Understanding Chemical Properties of Electrophoretically Deposited Graphene Oxide Films on Al Alloys

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Abstract

Adhesion between film and substrate is critical for electronic device and coating applications. Interfacial development between electrophoretically deposited graphene oxide films on Al 1100 and Al 5052 alloys were investigated using FT-IR and XPS depth profiling techniques. Obtained results suggest metal ion permeation from the substrates into deposited graphene oxide films. The interface between the films and the substrates were primarily composed of Al-O-C bonds from oxygenated defects on graphene oxide plane rather than expected Al-C formation. Films heat treated at 150 °C had change in microstructure and peak shifts in XPS spectra suggesting change in chemical structure of bonds between the films and the substrates.

Introduction

Electrophoretic deposition (EPD) is a promising technique for graphene oxide deposition with a number of advantages including simple experimental apparatus, economic cost, high throughput, fine control of film thicknesses, and broad selection of substrates [1, 2]. A recent review on graphene oxide EPD by Chavez-Valdez *et al*. have summarized potential applications of electrophoretically deposited graphene oxide as electrochemical electrodes, field emission devices, sensors, and composite materials [1]. From previous studies, graphene oxide films were deposited on various substrates including stainless steel [3, 4], p-type Si [4], SiO_2 [2], nickel foam [5], indium tin oxide (ITO) coated glass [6], and Al [4]. EPD has been proven to simultaneously reduce

oxygenated defects in graphene oxide during the deposition process. Ishikawa and co-workers deposited graphene oxide on SiO_2/Si and conductive glass substrates to obtain transparent conductive films [2]. They obtained graphene oxide films with lower relative ratio of oxygen-containing groups than ones that were reduced by hydrazine. The graphene oxide films produced with EPD had C – C content of ~ 81 %. In addition, An *et al.* observed anodic reduction of graphene oxide during EPD process [4]. EPD graphene oxide films had C/O atomic ratio of 6.2:1. This was ~ 5 times higher than the measured ratio of 1.2:1 for graphene oxide paper produced by vacuum filtration. In order to fine control graphene oxide deposition, Diva and co-workers performed quantitative evaluation of EPD kinetics of graphene oxide [6]. They used low voltages to avoid significant reduction of graphene oxide during the deposition processes. Experimental results displayed a good agreement with predictions from the Hamakers model. Hasan *et al.* studied the effect of suspension pH to graphene oxide film deposition and microstructure [3]. Although, there have been many studies on graphene oxide EPD, there has not been any study on interfacial development between EPD graphene oxide films and substrates.

Adhesion between substrates and films is very important to ensure good device and coating performances. Ogata *et al.* studied the chemical and physical properties of metal/graphene oxide interfaces and observed permeation of Au, Cu, Ni, and Pt into graphene oxide films [7]. From x-ray photoelectron spectroscopy (XPS) results, two main permeation paths were proposed – 1) metal ion permeation through simultaneous proton exchange and 2) metal atom permeation via defects and/or edges of graphene oxide sheets. Al is a well-known material for its lightweight, good electrical and thermal conductivity, ductility, and corrosion resistance [8]. Carbonaceous nanomaterials including graphene have been widely employed as reinforcement materials in Al alloy matrixes to increase its strength while preserving other desirable properties [9-12]. In addition, Al substrates-graphene films have potential applications in electronic devices [13, 14]. Previous study of carbon nanotube (CNT) surface in Al matrix has revealed that they are strongly bound by Al – C bond [15].

The scope of this paper is to observe interfacial chemical properties of EPD graphene oxide films and Al alloy substrates. Commercially available Al 1100 and Al 5052 plates were chosen as substrates of interest. Composition of Al 1100 is close to that of pure Al and Al 5052 is corrosion

resistance Al alloy with added Mg content. The films were subsequently annealed at temperature of 150 °C to observe effect of heat in bonding chemistry. The surface microstructures of deposited films were observed by scanning electron microscopy (SEM). Fourier-transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) with depth profiling were used to observe chemical characteristics of the specimens.

Experimental Procedures

All chemicals used in experiments were purchased from Sigma Aldrich, otherwise noted. graphene oxide (GO) sheets were synthesized using modified Hummer's method reported elsewhere [16]. Briefly, 0.5 g of expandable graphite (Grade 1721, Asbury Carbon) was microwaved for 30 s then 2 g of the expanded graphite was slowly added to 200 mL of concentrated H_2SO_4 while mechanically stirring. Then, 15 g of $KMnO_4$ was added to the mixture followed by stirring for 2 hr at 35 °C. 500 mL of deionized water was added gradually to the mixture in an ice bath. The temperature was maintained below 70 °C. The mixture was stirred for 1 hr followed by dilution with 3.0 L deionized water. 20 mL of H_2O_2 (30 wt. %) was slowly added to the diluted mixture, where the color of suspension changed from dark brown to yellow. The suspension was set overnight then the supernatant was decanted. The remained suspension was centrifuged at 3500 rpm for 15 min followed by 1 M HCl wash to remove manganese. This was repeated 3 to 4 times. Acid was removed by centrifugation at 12000 rpm for 30 min and wash with deionized water for 4 times. as-synthesized GO dispersion was a highly viscous paste. The paste was dried at 80 °C under vacuum for 24 h.

EPD of GO was carried out in a parallel two-electrodes cell. GO films were deposited on Al 1100 and Al 5052 plates (McMaster Carr) cut into 2 cm by 4 cm. Compositions of the substrates are presented in Table 1. The electrodes were cleaned by ultrasonication in Acetone for 20 min followed by Acetone and Isopropyl Alcohol (IPA) wash to remove impurities. Al 1100 electrodes were chemically polished prior to deposition to remove native oxide layer with a method reported elsewhere [17]. Briefly, Al 1100 electrodes were dipped in a mixture of 85:15 H_3PO_4 (87 wt. %) and HNO_3 (70 wt. %) at 85 °C for 5 mins followed by neutralization in 1 M NaOH for 5 mins. 2.0 mg/ml of graphene oxide in ethanol was used as suspension medium.

Counter electrode was Al 1100 plate. Deposited samples were dried at room temperature in air for at least 1 hr followed by desiccation. Selected samples were heat treated at temperatures of 150 °C.

Electrophoretic mobility and zeta potential of graphene oxide suspension in ethanol were measured with Malvern Dynamic Light Scattering (DLS) Zetasizer. Specimens were observed with optical microscopes and scanning electron microscopy (SEM, Hitachi S-4800 and S-3200) for their microstructure. Fourier transform infrared spectroscopy (FT-IR, Thermo Scientific Nicolet 6700) was used to observe chemical characteristics of the films. The obtained FT-IR spectra were baseline corrected with poly-fit. X-ray photoelectron spectroscopy (Al Kα XPS, Thermos Scientific) was used to obtain atomic composition and interfacial characteristics. The X-ray source had a spot size of 400 μm. For depth profiling, the graphene oxide films were etched with Ar ion with 3 keV. Obtained XPS spectra were peak fitted by using Avantage data system (Thermos Scientific) in Gaussian – Laurentzian peak shapes.

Results and Discussions

Electrophoretic mobility of GO sheets in ethanol was – 0.4325 um-cm/V-s with zeta potential of – 22 mV. Negative mobility of the colloidal GO sheets was confirmed again by formation of anodic deposits. Figure 1 shows typical current density plot of EPD of GO on Al alloys. Parabolic decrease in current density was observed in all samples. This is due to rise in resistivity of the electrode-suspension interface after the initial deposit of insulating GO layer [6]. They also present well-controlled EPD process without significant reduction of GO at the electrode surface observed in previous studies [4, 6]. Figure 2 (a) and (c) shows the photographs of samples pre- and post- heat treatment process respectively. Reduction of the deposited GO films was confirmed by color change from light brown to black after the heat treatment. SEM micrographs of sample surfaces pre- and post- heat treatment are presented in Figure 2 (b) and (d) respectively. The as deposited GO films consist of nearly flat stacks of GO with occasional wrinkles. Similar microstructure has been observed in previous studies on EPD GO [3, 6]. The wrinkling is due to overlapping of the individual sheets as well as distortion of the tetrahedral carbon plane due to –

OH defects [6, 18]. After heat treatment, these wrinkles were almost flattened out as depicted in Figure 2 (d).

All of FT-IR spectra in Figure 3 (a) and (b) have broad peaks at ~ 3380 cm^{-1}, which are from free –OH groups in deposited GO films. After heat treatment, we noticed dramatic decrease in the –OH peaks as seen in Figure 3 (c) and (d). FT-IR spectra of GO films on Al substrates (GO/Al) were compared with freestanding GO films to observe any peak shift. Detailed peak assignments for the obtained spectra are listed in Table 2. Sharper peaks at ~ 1650 cm^{-1} and ~ 1380 cm^{-1} were observed for GO/Al samples. We contend that they are asymmetric and symmetric C–O peaks respectively, although overlapping peaks reside within the same regions. Appearances of the two peaks are due to the deprotonation of C=O and C–O groups in carboxyl and may be evidence for the formation of bonds between aluminum metal and oxygen. Frequency differences ($\Delta\nu$) between the asymmetric and the symmetric peaks can reveal the coordination of the chemical bond. The difference can range from approximately 100 cm^{-1} to 300 cm^{-1}, increasing as the coordination changes from bidentate to monodentate [19]. Noticeable changes in peaks were observed after the heat treatment of GO/Al. The $\Delta\nu$ between the two peaks had changed to ~ 124 cm^{-1} from ~ 250 cm^{-1}, which indicates bonding coordination change after the heat treatment.

In order to observe change in bonding chemistry from surfaces to film–substrate interfaces, XPS depth profile analyses were performed on each specimen. Figure 4(a) is a schematic diagram of approximate point of XPS analyses depicted in Figure 4 (b) and (c). All presented spectra have been normalized for comparisons. C 1s spectra of graphene oxide have four main peaks; C–C from graphitic carbon at 284.6 eV, C–O from hydroxyl and epoxide at 286 eV, C=O at 287 eV, and COOH and COOR at 289 eV [20, 21]. An extended tail observed at 291 eV is from π–π^* carbon interaction [21]. C/O ratios for each specimen are listed in Table 3. For all samples, a reduction in oxygen-containing groups was observed after removal of the surface layer. Although, reduction of graphene oxide films during EPD has been reported previously [2, 4], we suspect Ar ion bombardment during the etching process is the main contributor in the reduction of oxygen. It has been reported repeatedly that even low energy Ar ions are sufficient to remove oxygen from graphene oxide films [22, 23]. Previous study has revealed that the reduction due to Ar ion

bombardment takes place in the first several minutes with ~ 20 °C temperature increase, which is not enough for thermal deoxygenation [23]. Ar is an inert gas, thus it does not chemically react with graphene oxide films [22]. Oxygen removal from the Ar etch is only from physical process. Atomic concentration of oxygen is highly affected by Ar bombardment, however, chemical bonding information obtained at each etch level should still be reliable.

Interpretation of O 1s spectra is rather difficult as many peaks are closely overlapping in the region from 531 eV to 534 eV. We used the following peak assignments from previous studies to obtain the best fit; C=O at 531.1 eV, metal oxide and C–OH at 531.9 eV, C–O–C and ether oxygen at 532.8 eV, and COOH/COOR at 534.1 eV [21]. A low intensity broad peak at 536.2 eV is from adsorbed water, which is in accordance with peaks at ~ 78 eV and ~ 1306 eV for metal binding to adsorbed water in Al 2p and Mg 1s spectra, respectively [24]. An example of O 1s peak fitting at different depth is shown in Figure 4(c). We see a dramatic decrease in C–OH after etching the surface away, which is congruent with the change in C 1s spectra presented in Figure 5(b). Through out the GO film, O 1s spectra portrayed mixed states of four different peaks. No significant change in elemental composition or chemical state was observed inside the films. However, near the film/substrate interface, C=O peak at 531 eV decreased with no significant change in COOH/COOR peak or ether oxygen peak. This change can suggest breakage of C=O bond to create C–O–Al bond.

Metal permeation in graphene oxide was present in all specimens. High-resolution Al 2p spectra in Figure 5 (a) was dominated with Al–O peak at ~ 74.5 eV. After heat treatment, the Al–O peak shifted towards 75 eV, which indicates change in chemical state. In previous studies on Al and polymer interface, peaks at ~ 74.5 eV were considered to be from Al–O–C bond instead of Al–O from native aluminum oxide [25, 26]. Mg 1s spectra in Figure 5 (b) had noticeable peak shift at film surfaces towards metallic Mg. Except at the surface level, all depth levels had peaks at ~ 1304 eV, which can be interpreted as MgO or Mg^{2+} peaks. From these results, we can conclude that the permeation of Al and Mg into graphene oxide films are via proton exchange rather than permeation of metal atoms [7]. The amount of Mg present at different levels of stacked graphene oxide sheets were consistent at ~ 0.7 ± at %. In contrast, the Al ions were distributed unevenly in a range of 0 at % and 2.0 at %. This discrepancy in Al distribution severed after heat treatment of

samples. From previous study of metal permeation into graphene oxide, the distribution of metal atoms or ions largely depends upon metal-carbon bonding strength and the transport is perturbed when a bond is made between C(O)O and metal atom [7]. Therefore, we can conclude that Al is the major contributor in adhering to graphene oxide films rather than Mg in Al–Mg alloys.

Conclusions

In conclusion, we attempted to study of chemical properties of EPD graphene oxide films on Al 1100 and Al 5052 substrates using FT-IR and XPS depth profiling. Results have shown formation of Al-O-C bonds between the films and both substrates. Moreover, metal ion permeation into graphene oxide films was observed. Upon heat treatment, the chemical structures involving metal atoms is suspected from peak shifts observed in high-resolution XPS spectra of Al and Mg. Finally, these findings provide useful information about chemical interactions between graphene oxide films and Al alloy substrates during EPD and heat treatment processes, which is important in optimizing graphene oxide films for functional coating applications on Al alloy substrates.

Acknowledgements

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