

The Solution Phase Aggregation of Graphene

Nanoplates

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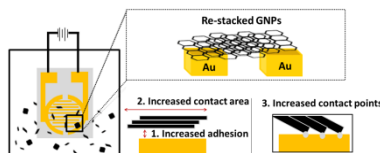
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The occurrence of particle aggregation, especially for two-dimensional (2D) nanoparticles, in the solution phase is an important practical problem. Aggregation influences the materials' properties and behaviour. This work studies the re-stacking process of graphene nanoplates (GNPs) in colloids and suspensions by a simple and highly sensitive technique in which the current responses resulting from the impacts of individual and aggregated particles which bridge across two interdigitated gold microbands are detected.

The magnitude of the steps in current varies as a function of time and yield clear in-situ information regarding the formation of GNP aggregation.

TOC GRAPHICS



KEYWORDS Graphene nanoplates, Aggregation, Namo-impacts

Two-dimensional (2D) materials are sheet-like structural materials typically larger than 100 nm in size but only a few nano-meters thick. These layer materials have potential for advanced technological applications such as catalysts, catalyst supports, energy storage, polymer composites, and biological molecule sensors[1-4]. Typically, a single 2D structure cannot exist in a freestanding system due to its poor thermodynamic stability with respect to aggregation[5]. The van der Waals and physical interactions between the 2D layers cause them to stack together leading to phase separation from solution by forming large aggregates. The multilayer structure of 2D materials significantly affects their electronic and physical properties[6, 7]. Hence it is important to gain a better understanding of the re-stacking and aggregation of the 2D material suspended in solution.

Graphene was the first 2D material available for practical uses[3, 4]. High quality graphene can be produced by scotch taping peeling and chemical vapour deposition methods, however, this method does not meet the demands of industry scale production[8]. Consequently, graphene derivatives have become an attractive alternative. Graphene nanoplates (GNPs) are a commercial graphene-based material with an average thickness of 5 – 10 nanometers. GNPs have graphitic structures making them durable to corrosion avoiding

the poor corrosive properties of single sheet graphene[9]. Nevertheless they also exhibit some of the advantageous properties of single-layer graphene notably a large surface area, high electro-conductivity, high thermal-conductivity, and strong mechanical properties[10, 11].

Evidencing in situ the degree of aggregation of 2D materials in the solution phase by conventional means is experimentally challenging. Traditional electron microscopy is often used for studying nanoparticle structures and morphologies ex-situ. However, the sample preparation method requires drying the material and the experiment is operated under vacuum. It is obviously not suitable for studying aggregation in solution. Liquid-phase transmission electron microscopy (LP-TEM) is an emerging technique allowing samples to be characterized under low-pressure (up to 20 Torr or 2.7 kPa). However, the complexity of the technique and further issue in terms of material radiation damage are recognised[12]. Alternatively, dynamic light scattering (DLS) is a common technique to measure the size of particles in colloidal suspensions. The method measures the diffusion coefficient of the particles and assuming a spherical particle, relates this value via the Stokes–Einstein equation to their effective radius[13]. In practice, the 2D material is, of course, far from spherical. DLS, therefore, in its most common implementations does not provide accurate sizing for the 2D materials. Nevertheless, work to develop the use of DLS for characterising such materials is ongoing. Lotya[14] found a relationship between the hydrodynamic radius and the thickness of 2D materials and developed an equation to calculate the mean thickness using data from DLS. This method can be used for roughly estimating the lateral size of any 2D nanosheets dispersed in a liquid with a reported relative error of 40%[14].

Recently, electrochemical “nano-impacts” has proved to be an effective approach for investigating single nanoparticle behaviour in solution[15, 16]. The area has been reviewed[15, 16] but one manifestation relates to the present work. The electrochemical characterization of a single carbon nanotube (CNT) can be achieved by immersing a wire

electrode in a dilute suspension of CNTs and waiting for a single tube to impact[17-21]. Such experiments allowed cyclic voltametry studies of single CNTs to be made and reactions such as the oxidation of hydrogen[18, 19] and of formate[20] investigated with the aim of comparing the single particle response to that of an ensemble of CNTs. In a further development[22, 23] bridging impacts were studied using an interdigitated microband electrode with a separation of a few microns between the bands. In this experiment the arrival and residence of a particle of sufficient length to electrically connect a pair of electrodes between which a potential difference is applied is indicated by a current flow between the electrodes for the duration of the particle residence. The latter type of experiment is explored in this paper and used to indicate particle aggregation.

Specifically we seek to investigate the aggregation of graphene nanoplates (GNPs) in an aqueous solution via bridging nano-impacts and observe the effect of the length of time over which GNPs are allowed to age in solution and their concentration. In the experiment, a current response is observed where each current step results from the arrival of an individual GNP entity which bridges between two micro-bands of a gold interdigitated electrode (IDE-Au) when a potential difference is applied between them. In order to corroborate the obtained result, dynamic light scattering (DLS) and optical microscopy techniques were also employed.

The GNPs used in this work have been previously characterised[24]. SEM images of the GNPs show rectangular or triangular plates with an average size of $16.5 \pm 5 \mu\text{m}$ which is in good agreement with data from the supplier Strem Chemicals, Massachusetts, United States ($15 \mu\text{m}$). In this work, $1.0 \times 10^{-6} \text{ mol dm}^{-3}$ GNPs were freely dispersed in deionized water without using any surfactant. Their sizes were initially assessed using a bright-field optical microscopy (Figure S1). The size distribution of GNPs was analyzed via using the ImageJ2 program[25] and the size distribution diagram is shown in an inset image of Figure

S1a. The size average from the optical microscopic image is $16.9 \pm 5.9 \text{ }\mu\text{m}$ (112 particles) which is consistent with the previously reported dimensions of this material.

In order to disperse GNPs in an aqueous solution, an ultrasound treatment was conducted in a Fisherbrand ultrasonic bath S60 (230 V 50/60 Hz 150W) for 10 minutes. After sonication, the obtained particles were well dispersed in the solution (Figure S1b and Figure S2) but the mean size was reduced to $6.3 \pm 3.2 \text{ }\mu\text{m}$ (111 particles). The treatment breaks the original larger GNPs into small particles. Moreover it may break the physical interaction between GNPs sheets leading to thinner structures[26].

Nano-impact experiments were conducted to investigate the electrical contact between single nanoplates and pairs of gold electrodes. A chronoamperogram was performed on a suspension of GNPs prepared as above at a constant potential of 0.8V across two microbands of a gold interdigitated electrode (IDE-Au). For freshly prepared suspension, the chronoamperometric profiles in Figure 1a show current steps above the background current with currents of magnitude, $0.8 \pm 0.1 \text{ nA}$, (inset image in Figure 1c). The effect of increased aging periods is shown in Figure 1b. The chronoamperometric profiles at 0.8V were recorded after the GNPs were aged in solution for 2 hours, during which time the electrode was not cleaned, it can be seen that the magnitude of the current step is notably larger. Some current steps switch between more than two discrete levels. This is interpreted as resulting from multiple platelet bridging collisions. The relative signal to noise ratio is also increased (Figure S3g) as more GNPs bridge the gaps between the IDE-Au bands.

To study the contact resistance between GNPs and gold electrode, the nano-impact chronoamperometry method was employed at different applied potentials (0.10-0.80 V) across two microbands of the gold electrode in a solution containing $1.0 \times 10^{-16} \text{ mol dm}^{-3}$ GNPs restricting the experiment to 10 minutes (section 3 in the Supporting Information). The obtained chronoamperometric profile is shown in Figure S5. The magnitude of the current

step relates to the contact resistance between the electrode and the carbon material[22, 23]. A plot of the average current step against potential is shown in Figure S7. The slope of linear fitting of the I-V curve reflects the average total resistance of a single nanoplate contacting between two bands of the gold electrode with a mean value of $5.9 \pm 0.1 \times 10^8 \Omega$. This value is similar in magnitude to the contact resistance (10-60 G Ω) reported in previous studies of a carbon nanotube (CNT) and a gold electrode contact[22, 23]. Based on the reported electrical resistivity of single crystals of graphite which ranges from 40 to 60 $\mu\Omega$ cm[27], the resistivity of individual GNP of 6.3 μm width and 7.0 nm thickness can be estimated to be the range of 50 - 90 Ω which is very much smaller than the contact resistance.

Next we investigated the effect of GNPs concentration and aggregation. For a newly prepared suspension as shown in Figure 1a, the current steps of all the concentrations of GNPs have a similar current range of magnitude. Increasing the concentration of GNPs results in an increase in the observed number of impacts, specifically 0.5, 0.6, and 1.1 events/second for 1.0×10^{-16} , 1.6×10^{-16} , and 2.2×10^{-16} mol dm⁻³ GNPs, respectively. Large current steps were seen for high concentrations of GNPs and long aging times (Figure 1b). The recorded collision events for all concentrations were plotted as a function of time (Figure 1c). The magnitude of the current step over the time clearly increases. Moreover, for same time, higher GNPs concentrations give higher steps. The magnitudes of the current steps indicate the aggregate level of GNPs on the electrode surface. High GNPs concentrations encourage particle collisions enhancing aggregate[28]. These observations demonstrate that the rate of aggregation significantly depends on both the age of a suspension and the particle concentration.

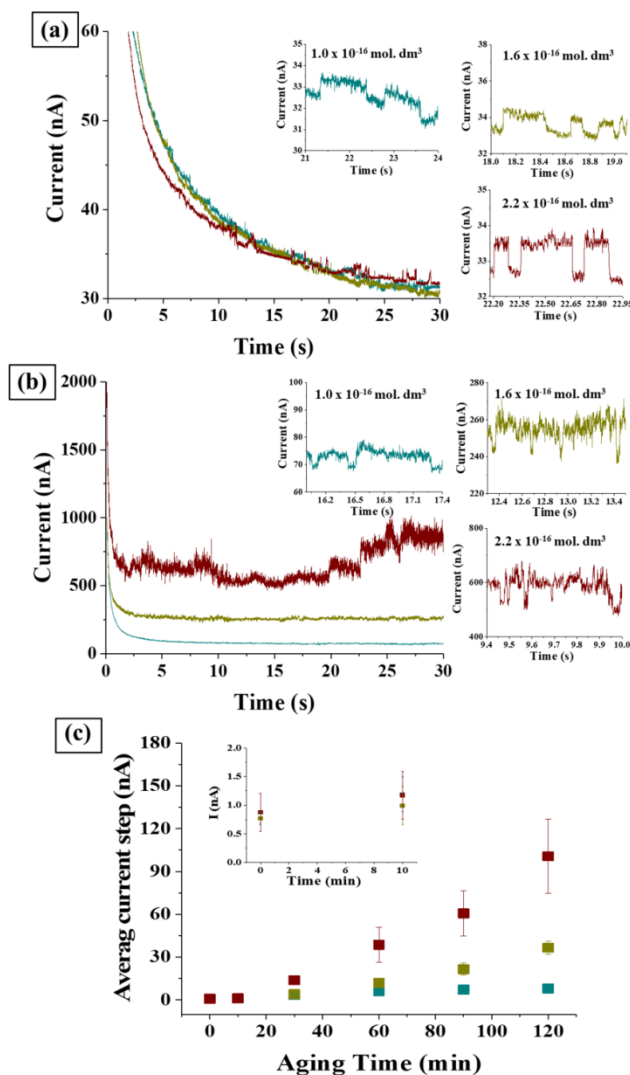


Figure 1 Chronoamperometric profiles of IDE-Au immersed in a solution containing different concentration of GNPs (■ 1.0 x 10⁻¹⁶, ■ 1.6 x 10⁻¹⁶, and ■ 2.2 x 10⁻¹⁶ mol dm⁻³) at a potential of 0.8V (a) fresh solution, (b) after GNPs are aged in the solution for 2h (inset shows the zoom-in images of the chronoamperometric profiles), and (c) Average step current at 0.8V against aging time of GNPs suspension from 15-35 collision events

Interestingly, for suspensions aged for a time longer than 2 hours (Figure S6), the contact resistance decreases to $2.0 \pm 0.2 \times 10^8 \Omega$. This plausibly results from the restacking and aggregation of GNPs. The observed increasing aggregation likely results in a decrease in the measured individual contact resistances. The GNPs aggregates may enhance the adhesive

forces resulting from the van der Waals' attraction between the large particle and the gold electrode. Consistent with the concept of increased adhesion is observation that the friction on multilayer graphene is smaller than on single graphene sheet [29, 30]. The increased adhesion of the GNPs to gold might be attributed to an increase of contact area. Also, when graphene sheets are brought into contact forming stacking layers, the layers do not overlay exactly one on top of each other, but are shifted relating to neighbouring layer increasing the size enhancing the GNPs area[31]. So that in addition to increasing adhesion and contact area, the particle may have increased multiple contact points which electrically act in parallel. Schematically, a single contact of GNP is shown by the simple equivalent circuit in Figure 2(a). Under the aggregating conditions the equivalent circuit of this situation is shown in Figure 2(b).

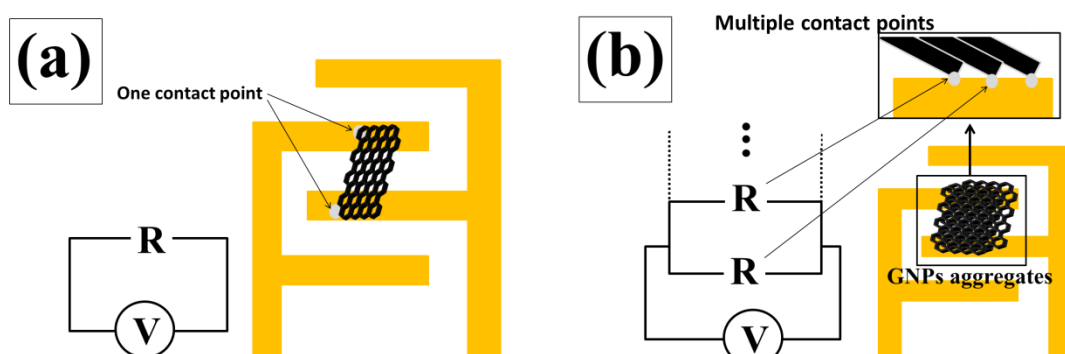


Figure 2 Schematic of (a) single and (b) multiple contacts of GNPs on IDE-Au and their equivalent circuits

Having evidenced the aggregation of GNPs via bridging impacts in solution dynamic light scattering (DLS) and optical microscopy techniques were next employed. Simple DLS measurements are shown in Figure S4 from which it was concluded that the high polydispersity of the samples precluded quantitative measurement. Accordingly, optical microscopy (Figure 3a and b) was preferentially used to characterize the nanoplates in the solution phase. As discussed earlier, the new preparation of GNPs suspension has highly

dispersed 2D particles with the uniform diameter of $6.3 \pm 3.2 \mu\text{m}$. Then, the GNPs suspension was aged for 2 hours. Some large particles precipitated which were visible to the naked eye after 30 minutes (Figure 3c). Aliquots were carefully taken from the middle of the container in order to be physically distant from the large particles. An image is shown in Figure 3b. A broad particle-size distribution (Figure 3d) is observed with the larger average diameter of $10.0 \pm 5.0 \mu\text{m}$ (117 samples). Even though the aggregation of nanoparticles in a solution phase is evidenced by the optical microscopy, it is difficult to provide an accurate quantitative estimation because of the change in particle size during the measurement time.

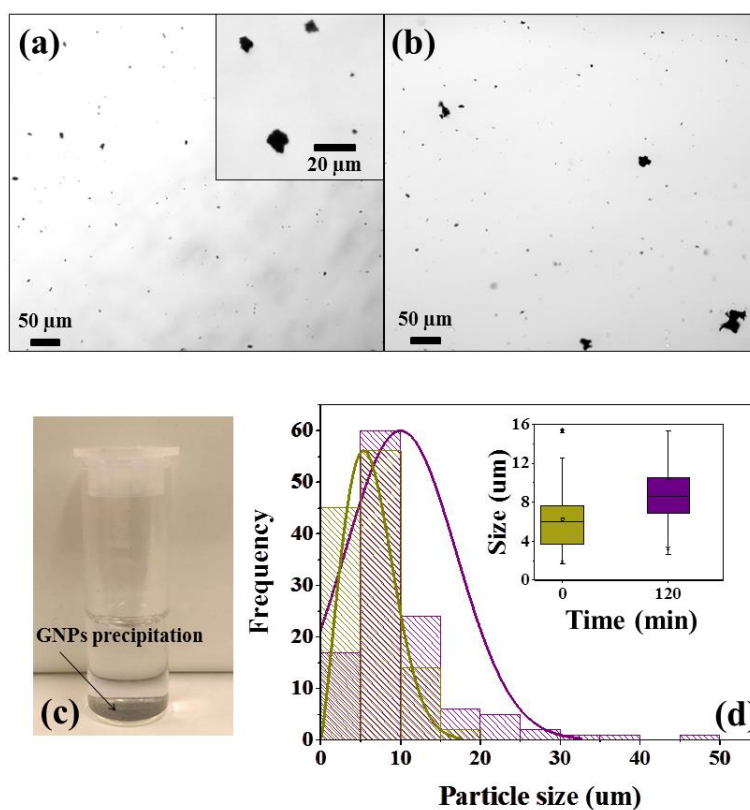


Figure 3 Bright-field optical microscopic images of graphene nanoplates in deionized water solution ($1.6 \times 10^{-16} \text{ mol dm}^{-3}$) subjected to 10 min sonication, (a) 0 min and (b) 2 h after sonication process, and (c) the size distribution profile of 0 min (■) and 2 h (■) aging time of graphene nanoplates in water solution (inset image is the box diagram of mean particle size and interquartile range)

In conclusion, a simple and rapid procedure has been developed to detect the re-stacking and aggregation of graphene nanoplates (GNPs) in solution by using the nano-impact method. In general, GNPs suspended in a solution have a time-dependent tendency to aggregate via overlaying on top of each other and growth in a perpendicular direction. The non-symmetrical shape high level of polydispersity makes them hard to detect via dynamic light scattering (DLS) which is commonly used to measure aggregation. Using nano-impacts, the current response shows a high sensitivity to the physical change of the impacting nanomaterials. Therefore, by increasing the processing time of the measurement at an applied potential, the current magnitude is increased significantly. The proposed electrochemical nano-impact allows an easy and feasible measurement of the re-stacking GNPs in the solution phase and enables rapid identification of the conditions under which suspensions of GNPs have metastability. In particular, we see the value of our approach as indicating the difference between non-aggregated and aggregated GNPs; in practice most applications will seek to use GNPs under the former conditions. Future work may address the relationship between the contact resistance and the extent of aggregation.

Supporting Information.

The supporting information consists of experiment and supporting figures. The supporting figures include bright-field optical microscopic images GNPs in solution with and without sonication, chronoamperometric profiles of IDE-Au in GNPs suspension at various potentials, and noise current vs. aging time, and hydrodynamic diameter obtained from DLS measurement.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

The research is sponsored by the funding from the European Research Council under European Union's Seventh Framework Programme (FP/207-2013), ERC Grant Agreement no. 320403. A.K. gratefully acknowledges funding from the Thailand Research Fund (RSA5880043) and Vidyasirimedhi Institute of Science and Technology.

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