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COMMUNICATION

Formation of Tunable Graphene Oxide Coating with High Adhesion

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Graphene oxide (GO) can be applied as a coating on metals, but few of these coatings have an adhesion suitable for practical applications. We demonstrate here how to form a GO coating on metals with a high adhesion (~10.6 MPa) and tuneable surface, which can be further applied using similar/modified techniques for special applications (e.g. anti-corrosion and anti-biofouling).

Graphene, a one atom thick carbon material with an aromatic substructure, has received much attention due to its remarkable properties.¹ Applications of graphene have been identified in which a homogenous graphene-based coating on metal surfaces is highly desirable,² such as coatings for anti-corrosion³ and anti-fouling.⁴ However, this requires graphene or its derivatives to be efficiently coated onto metals with strong adhesion and preferably with a highly chemically tunable surface.

Owing to its chemical inertness, graphene coatings (e.g. CVD graphene coating) are difficult to functionalize,¹ but its derivative, graphene oxide (GO) can be modified relatively easily.⁵ GO is therefore considered to be a promising source material for cost-effective, large-scale preparation of coatings.^{5,6} Many techniques, such as electrophoretic deposition (EPD), have been applied to obtain thick GO coatings.⁷ However, the adhesion of these GO coatings is rarely sufficient for practical applications, which may lead to desquamate of the coating in harsh environments (e.g. in marine and corroding systems).

Herein, we show a simple conceptual technique for achieving a highly adhered GO coating, which involves a simple formation and consolidation of a homogenous GO layer on a metal surface with chemical interactions. We demonstrate

how this high adhesion (up to 10.6 MPa) can be formed, and how this coating can be further functionalized *in situ* to change its surface properties (e.g. wettability). Discoveries here provide a simple way for obtaining robust GO coatings on metals for various purposes. Further development of this conceptual technique may include a modified method for coating large metal constructions (e.g. spray and immersion methods).

Initially, we investigated the formation and adhesion of GO coatings on polished steels (2×10 cm²) using the EPD application technique (see Supporting Information, 0.4 g.L⁻¹ GO concentration). During the EPD process, GO moves and adheres onto the surface of the positive electrode (driven by the added potential) since it is negatively charged. Nevertheless, a GO coating is also formed on the negative electrode, suggesting a possible spontaneous chemical reaction between the GO suspension and freshly polished steel before and during the full charge of the electrode (not driven by the added potential). After deposition, the adhesion of both dried (at 100 °C for 10 minutes) electrodes was measured and compared. As the deposition time was increased from 2 to 20 minutes, the average adhesion of GO on the positive electrode decreased from 4.8 to 3.0 MPa (see Table S1, for the negative electrode, the adhesion decreased from 3.9 to 3.0 MPa). The adhesion of GO on other metals (e.g. NAB, nickel aluminium bronze, see Supporting Information for more information) also behaved in a similar manner (Table S1). This highlights that the initially deposited layers are more strongly adhered to the metal than subsequent layers. The higher adhesion at the positive electrode also suggests that a positively charged surface can improve the adhesion of the GO coating. This is reasonable if a chemical interaction between metal and GO sheets is considered (metals and metal ions such as Fe²⁺, Ni⁺ and Cu⁺ can chemically bond with GO sheets),⁸ where the positive charge on the metal surface promotes the formation of the interaction.

Therefore, we propose to create a highly adhered GO coating by exploring the possible chemical interactions between clean metal surfaces (pure metals such as Cu, Ni, Al

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are more chemically active than their oxidized phases) and GO sheets (see diagram in Fig. 1a). NAB (> 78.5 wt% Cu, 4.5-5.5 wt% Ni, 4.0-5.0 wt% Fe, <1.0 wt% impurities) was then used to investigate this chemical interaction since it is more inert than pure steel when exposed to atmosphere and aqueous solution. We transferred GO (aqueous GO with concentration of 0.4 g L⁻¹) layers onto the freshly polished NAB surface (average 5×5 cm²) using filter paper (Whatman Grade 540). With suitable heating on a hot plate at 100 °C for 10 mins, the filter paper naturally peeled off, leaving a pure GO coating on the NAB surface (see Supporting Methods for more details). The characterization detailed below suggests that NAB can be fully coated with GO.

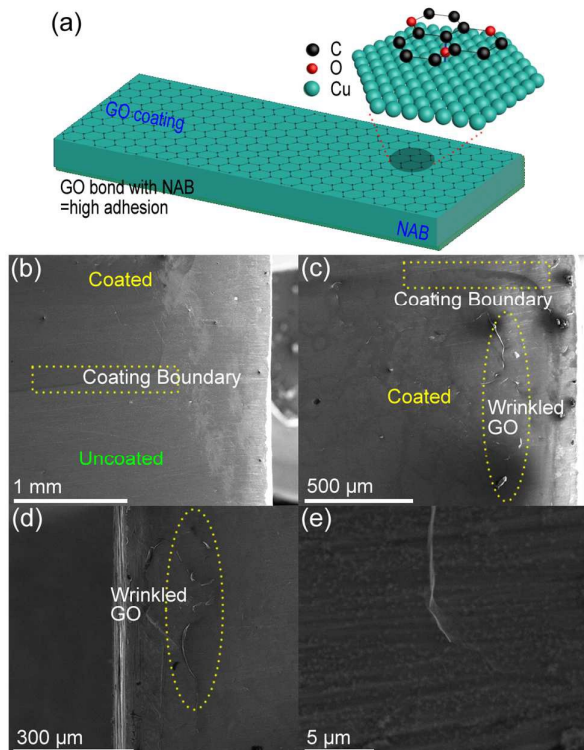


Figure 1. (a) Diagram of the bond between NAB and GO coating. (b-e) SEM images of transfer-2-100°C (NAB) show the coating boundary (b, c), and the raised GO edges at the edge of the NAB panel (c-d).

The thickness of the GO coating can be controlled by repeated transfers to add more GO layers (adding 2 transfers gives a thickness of around 12 nm), resulting in a darker surface (Figs. S2e&f and Fig. S3). Typically, two ('transfer-2-100°C') or more transfers (e.g. 10 transfers, defined as 'transfer-10-100°C') were required to achieve homogeneous coverage, as shown by SEM (Fig. 1b, also see Fig. S4 for more SEM images and Figs. S2c&d for photographs) and AFM phase contrast image (Fig. S5). The GO coating was optically darker (fewer surface charges) than the bare metal under SEM observations, suggesting that the GO has been reduced to a certain extent. SEM images (Figs. 1c-e) also indicate that the majority GO sheets were predominantly coplanar with the NAB surface; only at the edges were flakes occasionally found to have more random orientations. The adhesion of the GO

coating after 2 transfers ('transfer-2-100°C') was measured as 3.2 MPa. This decreased to around 2.9 (4 transfers), 2.6 (6 transfers), 2.3 (8 transfers), 1.9 (10 transfers) and 1.8 MPa (12 transfers) with more transfers, as expected as the additional layers are not in intimate contact and bound with the metal.

To understand the possible chemical interaction between the GO and NAB surface, we systematically conducted Raman investigations of the GO coating on both untreated and polished NAB (an average of 10 different positions were measured, separated by a distance larger than 2 mm). Noteworthy, Raman shift of the G peak can be used to determine the chemical environment of carbon based materials. For example, graphite and chemically reduced GO have a G peak at ~1587 cm⁻¹ which is blue shifted in both the free-standing GO and the GO bonding with metal.⁹ Fig. 2 shows the Raman spectra of the dried GO powder (dried at room temperature and at 100 °C, respectively) on untreated NAB (the surface was highly oxidized to avoid GO bonding with metal). Fringe Raman modes of the D and G peaks^{9,10} of the dried GO samples are evident (Fig. S6). Close examination (Fig. 2a) of the air-dried (room temperature) GO reveals a G peak at around 1602-1604 cm⁻¹ with low laser power (1%, ~1 mW, laser source of the Raman measurement) illumination. At higher laser power (10%), the G peak red-shifted to 1591-1593 cm⁻¹ (Fig. 2a). Fig. 2b shows that GO dried at 100 °C had a G peak at around 1598-1600 cm⁻¹ (1% laser power). Increasing the laser power to 10% again led to a red-shift of the G peak to <1592 cm⁻¹. In some occasional cases, the G peak shifted to as low as 1587 cm⁻¹, which is equal to the G peak of chemically reduced GO (1587 cm⁻¹).^{9,10} The above analyses show that the GO is reduced to a certain extent by both simple heating (100 °C) and laser illumination, giving red shift of the G peak.

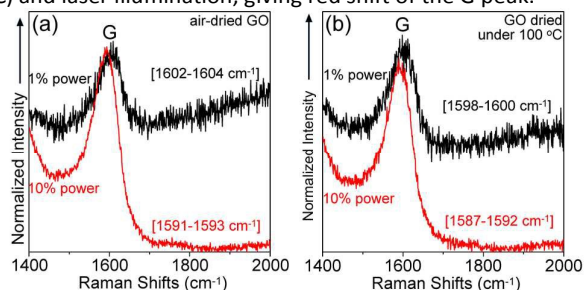


Figure 2. Raman spectra of different samples on untreated (pre-polished) NAB surface using different laser powers: (a) air-dried GO at room temperature and (b) GO dried at 100 °C for 10 minutes. For better comparison, the Raman intensity backgrounds were shifted.

It is anticipated that the G peak of the transferred GO coating (e.g. coating in Fig. 1) would also have a similar red shift under beam illumination if chemical bonds did not form between the GO and NAB. In the Raman spectra of transfer-2-100°C (Fig. 3, where the NAB has been polished to remove the oxide layer before GO transfer), the G peak at 1% beam power was at 1598-1601 cm⁻¹ (magnified in Fig. 3b), which is close to that found on the heated GO on untreated NAB (Fig. 2b). However, this G peak blue-shifted (rather than the red-shift on the non-bound GO on untreated NAB) to around 1603.5-1604.5 cm⁻¹ when the beam power was increased to 10% (Fig.

3b). Further Raman measurements with 50% and 100% beam powers (and with 5 accumulated scans of 100% beam power) showed no further shift of the G peak, suggesting that the chemical environment of the GO coating became steady after 10% beam illumination. The blue shift of the G peak is not an occasional case; we verified it at various different coating positions, which confirmed the formation of chemical interactions between the GO and freshly polished NAB. This interaction can be further consolidated due to the observed blue shift of the G peak under increasing beam illumination. In this case, like the C-C/C=C structure bound with oxygen, the bound metal atoms on GO (or partially reduced GO) would also suppress the rotation of C-C/C=C, leading the blue shift of the G band. *Note: Since GO coatings are not single layers, the Raman response is likely to be dominated by the lowest layer because it is in closest proximity to the metal and, therefore, subject to enhancement through surface-enhanced Raman scattering (SERS).*¹¹

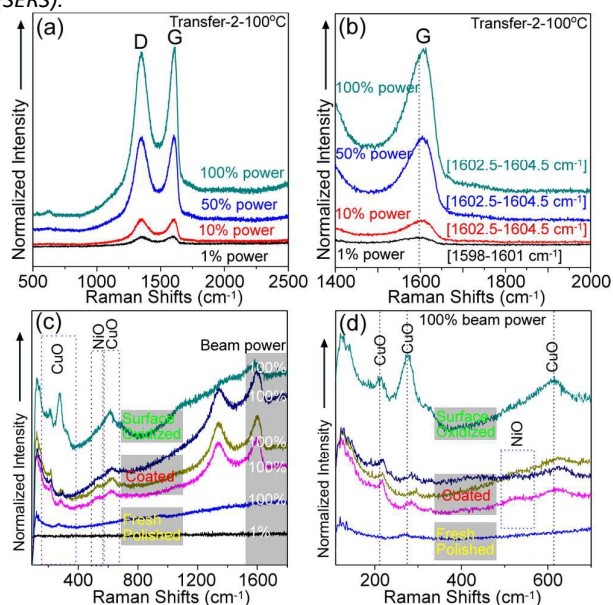


Figure 3. (a) Raman spectra of the transfer-2-100°C sample with different laser powers, showing D and G bands of GO. (b) Raman spectra of the transfer-2-100°C sample, showing G peak shift under different beam powers. (c) Raman spectra of freshly polished NAB, transfer-2-100°C and surface oxidized NAB (no GO coating) with different beam powers. (d) Local enlarged Raman spectra of freshly polished NAB, transfer-2-100°C sample and surface oxidized NAB (no GO coating, 100% beam power).

The chemical interaction between GO and freshly polished NAB was further confirmed by Raman examinations of the oxidized metal atoms on NAB. Fig. 3c shows that freshly polished NAB (washed with acetone) has no Raman response with 1% beam illumination. With 100% beam illumination, the untreated NAB gave more intense Raman peaks of the CuO phase at around 212.5, 276, 319 and 619.3 cm⁻¹ (Fig. 3d).¹² These oxidized phases originate from the pristine untreated NAB surface as opposed to being induced by beam illumination, since only one weak response (276 cm⁻¹) was found on the polished NAB (Figs. 3c&d) under identical measurement conditions. Raman spectra of the transfer-2-100°C (100%

beam power) are also shown in Figs. 3c&d, which are clearly different with that of oxidized metal on untreated NAB, giving slightly blue shifted responses to around 217.9, 284.5, 330, 623.6 cm⁻¹ respectively. In addition, a new weak Raman response for transfer-2-100°C was found at ~528.6 cm⁻¹, which absent on the untreated NAB, but corresponds well with the oxidized Ni phase (Ni-O).¹³

The X-ray photoelectron spectroscopy (XPS) of different samples were measured to confirm the precise bond between NAB and GO. As shown in Fig. 4a, pristine GO shows C1s peaks assigned to C-C/C=C (~284.6 eV), hydroxyl and epoxy C-O (~286.6 eV), carbonyl C=O (~287.4 eV) and carboxyl C-OH (~288.8 eV).⁹ C1s XPS of transfer-2-100°C (Fig. 4a) still shows a significant amount of O-containing groups (but much lower than that of pristine GO) and a new peak at ~289.5 eV which is assigned to C-O-Cu.¹⁴ The intensity of this new C-O-Cu peak significantly increased (Fig. 4a, O-containing groups still remain but are weakened from that of transfer-2-100°C) once the transfer-2-100°C sample was further heated at 200 °C for 10 minutes (defined as 'transfer-2-200°C'), suggesting that the bond formation of C-O-Cu was improved and consolidated. Fig. 4b is the Cu 2p_{3/2} XPS spectra of freshly polished NAB, transfer-2-100°C and transfer-2-200°C. The Cu(0) of polished NAB appears at around 932.2 eV.¹⁴ Slight oxidization of the polished NAB is also observed with a peak at around 935.8 eV, corresponding to Cu (2+).¹⁴ Nevertheless, transfer-2-100°C has an evidently different oxidized Cu state at ~934.5 eV [between Cu(0) and Cu(2+)], which is normally assigned to Cu (1+) and becomes more intense in transfer-2-200°C. This result corresponds well with that of C1s spectra (Fig. 4a), emphasizing that further heating at the elevated temperature consolidated the formation of C-O-Cu. Together with Raman results, the data suggests that the polished NAB has reacted with (oxidized by) GO, leading to different Raman responses and XPS states to that of GO and untreated NAB (oxidized by atmosphere with oxygen and H₂O).

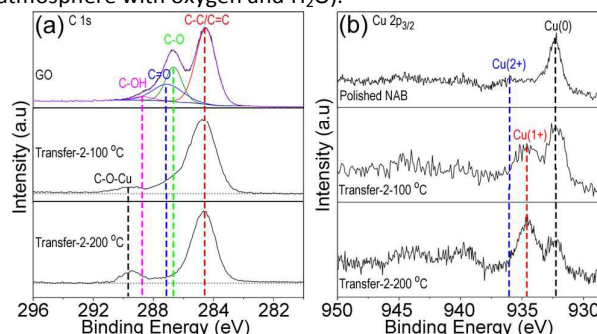


Figure 4. XPS spectra of GO, bare NAB, transfer-2-100 °C and transfer-2-200 °C. (a) C 1s XPS spectra. (b) Cu 2p_{3/2} XPS spectra.

The results obtained to date are promising for the creation of a highly adhered GO coating as these chemical interactions can be consolidated by simple thermal treatment. As result, transfer-2-200°C shows a high adhesion of 10.6 MPa, which is largely increased from the initial 3.2 MPa measured for transfer-2-100°C. This adhesion is much higher than that reported for other GO based coatings (e.g. few coatings have

been achieved with an adhesion of 3.3 MPa,⁷ and is comparable to many commercially available adhesives.¹⁵

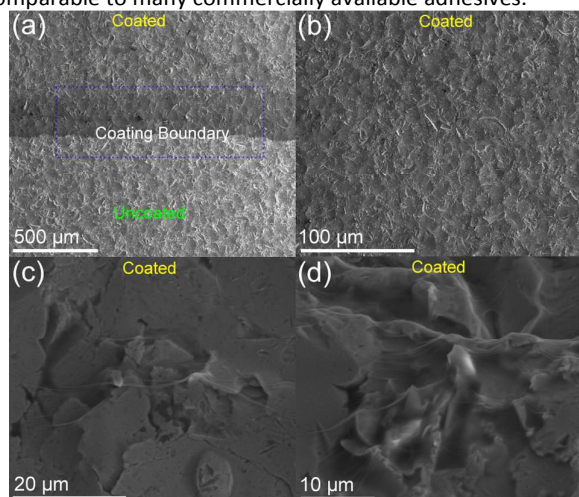


Figure 5. SEM images of transfer-2B-100°C: (a) shows the coating boundary, (b) homogenous coating and (c,d) wrinkled GO at the areas with valleys.

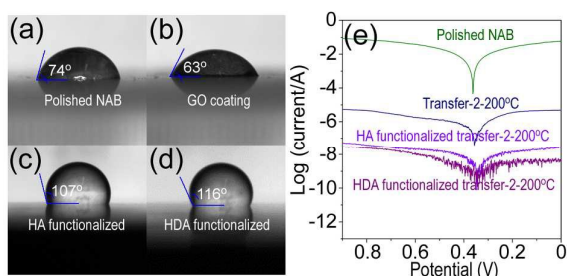


Figure 6. Water contact angle measurement of (a) polished NAB, (b) transfer-2-200°C, (c) HA functionalized transfer-2-200°C and (d) HDA functionalized transfer-2-200°C. (e) Potentiodynamic polarization curves of bare NAB, transfer-2-200°C, HA and HDA functionalized transfer-2-200°C samples.

This highly adhered GO coating can also be achieved on rough NAB surfaces. As shown in Figure 5, we roughened the NAB surface with bead blasting and transferred GO onto the surface (see Supporting Method) using the same transfer method as for transfer-2-100°C (sample is defined as 'transfer-2B-100°C'). GO coating is homogenous and fully covers the surface of the rough NAB (Figs. 5a&b). Some areas, containing wrinkled GO sheets, are not coplanar with the metal surface. The Raman response of this coating (transfer-2B-100°C) was largely similar to that of transfer-2-100°C, with a blue shift of the G band with increasing beam power. In some positions, particularly in the valleys (Figs. 5c-d), we found a red shift of the G band with increasing beam power, suggesting that some GO flake faces are not in sufficient contact with the metal to form a bond. Nevertheless, adhesion of up to 9.4 MPa was achieved once this sample was further heated at 200 °C for 10 minutes (transfer-2B-200°C). This value is slightly lower than that for transfer-2-200°C, which was subjected to the same thermal treatment, but can be explained as some areas of the GO sheets are not well bound with rough NAB surface. We

have also transferred GO on to polished steel (5x5 cm², 2 transfers), and the result is similar to that for NAB (adhesion improved from ~4.5 to 10.2 MPa once sample was further heated at 200 °C for 10 mins).

We have shown that highly adhered GO sheets can be formed on metal surfaces using a suitable treatment (*e.g.* removal of surface oxidized phases and thermal treatment). The transfer-2-200°C sample contains a significant number of oxygen-containing groups (*e.g.* epoxy and hydroxyl groups, also confirmed with our XPS analysis), which is suggested by a water contact angle of ~63° [close to that of NAB (74°, Figs. 6a-b), lower than graphite (98°) and graphene (127°)].^{16,17} These groups enable functionalization (and further reduction) of the coating using hexylamine (HA) and hexadecylamine (HDA) (see Figs. S7&8 for the successful functionalization), which increased the water contact angle to 107° and 116°, respectively (Figs. 6c-d). We further evaluated anti-corrosive behaviors (in 0.1 M NaCl solution) of different samples with a potentiodynamic test in Tafel model (see Supporting Methods for more details). As suggested in Fig. 6e, corrosion potential of coated samples slightly shifted to lower potentials (0.346 V vs 1M Ag/AgCl) from that of bare NAB (~0.363 V vs 1M Ag/AgCl), but the current are significantly reduced. Transfer-2-200°C showed an increased anti-corrosion performance with a lower corrosion current density of ~13.84 μA.cm⁻², compared with that of polished NAB (high corrosion current density of ~2.03×10⁵ μA.cm⁻²). The corrosion current density was further decreased to around 0.14 and 0.08 μA.cm⁻² once the coating was further functionalized by HA and HAD, respectively. This improvement in the anti-corrosion properties is considered to be due to the increased number of hydrophilic features in the functionalized coating.

Conclusions

Adhesion tests of EPD coatings of GO on steel and NAB have shown that the intimately contacted material is more strongly bound than subsequent layers. The GO coating was formed on both positive and negative electrodes. Both features suggest that a chemical interaction may be formed between GO and freshly polished metal surfaces. Our systematical Raman and XPS investigations confirmed the presence of chemical interactions between GO and pre-treated NAB metals, which can be further consolidated by a simple thermal treatment (GO is also reduced to certain extent). A simple but robust conceptual method has therefore been established for a highly adhered (adhesion up to 10.6 MPa) GO coating on metals with different surface roughnesses, which includes the formation (*e.g.* transfer GO onto clean metal surface) and consolidation of the chemical interaction (*e.g.* heat at 200 °C for 10 mins). With this process, sufficient oxygen containing groups still remain on the GO to permit its chemical functionalization. This demonstrated conceptual process could open new practical approaches for highly adhered GO coatings on metals for various aims. This may include a modified process such as immersion or spraying large pre-treated metal constructions with GO suspension and tuning the thickness of the coating (by

changing the GO concentration) followed by a simple thermal treatment and functionalization.

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