

Supplementary Information to

Formation of Tunable Graphene Oxide Coating with High Adhesion

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SUPPLEMENTARY METHODS

Preparation of GO: preparation of exfoliated GO followed a previously published, modified Hummers method,¹ with same materials and setup. This method gave GO flakes with lateral size and thickness ~ 0.5 - $20 \mu\text{m}$ and $\sim 1.5 \text{ nm}$, respectively.¹ The concentration of GO (0.4 g L^{-1}) is defined here as the net carbon weight, excluding the weight of oxygen containing groups, divided by volume.

Surface treatment of NAB panels: Before coating, the NAB ($> 78.5 \text{ wt}\%$ Cu, 4.5 - $5.5 \text{ wt}\%$ Ni, 4.0 - $5.0 \text{ wt}\%$ Fe, $< 1.0 \text{ wt}\%$ impurities) surface was polished using sand paper ($12.5 \mu\text{m}$ grain size) to remove surface oxides, sonicated in acetone to remove small particles and contamination, and then immersed in fresh acetone to suppress surface oxidation. Some polished panels were further polished by glass bead blasting (bead size of $\sim 75 \mu\text{m}$) and then cleaned and stored in acetone. Polished steel panels were also produced using this method.

GO coating by EPD technique: GO (0.4 g L^{-1} aqueous suspension) was coated on both steel (2 cm width, 10 cm length) and NAB (both positive and negative electrodes, 5 cm width, 5 cm length), which were then dried at $100 \text{ }^\circ\text{C}$ for 10 minutes before the adhesion test was completed. The inter-electrode distance and the electrical potential were fixed at 3 cm and 3 V , respectively. To create samples of NAB with a thin GO coating, a thick layer was first created, heated at $100 \text{ }^\circ\text{C}$ for 10 minutes, then at $200 \text{ }^\circ\text{C}$ for a further 10 minutes and then the loosely attached GO was peeled off to leave a thin coating. This was used for later comparison with samples created using the transfer method described below.

GO coating by transfer technique: Filter paper (Whatman Grade 540) was immersed into 0.4 g.L^{-1} GO suspension to coat it with GO. The NAB panel was removed from acetone and air dried for 10 seconds. The GO coated filter paper was removed from the suspension (vertically attach the edge onto clean filter paper until no clear visible droplet on the immersed filter paper), and then put onto the panel. The panel was placed onto a hot plate at $100 \text{ }^\circ\text{C}$ until the filter paper naturally peeled off with 10 minutes. The panel was then removed from the hot plate and allowed to cool with 10 minutes. This transfer process was repeated a second time to obtain a uniform coverage of GO. Some coated panels were further heated at $200 \text{ }^\circ\text{C}$ for 10 minutes. In some cases, further repeated transfers were used in order to build up thicker

layers of the coating. Application of GO onto steel (5 cm width, 5 cm length) using the transfer method also followed this process.

Functionalization of the GO coating: Separate solutions were prepared of 0.5 mL hexylamine (HA, Sigma-Aldrich, product No. 219703) and 30 mg hexadecylamine (HDA, Sigma-Aldrich, product No. 445312) both in 150 mL absolute ethanol. GO coated NAB panels were immersed into these solutions. The solution was gently stirred and heated at around 60 °C for 2 h, to allow any reaction. After this, the panel was dried at 80 °C for 5 minutes in an oven and washed thoroughly with warm ethanol (around 50 °C) to remove any residual chemicals (un-functionalized HA and HDA) from the coated surface. The panel was then dried at room temperature.

Characterization: Raman spectra were recorded on a Renishaw Raman spectrometer with an excitation wavelength of 532 nm and different beam powers (100 % power equals 100 mW beam power; same objective lens was used for all measurements; Raman shift of Si was calibrated as 520 cm^{-1}). Since GO coated NAB is not transparent, reflectance FT-IR of the coating was performed at room temperature on a Bruker Optics Tensor-27 Fourier transform infrared spectrometer. Scanning electron microscopy (SEM) was performed using a commercial Nova 600 NanoSEM without any additional conductive surface coating. X-ray photoelectron spectroscopy (XPS) was performed on a Kratos AXIS Ultra DLD X-ray photoelectron spectroscopy with an excitation source of Al Ka. The binding energy of XPS was calibrated based on C1s (284.6 eV). Ion gas etching was used to reduce the thickness of GO coating, which was required for obtaining the binding environment of the GO/NAB interlayer. The wettability of the coated metal surface was determined using a contact angle goniometer. The adhesion of the coating to the panel was measured using a dolly pull test technique. Before each adhesion measurement, the dollies (1.27 cm diameter) were cleaned using acetone, air dried for 20 minutes, grit blasted with p320 alumina grit, rewashed using acetone and then re-dried in air for 20 minutes. The surface of the sample was prepared by gently wiping it with tissue soaked in 2-propanol and air-dried for 20 minutes. Following this, 1.8 g (\pm 0.1 g) of Loctite 907 epoxy adhesive was mixed and applied to bond the dolly to the sample. The sample was placed in a fume cupboard for 72 hours at room temperature to cure the epoxy. The pull tests were

made using a PosiTest AT-A (with a pressure increase rate of 0.7 MPa s^{-1}). A photograph of one GO coated NAB sample and the face of one dolly after an adhesion test had been completed are shown in Fig. S1. Potentiodynamic polarization tests of different samples were performed on on a CHI 650C electrochemical workstation with three electrodes [reference electrode: Ag/AgCl, 1M KCl; counter electrode: glassy carbon; working electrode: $4 \times 10 \text{ mm}^2$ coated and uncoated NAB] in 0.1 M aqueous NaCl solution.

Table S1. Adhesion of EPD coatings of GO on steel and NAB.

Time (mins)	Steel (MPa)		NAB(MPa)	
	positive	negative	positive	negative
2	4.8	3.9	3.1	2.8
20	3.0	3.0	2.4	1.7

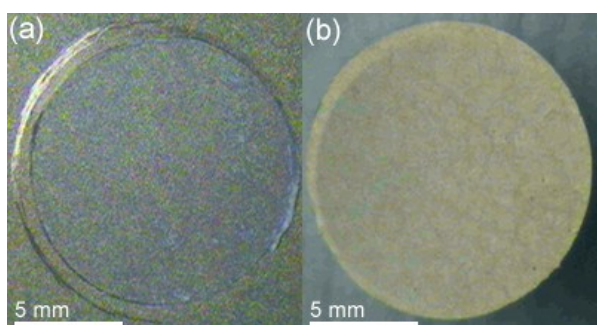


Figure S1. Photographs of one GO coated NAB (bead blasted) and the face of one dolly after adhesion (pull) test.

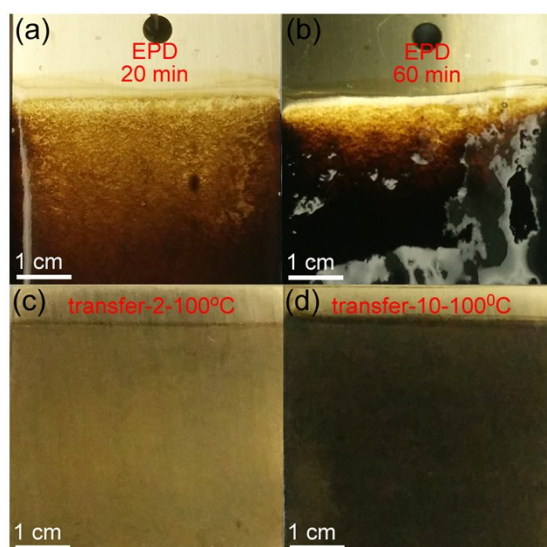


Figure S2. (a-b) Photographs of NAB coated with GO using the EPD method. (c-d) Photographs of transfer-2-100°C and transfer-10-100°C samples, showing that the thickness of the GO coating can be well controlled (darker surface means thicker coating).

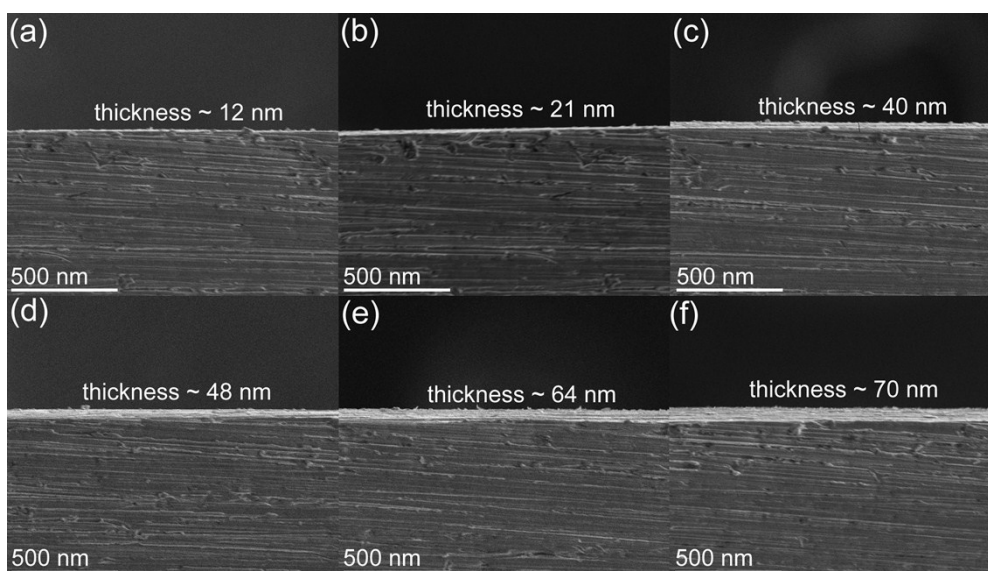


Figure S3. Cross-section SEM images of (a) transfer-2-100°C, (b) transfer-4-100°C, (c) transfer-6-100°C, (d) transfer-8-100°C, (e) transfer-10-100°C, and (f) transfer-12-100°C, suggesting that thickness of GO film is dependent on number of transfers.

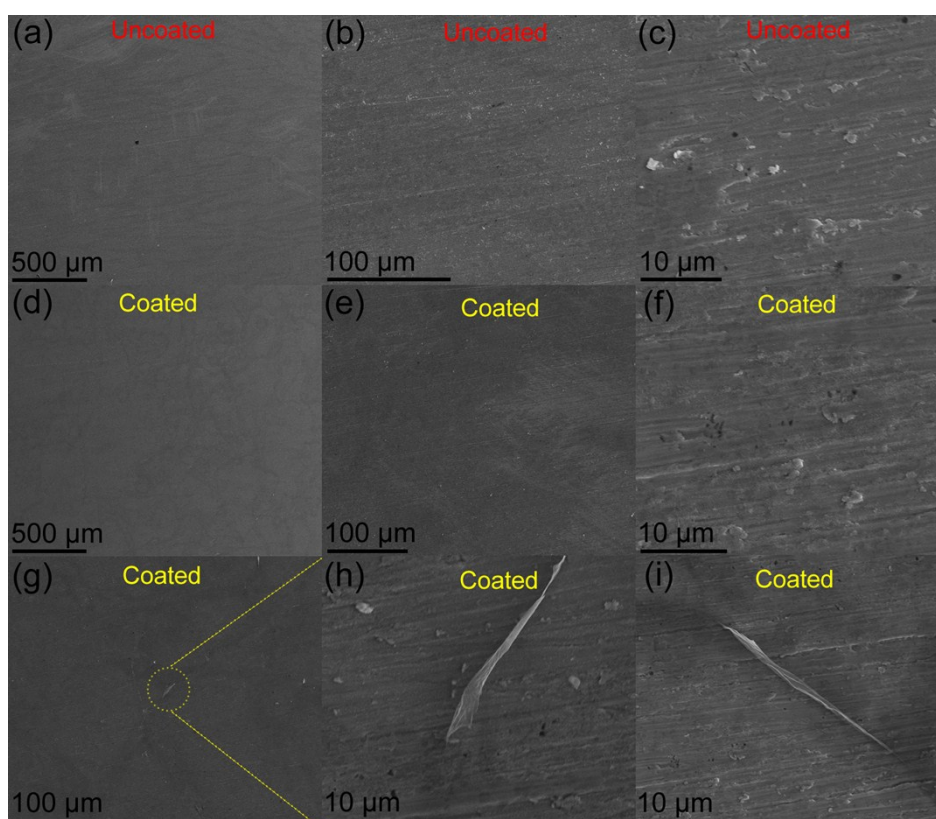


Figure S4. (a-c) SEM images of polished NAB. (d-i) SEM images of transfer-2-100°C. The marked position in image g was enlarged in image h.

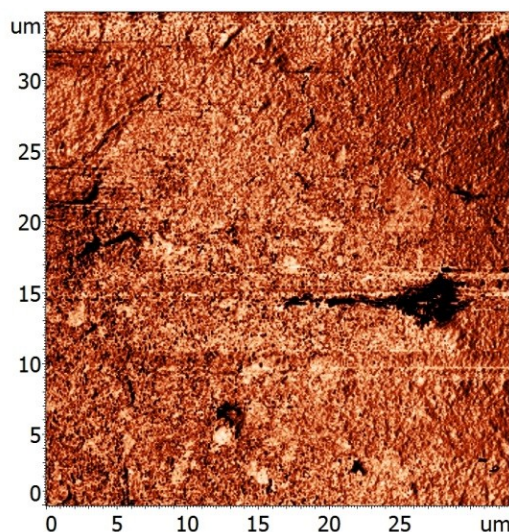


Figure S5. AFM phase contrast map of transfer-2-100°C. Very little contrast over the area was observed, which suggests that the coating is uniform and fully covered the NAB surface. The black area is induced by the erupted particle.

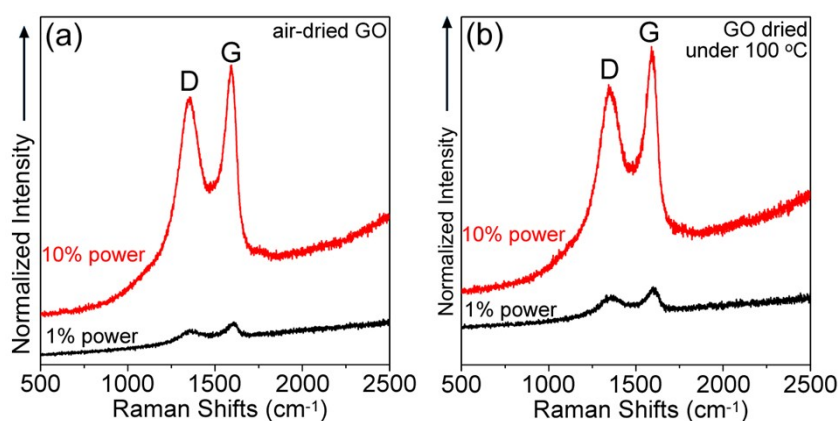


Figure S6. Raman spectra of different samples on untreated NAB surface (the surface was not polished or bead blasted) using different laser powers: (a) air-dried GO powder at room temperature and (c) GO powder dried at 100 °C for 10 minutes.

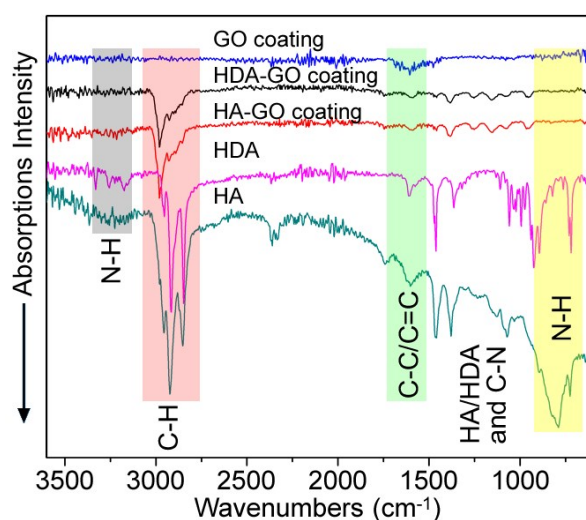


Figure S7. FT-IR absorption spectra of GO, HA, HDA, HA functionalized GO (HA-GO) and HDA functionalized GO coatings (HDA-GO). The absorption intensities of HA and HDA were weakened for better comparison. FT-IR spectra of the functionalized GO are similar with each other. Although the signal (coated samples) from this measurement is really weak (e.g. the C-O and C=O vibrations of GO

coating are not well resolved), characteristic peaks of C-C/C=C of all these samples (highlighted as faint green) were detected at around 1600 cm^{-1} , which is close to some GO materials and red-shifted from that of highly reduced GO ($\sim 1640\text{ cm}^{-1}$).^{1,2} Vibrations from HA and HDA are also evident in the functionalized samples (e.g. C-H bond at around 2982 cm^{-1}), but both blue shifted from that of HA and HDA (highlighted as faint red region). Absorption peaks in the region of $1500\text{-}900\text{ cm}^{-1}$ are also clear which contains the vibrations from HA, HDA.³⁻⁴ Besides, in comparing with our measured (in this figure) and previously reported FT-IR spectra of HA and HDA,³⁻⁴ two new absorptions appeared at around 1252 and 1151 cm^{-1} , which were induced by the newly formed bond between GO and HA/HDA. Although precise assignments of these peaks (in the region of $1500\text{-}900\text{ cm}^{-1}$) are difficult at this stage since chemical environment changes may also lead the shift of absorptions (e.g. C-O, C-N), successful functionalization of the GO coating is evident. This was further confirmed by the disappearance of N-H vibrations of the functionalized GO coating, which should appear at around 3288 (weak in HA and HDA, highlighted as gray region) and $894\text{-}718\text{ cm}^{-1}$ (strong in HA and HDA, highlighted as faint yellow region).³⁻⁵

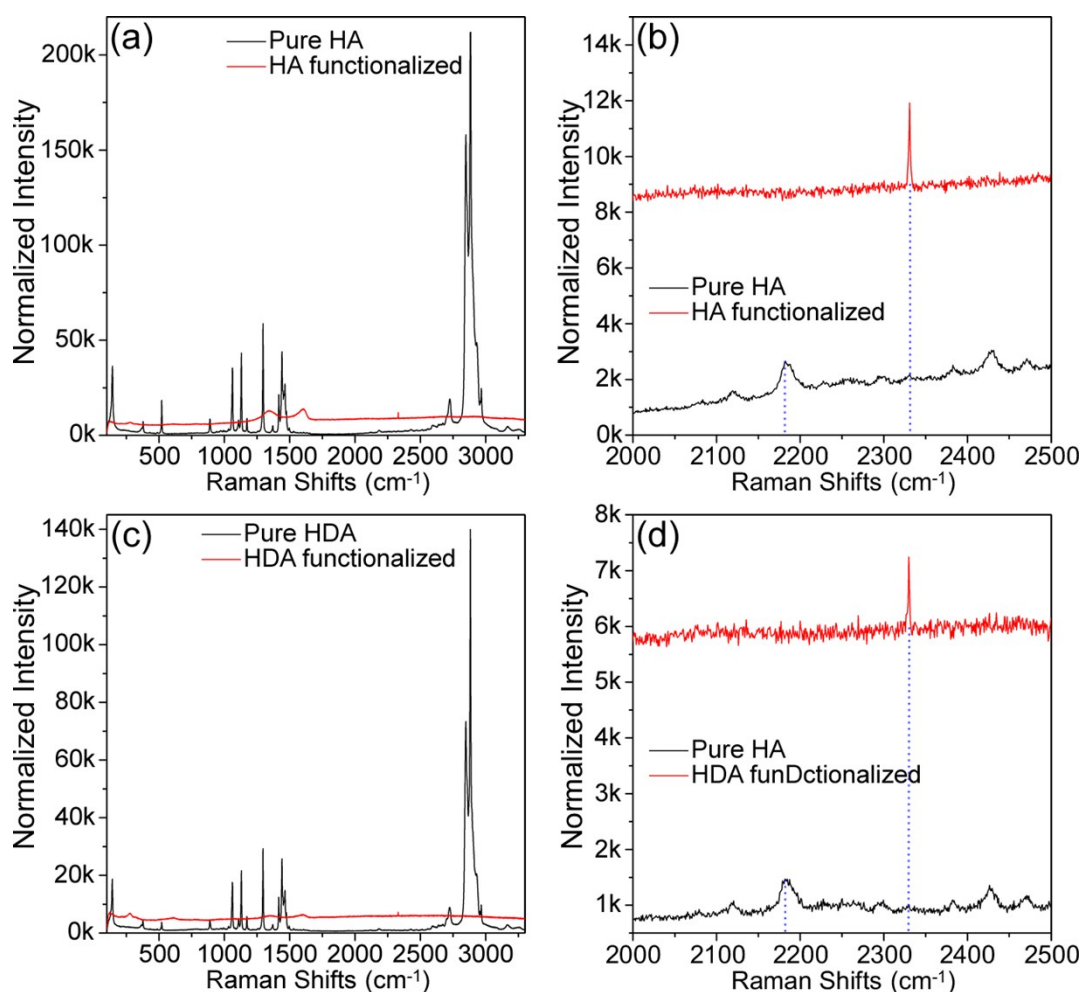


Figure S8. (a,b) Raman spectra of pure HA and HA functionalized GO coating. (c,d) Raman spectra of pure HDA and HDA functionalized GO coating. Raman analyses (all with 100% beam power) of HA and HDA were performed on powder sample (HA is in solution form and was dried at room temperature) on polished NAB surface. The Raman response of pure HA and HDA are intense and evident (a,c). These responses from functionalized GO coating are weak since only one HA/HAD layer grafted on the GO surface and edge in principle. Nevertheless, we found Raman response of C-N bond changed upon this functionalization (b,d). Previous Raman studies on C-NH₂ suggested a C-N Raman response at around $2150\text{-}2190\text{ cm}^{-1}$,⁶ which presented at around 2180 cm^{-1} in both HA and HDA (b,d). After functionalization, such C-N peak (at around 2180 cm^{-1}) disappeared and a new Raman response appeared at around 2330 cm^{-1} , suggesting that HA and HDA have bonded with GO coating and changed the

chemical environment of C-N (we have not found such Raman of GO and polished NAB). Together with FT-IR characterizations in Figure S7, it is clear that the GO coating has been successfully functionalized by HA and HDA.

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