Supporting Information

The Solution Phase Aggregation of Graphene Nanoplates

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Section 1: Experimental Section

1. Chemicals and reagents

Graphene nanoplatelets (GNPs, 15 µm in width, 6-8 nm in thickness, bulk density of 1×10^5 g m^{-3}) were purchased from Strem Chemicals (Newburyport, MA, USA). They were of analytical grade and used without any further purification. All solutions were made up with deionised water (DI water) of resistivity not less than 18.2 MΩ cm at 298 K (Millipore, Billerica, MA). The prepared solution was degassed thoroughly with pure nitrogen (BOC Gases plc, UK) for 5 min before use.

2. Suspension preparation

The GNPs suspension was prepared via first adding 1 mg GNPs into 10 mL DI water. The sonication process was employed using a Fisher Scientific FB15050 ultrasonic bath for 10 min in order to disperse the nanoplatelet and break up any aggregation. Then, 200 µL of the stock solution was then added into 2 mL DI water. The concentration of GNPs is 10µg/mL or $\approx 5.95 \times 10^{-15}$ mol. dm^3 GNPs assuming a relative molecular mass of 1.7×10^{12} g. mol^{-1} for GNPs which is calculated from a powder density of graphite (2.3×10^6 g m^{-3})[1]. Similarly, suspensions with higher GNPs concentrations (1.6×10^{-6} and 2.2×10^{-6} mol. dm^3) were carried out without any further sonication. Note that a fresh stock suspension was prepared daily.

3. Nano-impact experiments of graphene nanoplates (GNPs) on a gold interdigitated array electrode (IDE-Au)

Nano-impact chronoamperometry was conducted at a gold interdigitated electrode (ED-IDA3-Au, Micrux Technologies, Oviedo, Spain). The electrode consists of 180 pairs of gold bands that are 5.0 µm width and separated by 5.0 µm gaps. The experiment was carried out by the µ-Autolab II potentiostat (Metrohm-Autolab, Utrecht, The Netherlands) in a Faraday cage thermostated at 25.0 ± 1.0 °C. Different GNP concentrations and potentials were investigated.

4. Optical microscopy

Bright-field optical microscopic images were recorded using a Zeiss Axio Examiner microscope using a 20x oil immersion objective (NA = 0.5, EC Plan-Neofluar). A Hamamatsu ORCA-Flash 4.0 Digital CMOS camera (Hamamatsu, Japan) was applied to

provide 16-bit images with 4 megapixel resolution. Camera exposure control was carried out with the software Zen 2 (blue edition, Carl Zeiss Ltd., Cambridge UK). 40 µL aliquot was dropped on a cleaned slide and covered with a thin cover slide.

5. Dynamic light scattering (DLS)

The DLS experiments were performed using Malvern Zetasizer Nano ZS (Malvern instrument Ltd, Worcestershire, United Kingdom) at 25°C. Measurement parameters were as follows: He– Ne laser with a wavelength of 633 nm, fixed scattering angle of 173°, a medium viscosity of 0.8872 mPa.s and a medium refractive index of 1.330, and material refractive index of 2.42 (graphite refractive index). The sample was loaded into a disposable micro cuvette. In order to observe an effect of aging time, 2.2 x 10^{-16} mol. dm^{-3} GNPs in deionized water was first sonicated for 10.0 min and then aged for 30.0, 60.0, and 120.0 min. Each experiment was repeated three times.

Section 2: Supporting Figures

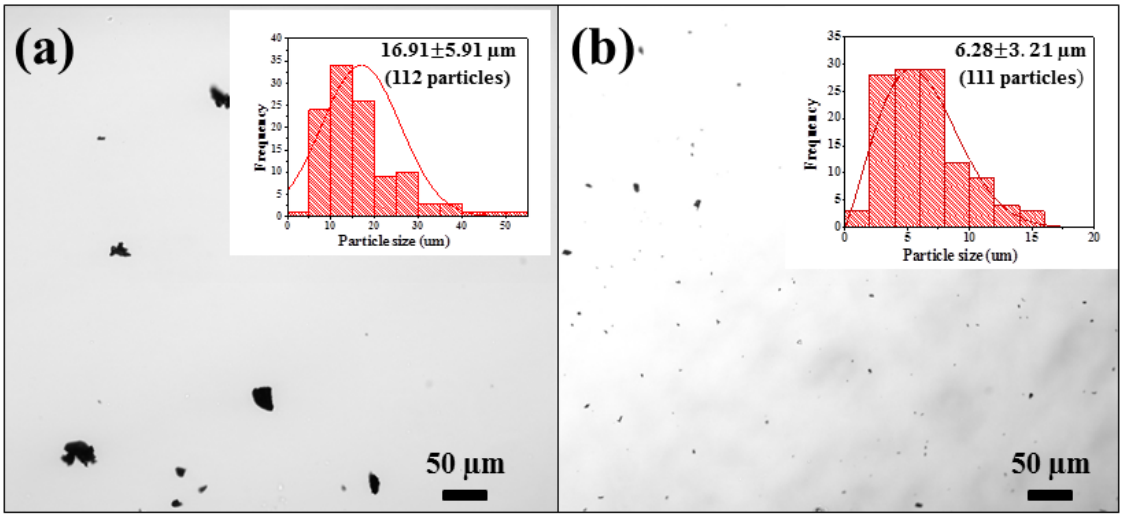


Figure S1 Bright-field optical microscopic images of 1.0 x 10^{-16} mol. dm^{-3} graphene nanoplates in deionized water solution (a) without sonication, and (d) subjected to 10.0 min sonication (inset image: the size distribution)

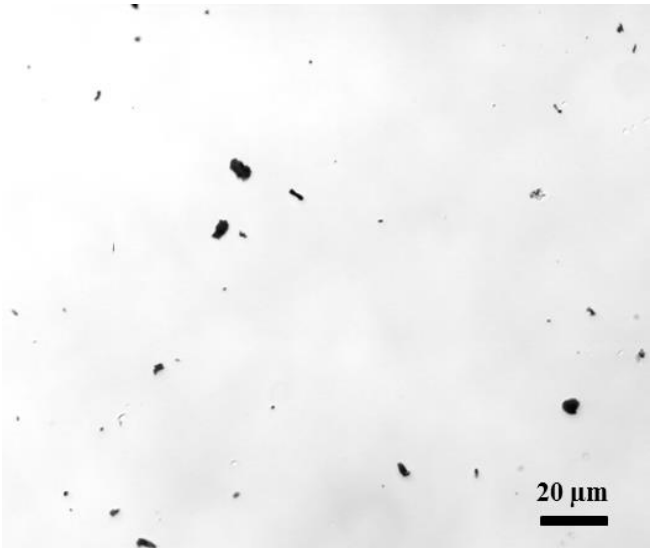


Figure S2 High magnification of bright-field optical microscopic images of 1.0 x 10^{-16} mol. dm^{-3} graphene nanoplates in deionized water solution subjected to 10 min sonication

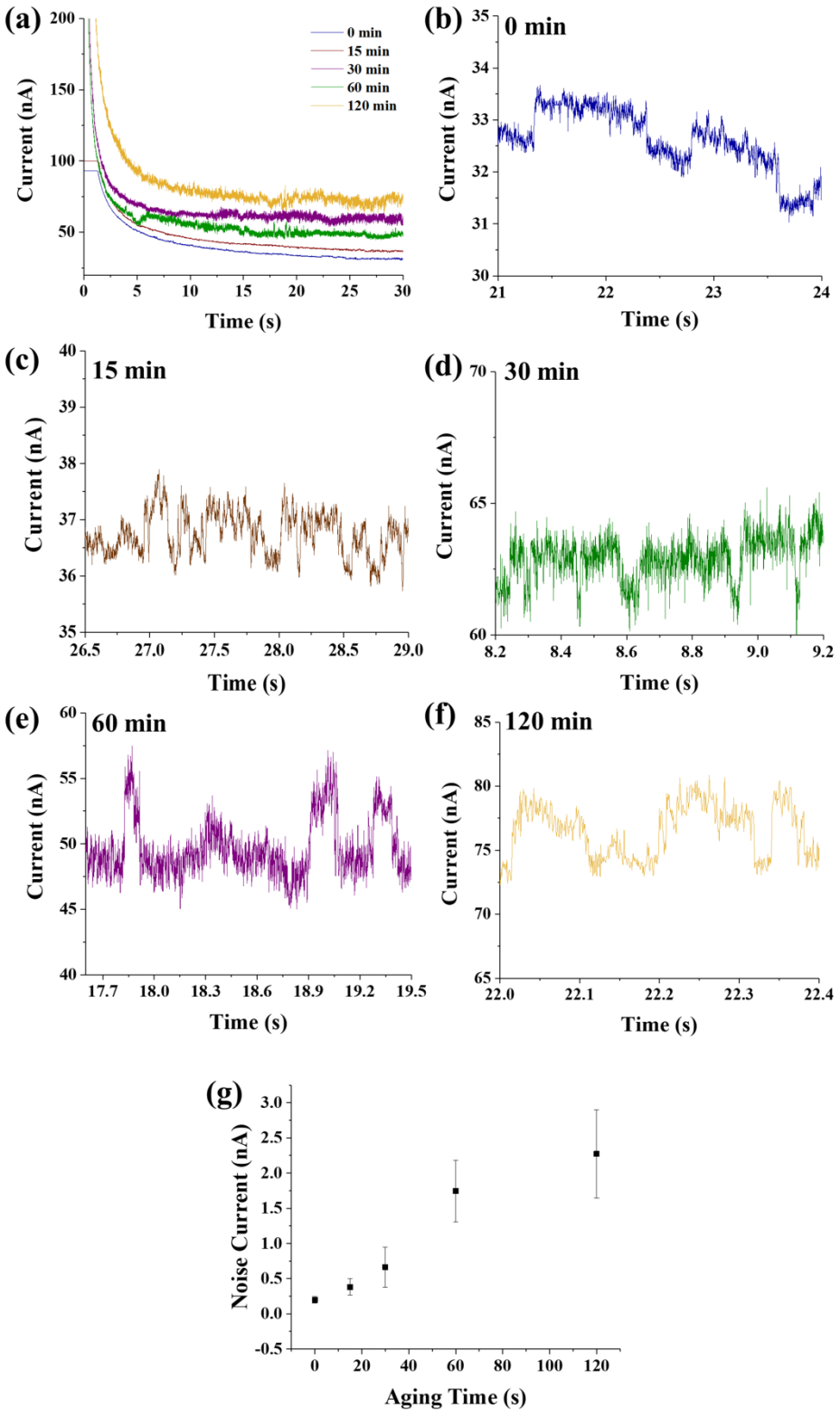


Figure S3 (a) Chronoamperometric profiles of IDE-Au immersed in a solution containing 1.0 x 10^{-16} mol. dm^{-3} GNPs and GNPs aged for 2 h; Zoom on the chronoamperometric profiles (Figure S5a) at different aging times, (b) 0.0 min, (c) 15.0 min, (d) 30.0 min, (e) 60.0 min, (f) 120.0 min, and (g) Noise current vs. aging time

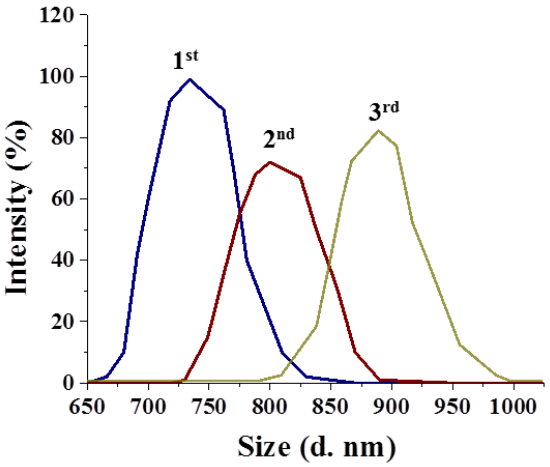


Figure S4 Hydrodynamic diameter profile at 0 min obtained by DLS analysis

Section 3: Contact resistance study

In order to study the contact resistance, the nano-impact chronoamperometry method was employed at different applied potentials (0.1-0.8 V) across two microbands of a gold electrode in a solution containing 1.0 x 10^{-16} mol dm^{-3} GNPs. The suspension was sonicated for 10 min. As discussed in the main text, the effect of aging times (10 min and 2 h) after the sonication process was observed. Firstly, the experiment was conducted within 10 min to minimize the aggregation (**Figure** S5). The first chronoamperometric scan of each potential was recorded. An example response of 0.2, 0.4, and 0.6 V is shown in inset images in **Figure** S5 (b), (c), and (d) respectively. The impact features of GNPs are in the form of current 'steps', with their impact duration in the range of 90 ms to 350 ms.

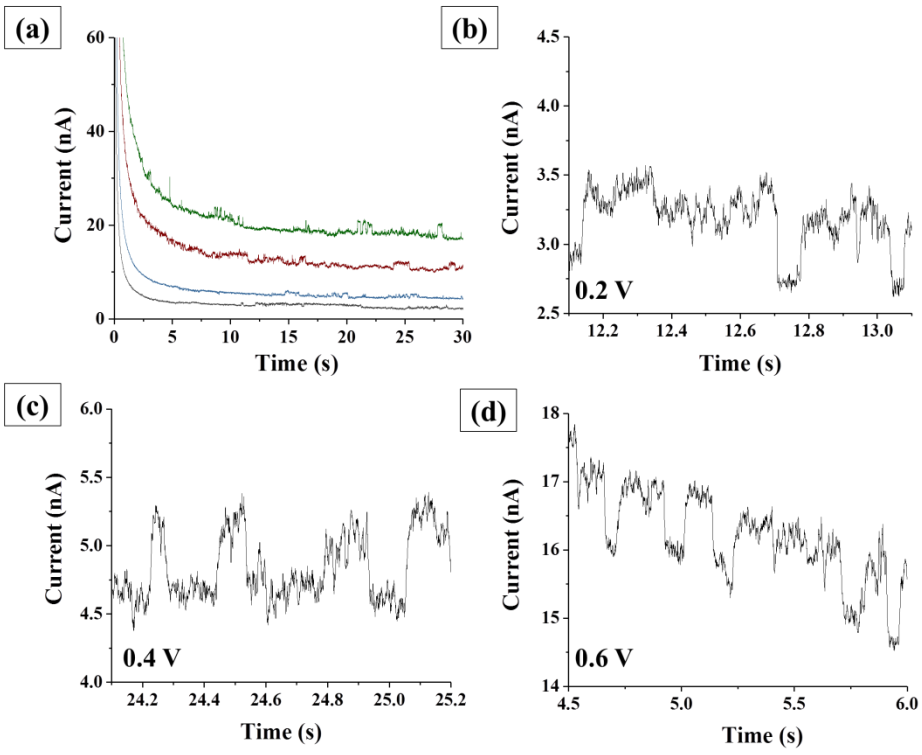


Figure S5 (a) Chronoamperometric profiles (1st scan) of IDE-Au in DI water containing graphene nanoplate (1.0 x 10^{-16} mol. dm^{-3}) at different applied potentials (■ 0.2, ■ 0.4, ■ 0.6 and ■ 0.8V), Zoom in image of applied potentials (b) 0.2, (b) 0.4, and (d) 0.6 V

The second experiment was after 2 h to allow the GNPs to aggregate (**Figure** S6). Again, the response from the chronoamperometry method was recorded at different applied potentials (0.10-0.80 V) across two microbands of the IDE-Au in a solution containing 1.00 x 10^{-16} mol dm^{-3} GNPs. Each potential in this experiment was consecutively repeated for 18 scans. The current steps switch between two or more apparently discrete levels (inset image of **Figure** S6 (d)) above the background current which is an evidence of GNPs re-aggregation. Some of them have about double current magnitude (inset image of **Figure** S6 (c)).

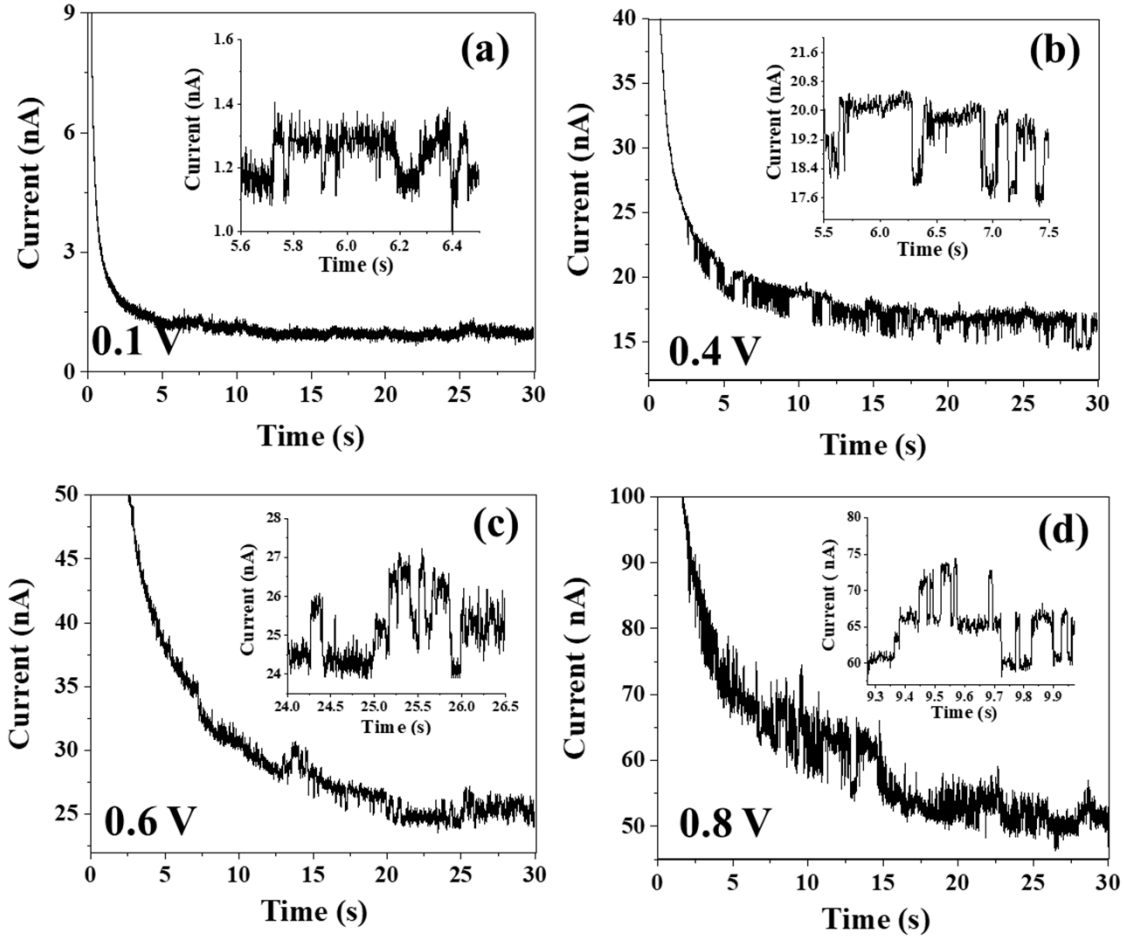


Figure S6 Chronoamperometric profiles of IDE-Au in DI water containing graphene nanoplates (1.0 x 10^{-16} mol dm^{-3}) at different applied potentials, (a) 0.1 V, (b) 0.4 V, (c) 0.6 V, and (d) 0.8 V, and (e) Average step current of graphene nanoplates (1.0 x 10^{-16} mol. dm^{-3}) at various potentials across two microbands of the IDE-Au

During the measurements, 15-150 collision events were observed and analyzed at each potential. The average values of current steps are plotted as a function of the applied potential, as shown in **Figure** S7. Black dots represent the result from the first experiment (10 min aging time), while green dots belong to the second experiment (2h aging time). The result is fitted with a linear curve. The slope of linear fitting I−V curve represents the average total resistance of a single nanoplate contacting between two bands of the gold electrode with a mean value of $5.9 \pm 0.1 \times 10^8$ Ω and $2.0 \pm 0.2 \times 10^8$ Ω for the experiment with 10 min and 2 h aging time, respectively. Compared to previous studies of a carbon nanotube (CNT) and gold electrode contact[2-3], the contact resistance in this work reports is the similar magnitude of 10−60 GΩ.

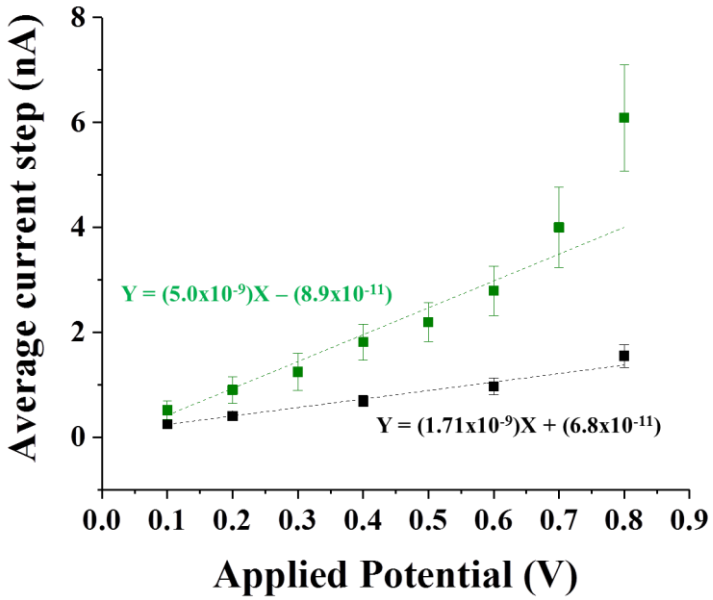


Figure S7 Average step current obtained from the 1st scan chronoamperometric profiles (blank dots) of graphene nanoplates (1.0 x 10^{-16} mol. dm^3) at various potentials across two microbands of IDE-Au compared with the average step current obtained from the several scans chronoamperometric profiles, consuming more than 2 hrs for the experiment, (green dots) (inset image: schematic showing a detection of re-stacking GNPs on IDE-Au)

Section 4: References

1. Wu, H.; Lin, Q.; Batchelor-McAuley, C.; Goncalves, L. M.; Lima, C. F. R. A. C.; Compton, R. G. Stochastic Detection and Characterisation of Individual Ferrocene Derivative Tagged Graphene Nanoplatelets. *Analyst.* **2016,** *141*, 2696-2703.

2. Krittayavathananon, A.; Ngamchuea, K.; Li, X.; Batchelor-McAuley, C.; Kätelhön, E.; Chaisiwamongkhol, K.; Sawangphruk, M.; Compton, R. G. Improving Single-Carbon-Nanotube–Electrode Contacts Using Molecular Electronics. *J. Phys. Chem. Lett.* **2017,** *8*, 3908-3911.

3. Li, X.; Batchelor-McAuley, C.; Shao, L.; Sokolov, S. V.; Young, N. P.; Compton, R. G. Quantifying Single-Carbon Nanotube–Electrode Contact Via the Nanoimpact Method. *J. Phys. Chem. Lett.* **2017,** *8*, 507-511.