Optimization of Immobilization of Nanodiamonds on Graphene

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Abstract. We report using simple dip-coating method to cover the surface of graphene with nanodiamonds for future optical detection of defects on graphene. Most important part of the immobilization process is the pre-functionalization of both, nanodiamond and graphene surfaces to obtain the selectiveness of the method. This work focuses on an example of using electrostatic attraction to confine nanodiamonds to graphene. Raman spectroscopy, micro-luminescence imaging and scanning electron microscopy were applied to characterize obtained samples.

1. Introduction
Graphene is a two-dimensional atomically thin semi-metallic film, where carbon atoms are arranged into \( \text{sp}^2 \) honeycomb lattice. Graphene has excellent mechanical, optical, thermal and electrical properties and finding a way to employ them easily is of most importance. There have been reports on graphene oxide-semiconductor/metal nanoparticle composites as a probable tool for water splitting, solar cells and fuel cells [1]. Learning to prepare and functionalize graphene surface with desired properties easily and cost-efficiently holds great potential for future bottom-up electronics.

Dealing with graphene means manipulating it in nano-scale, which makes the process time-consuming, expensive and prone to defect creation. Defects in graphene can manifest in many forms and at different scale. Atomic scale defects like mono- and multi-atom vacancies can seriously disturb graphene electron structure leading to reduced conductivity [2]. More sophisticated defects like dislocations, edges or Stone-Wales defects can enhance the chemical reactivity of graphene compared to perfect lattice [3]. Micro-scale defects are also relatively common and naturally occur due to stresses caused by substrate thermal expansion or mechanical manipulation (e.g. Scotch tape technique) [4]. Uneven growth thickness of graphene can often form islands of multilayer graphene in micro-scale.

In all cases a robust and easy method for defect detection and quantification is desired. As graphene sheets are usually grown in an atom thick layer, it is very difficult to distinguish between mono- and multilayer graphene solely by looking at optical or SEM micrographs. This leads to Raman spectroscopy being a commonly used tool in graphene investigations [5].

In present report a spectroscopic method for optical identification of micro-scale defects on graphene is introduced via selective marking of defective areas with luminescent nanodiamonds (ND). The selective adhesion of ND-s is achieved via zeta potential modification of both graphene or its defects and the ND-s to introduce electrostatic attraction in a liquid solvent.

Nanodiamonds with nitrogen-vacancy (N-V) centers are selected as markers because of their well-known luminescence properties. They are readily used as fluorescent markers in drug delivery and...
bio-imaging [6] but also as single photon sources with high quantum yield and photostability in quantum computing [7]. Furthermore, the combination of graphene and ND-s is in early stages of scientific interest. Said composites have been featured for uses in supercapacitor electrodes [8] and as a scanning probe in optical microscopy of graphene [9].

The mechanism of ND self-assembly onto graphene surface via electrostatic attraction is based on observations in several earlier works showing the possibility of attracting small (d~5 nm) detonation ND-s to graphene surface via appropriate pretreatment of the adsorbates and graphene. It has been shown that nanoparticles tend to obtain the potential of the substrate [10] and also, there is a certain pH window for electrostatic attraction [11]. One of the goals of the work is to observe how well bigger ND-s (d~40 nm) function in similar conditions.

2. Experimental procedure
The ND-s used in this study were commercially available (Adamas Nanotechnologies Inc) detonation ND solution in water, containing 0.1% ND-s with average d~40 nm, zeta potential +30 mV, containing 1-4 N-V centers. The ND-s were first treated with H₂ plasma at 100 W power for 15 min (Diener Electronic Plasma Surface Technology Femto) to enhance positive zeta potential [5]. Then, the ND-s were dispersed in methanol via ultrasound (40 W, 30 min).

The substrate used was commercially available graphene on SiO₂/Si surface (Graphene Square Inc). To obtain negative zeta potential, the graphene surface was treated with O₂ plasma at 25 W for 15/30/60/120 s followed by dipping the treated substrate vertically into the ND-methanol solution for 1 minute.

It is expected that treatment with hydrogen and oxygen plasmas leads to vastly different zeta potentials, since oxygen plasma forms negatively charged surface (O⁻ terminated) whereas hydrogen plasma forms positively charged surface (H⁺ terminated). By dispersing ND-s in methanol, alcy groups are removed from the ND surface, leaving it hydroxylated, which leads to positive zeta potential [12]. Oxidized surface has negative potential, so the ND self-assembly is caused by electrostatical attraction. The efficiency of the surface covering and plasma treatment effect were estimated with scanning electron microscopy (SEM, type FEI Helios).

Additionally, luminescence (532 nm laser excitation, custom micro-luminescence setup) and Raman scattering measurements (Renishaw inVia Raman spectrometer) were carried out to estimate the applicability of optical detection of ND-s and graphene quality before and after plasma treatments.

3. Results and discussion
In Raman spectra of the plasma treated graphene (figure 1) the FWHM of 2D band (29 cm⁻¹) and intensity ratio of 2D/G (≈2.8) show that the initial graphene is monolayer and the absence of D band hints good crystallinity. Relatively featureless graphene surface is also seen under optical microscope (figure 2). After treating the surface with O₂ plasma, high concentration of defects (or graphene edges) is indicated by an intense D band. Randomly distributed impurities and surface charges occurring during plasma treatment in graphene cause the G band to split into G and D’ bands [13]. The merging of D’ band into the G peak also implies high concentration of defects and the intensity ratio of D and D’ band of ~3 indicates that the most common defects present are graphene edges [2].
D band observed after O$_2$ plasma treatment has been suggested to arise from two competing processes: (a) introduction of covalently bonded oxygen (epoxy, hydroxyl and carboxyl groups) onto the graphene lattice; (b) progressive amorphization of the sp$^2$ lattice [14]. Since the D'/D intensity ratio is small, the latter is less dominant in our case [2].

ND-s tend to accumulate at physical defects in graphene structure (figure 3). This is most likely due to the fact that the electrical field is concentrated onto sharp graphene features during surface plasma treatment and that defects are chemically more active, leaving them more/highly functionalized.

Single ND-s are not fluorescent on the graphene substrate due to fluorescence resonance energy transfer (FRET). Previous works have shown that single N-V center has lower fluorescence intensity and shorter lifetime on graphene compared to quartz due to FRET [15]. Fluorescence occurs only when there is a larger cluster of ND-s present on the graphene surface, for example at the edges of solvent droplet (figures 4 and 5).
Although the substrate shows significant loss of graphene layer as the plasma treatment time increases, ND-s still accumulate in the same places. ND-s tend to attach to graphene boundaries, regardless of progressive plasma etching (figure 6).

![Figure 6. SEM micrograph of graphene-ND samples with different duration of O\textsubscript{2} surface plasma treatments. NDs attach preferably to graphene island edges (a defect).](image)

The process of ND self-assembly by electrostatic attraction onto pretreated graphene surface is relatively random and challenging to control. Hees et al. [11] have shown that using centrifugation in addition to ultrasonic mixing and coating the substrate in an ultrasonic bath lead to an even covering of silicon with ND-s (RMS roughness 2 nm). In addition, their measurements show that hydrogenation leads to smaller degree of agglomeration, decreasing the mean particle size in solution from 100 nm to 3 nm. In our case the hydrogenation process had a smaller effect, SEM observations showed that there were no ND-s with diameter larger than 40 nm on the substrate, although they were present in the untreated solution.

The estimation of the optimum parameters for selective coverage of substrate’s particular defects is highly complicated, most problematic being the determination of the potential between the intended target defect and the nanoparticle. Stehlik et al. [10] report that the reliable potential characteristic of a nanoparticle on any substrate is more dependent on the substrate than the particle’s chemical termination and manifests as a linear function of the adhered particle’s size. This means that already bound particles can alter the potential of the target during the electrostatic adhesion process, thus rendering simple zeta potential difference as a temporary indicator of attraction strength.

4. Conclusion
In this work we demonstrated a simple method for covering graphene surface defects with ND-s. The electrostatic attraction of different graphene defects and ND-s lead to accumulation of ND-s onto different micro-scale defects on graphene surface after plasma treatment. The coverage was only observable via SEM micrographs as the ND-s were not luminescent on graphene due to its quenching effect.

Current results suggest that zeta potential manipulation is a usable but complex tool for controlling ND immobilization on graphene. Further work using larger ND-s, preferably with dielectric shell, is needed to enable luminescent detection of graphene defects.

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