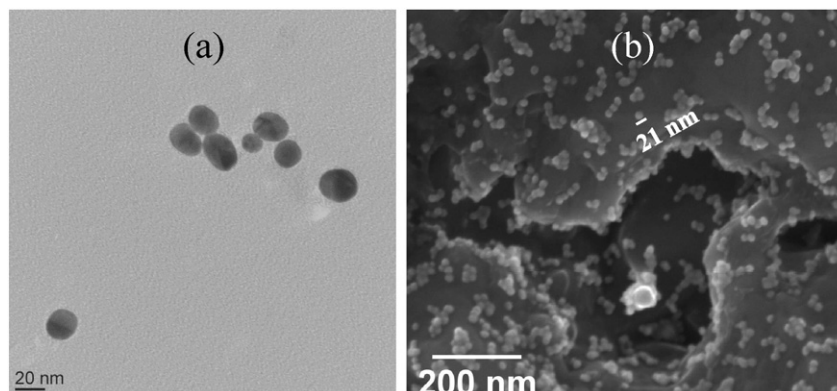


Fig. 3. (a) TEM image of Au nanoparticles; (b) typical SEM image of Au NPs decorated few-layer graphene.

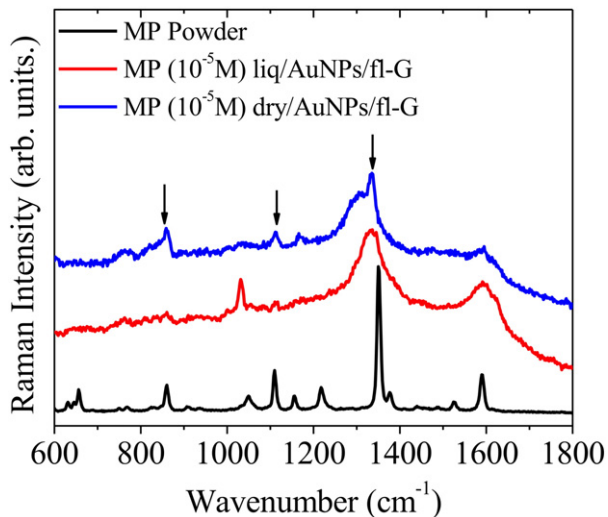


Fig. 4. Raman spectra at 633 nm of methyl parathion (MP) on Au-fl-G concentrated at 10⁻⁵ M and 10⁻⁴ M at liquid and dry states. Raman spectrum of MP powder is added for reference. The arrows indicate the peaks signature of methyl parathion.

The SERS activity on the samples is interpreted as a combination between the EM and CM mechanisms. By referring to the SEM images, rough regions (as observed in Fig. 1b) can have high density coverage of Au NPs and short inter-particles distance (Fig. 3b), leading to large EM field at junction sites that give rise to the enhancement of the SERS signal [44,51]. This is clearly evidenced by Raman mapping at 1073 cm⁻¹ over a large scale (Fig. 5b) which indicates an enhanced SERS signal in rougher regions. However, the Raman mapping indicates a good SERS detection of p-ATP at low concentration (10⁻⁵) over the entire platform surface, as presented on the SERS spectra of Fig. 5c from the area marked with corresponding colored cross in Fig. 5b.

It is worth noting that the large-scale AuNPs/fl-G device is found very sensitive, fast and robust to detect the molecules in regards to the low concentration of p-ATP and low laser power density (6×10^2 W/cm²) with a short acquisition time (~10 s) used. This is a good evidence of the large scale and robust features of the as-grown platform.

As a final proof of competitiveness of such platforms for SERS detection, we have investigated the stability of the detection over one year of storage. A stabilized substrate with monolayer of graphene stabilizing silver NPs was recently proposed for enhanced SERS signal for up to 28 days [52]. It has been widely recognized that silver NPs were more sensitive to oxidation than gold NPs, with however a higher enhancement. Fig. 6a presents the stability of our platform for up to one year under ambient conditions. Fig. 6b presents the Raman mapping after 1 year of storage and Fig. 6c presents the SERS spectra from the spots identified as crosses in Fig. 6b. Those results confirm the good uniformity of the SERS platform after 1 year storage. The good anchoring of the NPs as well as the chemical inertness of Au NPs allow us to improve the stability of the platform without compromising its SERS sensitivity to various molecules at low concentration, comparable to the state of the art and reported previously [53–54].

Although further investigations are still needed, our results are rather encouraging in SERS detection and coupled with a portable Raman spectrometer, this approach can be easily used to detect in-situ various molecules and pollutants.

4. Conclusion

It has been shown that fl-graphene films, synthesized at low temperature from solid-state amorphous carbon source based on the emerging PLD technique, appear like a SERS devices through the functionalization

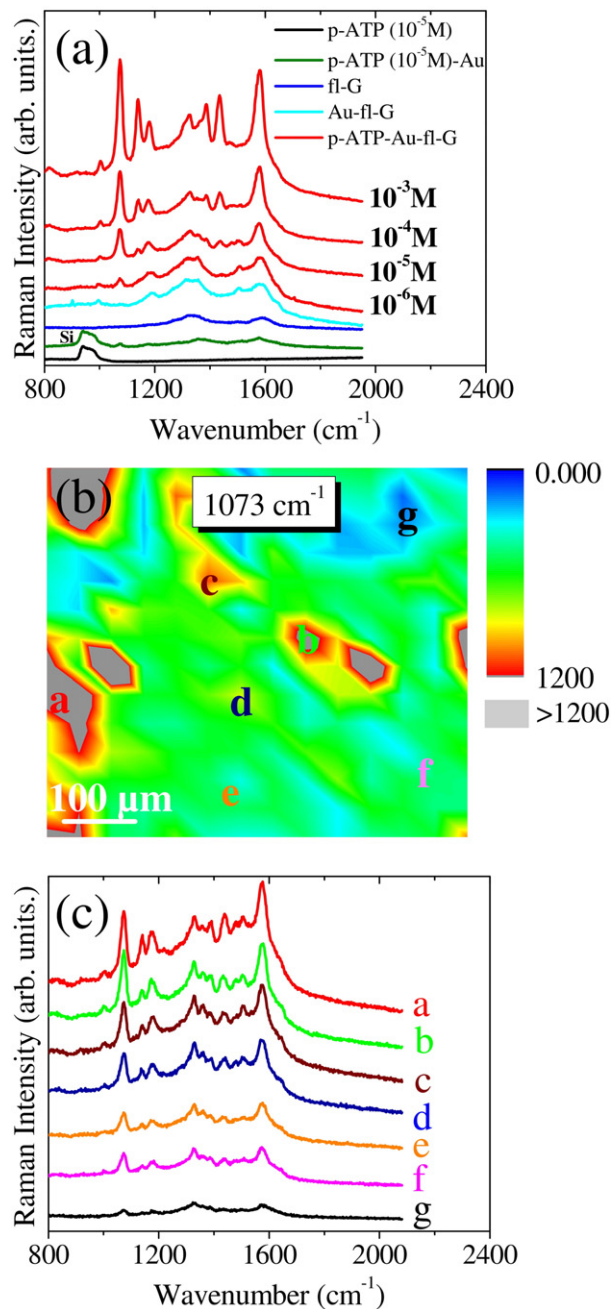


Fig. 5. (a) Raman spectra at 633 nm of p-ATP(10⁻⁵ M) on Si, p-ATP(10⁻⁵ M) on AuNPs deposited on Si, fl-graphene, AuNPs/fl-G, and p-ATP on AuNPs/fl-G at different p-ATP concentration (10⁻⁶ M, 10⁻⁵ M, 10⁻⁴ M, 10⁻³ M). The arrows indicate the peak signature of p-ATP used for Raman mapping; (b) Raman mapping at 633 nm of p-ATP(10⁻⁵ M) dropped on AuNPs/fl-G (objective $\times 10$); (c) typical SERS spectra from the spots marked with corresponding letters in (b).

of its surface via gold nanoparticles. Through the diffusion of Ni atoms into a Si substrate and the concomitant formation of nickel silicide compounds, such as Ni₃Si₂, large scale textured fl-graphene films have been designed with nanoscale roughness. Thanks to their unique surface architecture at nanoscale we were able to detect by SERS various molecules at low concentration with high sensitivity and good uniformity such as para-aminothiophenol and an organophosphate insecticide, the methyl parathion. The method developed is simple, fast and cost effective, and presents stability over up to one year. We expected that the as-grown textured fl-graphene will serve as an alternative SERS platform for molecular diagnostics and will open new avenues for graphene applications.

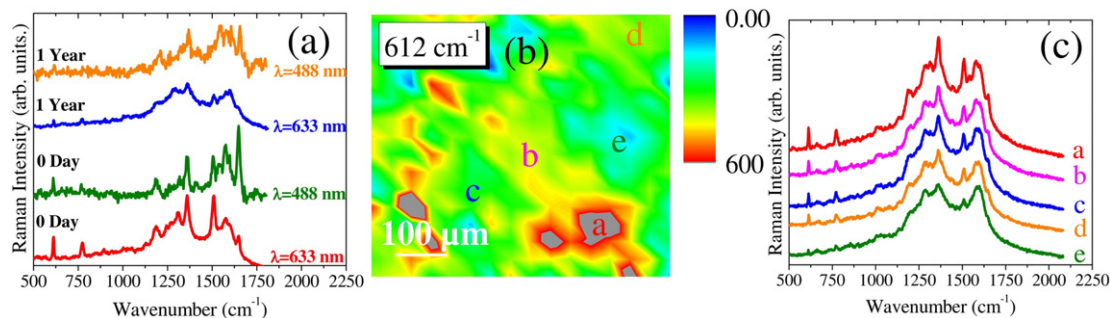


Fig. 6. (a) SERS Raman at 488 and 633 nm of R6G (10^{-6} M) on AuNPs/fl-G freshly obtained and after 1-year; (b) Raman intensity map (at 633 nm) of 632 cm^{-1} mode of R6G (10^{-6} M) on AuNPs/fl-G after 1-year; (c) typical SERS spectra from the spots marked with corresponding letters in (b).

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