

Nano-micro-structured Graphene Film Electrodes for Enhanced Performance of Supercapacitors

Gyoung Gug Jang,¹ Jong Kahk Keum,² Bo Song,³ Liyi Li,³ Dale K. Hensley,² Yongdong Jiang,⁴ Andrew Hunt,⁴ Kyoung-Sik Moon,³ Ching-Ping Wong,³ Michael Z. Hu^{1*}

¹ Energy and Transportation Science Division,
Oak Ridge National Laboratory (ORNL), Oak Ridge, TN 37831

² Center for Nanophase Materials Sciences, Chemical and Engineering Materials Division ORNL

³ School of Material Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332

⁴ nGimat Co., Norcross, GA 30093

ABSTRACT

The graphene structures at either nanoscale or microscale are important to the film electrode performance. At nanoscale, a molecular engineering approach (i.e., molecular ligand grafting) was used to control the interspacing between restacked graphene sheets. At microscale, this work applied an external field to align the graphene sheets along the field direction during the film deposition from liquid slurry of molecularly engineered graphene. Five different ligand molecules were effectively grafted on the surfaces of well-dispersed graphene oxides (GOs) in liquid suspension and the grafted GOs were chemically reduced to form molecules modified graphene or reduced GOs (m-rGOs). XRD data shows well controlled nanometer sized interlayer spacings between the re-stacked sheets of m-rGOs. Then, we investigated the effects of ligand grafting on the deposited film structure. Their baseline electrochemical cell performance was evaluated by different aqueous electrolytes (e.g., H₂SO₄ vs. KOH) for the following external field alignment. Initially, the m-rGO film electrodes exhibited higher capacitance performance with H₂SO₄ electrolyte, compared with KOH. Also, the external field has rendered the graphene sheets to be oriented vertically to the film surface, resulting in enhanced capacitance due to enhanced diffusion and accessibility of electrolyte ions into the graphene film structure. Aligning graphene nanosheets in film deposits via external field could be a novel versatile fabrication technique to tailor microscopic architecture of graphene coatings for high performance supercapacitor.

Keywords: Vertical alignment, Graphene, Supercapacitor

1 INTRODUCTION

Graphene-based supercapacitors have been considered very promising energy storage devices with advantages beyond rechargeable batteries in terms of power density, high rates of charge/discharge and long cyclic stability due

to superior electrical conductivity, a high theoretical surface area and chemical resistance of graphene. Currently, GO is mostly considered as a practical graphene platform because it can be easily produced by chemical oxidation of graphite on a large scale. The oxygen functional groups of GO must be removed to improve inherent conductivity. However, the quick and irreversible agglomeration into graphite during hydrothermal reduction is still problematic [1]. Various additional ligand molecules have been introduced to inhibit aggregation of graphene sheets for effective surface area of charge storage and to improve the wettability of the electrode surface/electrolyte [1]. Nevertheless, these graphene electrode structure is usually limited to horizontally packed films, resulting in slow kinetics due to long path lengths of electrolyte ions diffusion and limited contact points between active material and current collector.

Architected graphene films, e.g. porous/holey and vertically oriented sheets, have been developed for improving kinetics of electron and electrolyte ion in their structure. Especially, vertically-aligned graphene sheets have high kinetic performance due to 1) open edge structure to facilitate electron transfer between active material and current-collector 2) a large interlayer space to facilitate mobility of electrolyte ion 3) short paths of electrolyte ions to the graphene layers [2]. In spite of these advantages, designing approach of these structures such as plasma-enhanced chemical vapour deposition and cutting of graphene sheet roll have a difficulty in fabrication cost and scale-up for large sized films.

Due to the fact that intensive research on external field aligned electrode material are still in progress, this work attempts to find the ligand grafting effect on controlling interlayer gap of restacked graphenes, their binder-free film deposit morphology and a suitable electrolyte. Typically, GO was first treated with five different ligand molecules (Figure 1). The morphology and interlayer gap of m-rGO films were studied by XRD and SEM. Then, the electrochemical performance of electrode films were studied by different electrolytes. Under external field

assisted deposition, a m-rGO exhibited vertically alignment, resulting in capacitance improvement.

2 EXPERIMENTAL SECTION

Synthesis of m-rGOs: GO was synthesized from natural graphite powders (230U from Asbury Carbons, PA) by a modified Hummers method. GO slurry was prepared by dispersing GO solid sheet flakes in ethanol and was sonicated to homogenize. HCl was added into the slurry and also mixed with 2,5-Diamino-1,4-dihydroxylbenzene dihydrochloride (DDDC) or octadecyltrichlorosilane (ODTS) in a reaction vessel sealed with a cap. The mixture was kept at 120 °C in an oven overnight. For chemical reduction of the ligand-grafted GO, NH_3 and hydrazine was dropped into the reaction vessel and the mixture was held at 95 °C for 3 hrs. After cooling to room temperature, the slurry was washed by centrifugation. Synthesis of the p-phenylenediamine (PPD)-rGO was made by a previously reported procedure [3]. Synthesis of ethylenediamen (EDA)-rGO was followed by the PPD-rGO synthesis. For the synthesis of polyaniline (PANI)-rGO, GO was dispersed in 1 M HCl solution by sonication. Then 100 mg aniline was added into the solution and the polymerization of PANI was initiated by adding $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as catalyst.

The reaction was carried out for 12 hr in ice bath. The slurry was washed by centrifugation

Characterization: Scanning electron microscopy (SEM) measurement was carried out on a field emission scanning electron microanalyzer (Merlin, Carl Zeiss AG). X-ray diffraction (XRD) measurements were conducted using a PANalytical X'Pert Pro MPD equipped with an X'Celerator solid-state detector. Electrochemical cell performance tests were carried out with a Versastat 2-channel system (Princeton Applied Research).

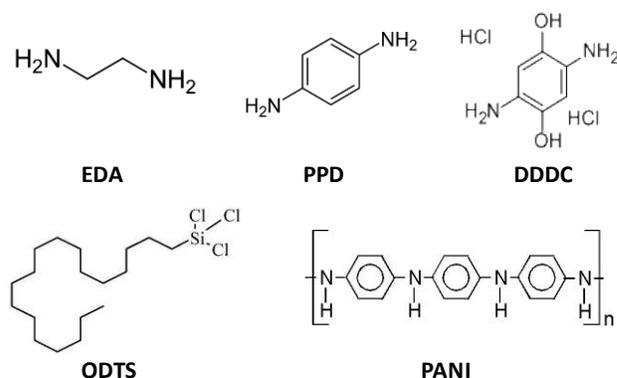


Figure 1 Ligand molecules grafted on rGOs.

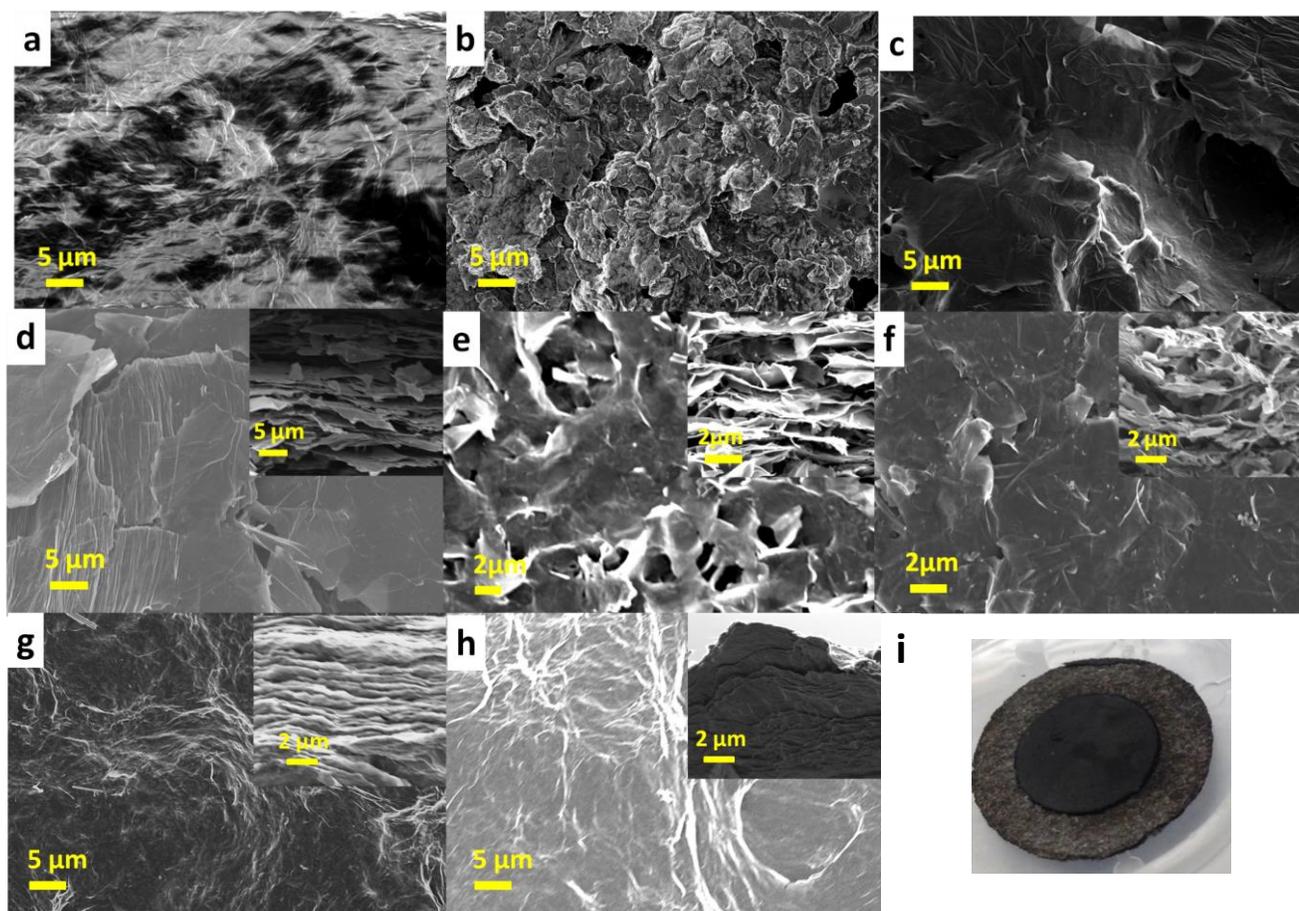


Figure 2 Surface and internal morphology of binder-free deposit graphene films. a) GO, b) rGO, c) ODTS-GO, d) ODTS-rGO, e) PANI-rGO, f) DDDC-rGO, g) EDA-rGO, h) PPD-rGO, i) graphene electrode on carbon fiber paper (current collector)

3 RESULTS AND DISCUSSION

Figure 2 shows the surface morphology of m-rGOs and their cross section view of deposit films. To investigate the deposit film morphology, all wet m-rGOs slurry were evaporately deposited on carbon fiber substrates (Figure 2i). GO deposit exhibits smooth surface sheets (Figure 2a). Due to oxygenates groups, the low conductivity of GO renders blurred in the SEM image. The rGO shows stacks of particles due to irreversible agglomeration during chemical (hydrazine) reduction and drying (Figure 2b). After ODTS grafting on GO, the ODTS-GO can be dispersed well in the non-polar solvent like hexane, and film deposit shows individual sheets without severe agglomeration (Figure 2c). Octadecyltrichlorosilane (ODTS, molecular weight (MW)=388 g/mol) is an amphiphilic molecule consisting of a long-chain alkyl group ($C_{18}H_{37}$) and a polar head group ($SiCl_3$), which forms self-assembled monolayers on oxidic substrates. The functional long-chain alkyl group exhibits a strong hydrophobic property. For ODTS-rGO (reduced ODTS-GO), the deposit films showed clearly separated sheets, relative to ODTS-GO (Figure 2d). As expected, the binder-free ODTS-rGO deposits shows horizontally stacked films (Inset of Figure 2d). However, due to a long carbon chain ligand intercalation between sheets and its hydrophobicity of ODTS molecules, the internal ODTS-rGO film shows clear spaces between stacked films.

Interestingly, more porous film structure was obtained in PANI-rGO (Figure 2e). Polyaniline (PANI) is a conducting polymer of the semi-flexible rod polymer family. The MW is $>15,000$ g/mol. Especially, PANI-rGO shows clear pores on the top surface and the packed films have porous bend film structures (Inset of Figure 2e). DDDC-rGO shows a similar surfac morphology to ODTS-rGO (Figure 2f). 2,5-Diamino-1,4-dihydroxyl benzene dihydrochloride (DDDC, MW=213) has two types of functional groups, amine and hydroxyl groups. The internal DDDC-rGO film also shows clear large spaces between stacked sheets. *P*-phenylenediamine (PPD, MW=108) has similar structure to DDDC molecule without hydroxyl groups. However, the morphology of deposits shows clear difference from DDDC-rGO. The cross-sectional view of PPD-rGO shows a more closely stacked films, relative to DDDC-rGO (Figure 2g). The additional hydroxyl group of DDDC is attributed to the porous film structure. Also, small size molecules of ethylenediamine (EDA, MW=60) grafting on GO forms closely packed films (Figure 1h). Specifically, as shown of the top view of SEMs, the edge line of planar sheets of EDA- and PPD-rGO film was not distinguishable between stacked sheets, resulting in continuous films.

From these above observations, with increasing MW of grafted ligands (*i.e.* PANI>ODTS>DDDC>PPD>EDA), m-rGOs exhibited more porous and spacy structured deposit films. Ligand grafting increases interlayer spacing between re-stacked graphene sheets inside the film. The crystalline structures of m-rGOs such as PPD, PANI, EDA,

ODTS and DDDC were characterized by XRD measurement. (Figure 3) The XRD diffraction peaks of the GO and rGO films corresponds to the interlayer distance of restacked GO and rGO nanosheets. Grafting with additional ligand molecules on GO sheet increases the interlayer distance, indicating in shift of XRD diffraction to small angles from GO or rGO peaks or disappearance of crystalline peaks [1].

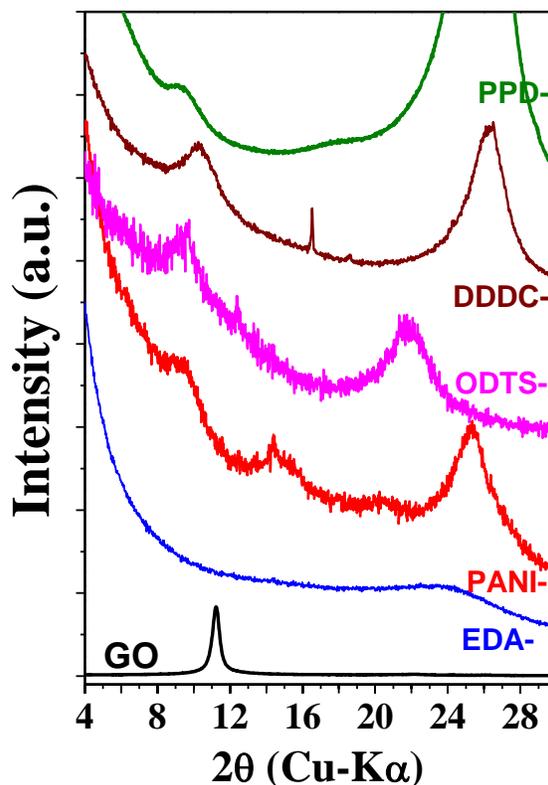


Figure 3 XRD patterns of m-rGOs

A referential GO slurry deposits exhibit a reflection peak at $2\theta=11.3^\circ$, which is assigned to the [001] reflection peak corresponding to an average interlayer distance of 0.78 nm, resulting from intercalated water molecules and the oxygen-containing functional group. After EDA ligand functionalization on GO sheets and its following reduction, the EDA-rGO shows a broad peaks at $2\theta=24.3^\circ$ which correspond to the moderately aligned graphitic arrays along the [002] direction. It suggests the restacked interlayer of GO sheets is intercalated by EDA molecules, resulting in disappearance of crystalline at [001] direction. Other ligand molecule intercalation shifted a crystalline peak at [001] direction to small angle relative to GO peak, indicating enlarged interlayer space between restacked layers. PANI-, ODTS-, DDDC- and PPD-rGO exhibited [001] crystalline peaks at $9.6^\circ(0.92\text{ nm})$, $9.8^\circ(0.90\text{ nm})$, $10.4^\circ(0.85\text{ nm})$ and $9.4^\circ(0.93\text{ nm})$, respectively. XRD of PPD-rGO was measured on deposit on carbon fiber. Due to a strong graphite peak from the carbon paper, a peak graphene crystalline peak is no observable after 20° .

In order to assess the ligand molecule grafting effect on electrochemical cell performance, we have evaluated the film deposits of m-rGOs on carbon fiber paper substrate. The m-rGO film deposits serve as active materials of supercapacitor electrodes in a two-electrode system as the form of coin-cells and split-cells. Table 1 shows the average specific capacitance of all m-rGOs electrodes with two aqueous and an organic electrolytes. We found aqueous electrolyte significantly affects specific capacitance. For 6M KOH, m-rGOs (i.e. PPD, PANI, EDA) exhibited relatively lower capacitance than rGO. However, for 1M H₂SO₄, m-rGOs show significant improvement on capacitance compared with rGO. Hydrothermally reduced GO has a specific capacitance of ~90 F/g with H₂SO₄ [3]. The higher specific capacitance may be attributed to synergistic effect of large ionic accessible surface area and good wettability of the H₂SO₄ electrolyte. We also found that either ligand grafting amount and deposit loading amount are significantly factors on specific capacitance. Further optimization of surface functionalization is still in progress.

Table 1. Summary of specific capacitance of m-rGO film electrodes

	PPD		PANI		DDDC	
Specific capacitance (F/g @ 10mV/s)	241	49	198	33	151	87
Loading amount (mg/cm ²)	2.2	2.4	3.9	5.3	2.5	2.7
Electrolyte	H ₂ SO ₄	KOH	H ₂ SO ₄	KOH	H ₂ SO ₄	KOH

	EDA	ODTS	rGO
Specific capacitance (F/g @ 10mV/s)	50	31	71
Loading amount (mg/cm ²)	3.9	9.6	9.7
Electrolyte	KOH	Tetraethylammonium fluoride	KOH

The external field effect on the nano-micro-structures and the electrochemical properties of the graphene film deposits nanosheets are underway to develop for further optimization. Thus, we only highlight a few significant results. Figure 4 shows vertically aligned m-rGO sheets in the field assisted depositions on carbon fiber paper substrate. Inset of Figure 4 shows the galvanostatic charge/discharge plots in the potential range (0-0.8V) at a low current density of 1 A/g. The longer charging and discharging duration for an aligned m-rGO electrode indicates its superior capacitance to that of non-aligned. It also showed that the voltage (IR) drop of aligned m-rGO is much lower than non-aligned one. The reduced IR drop indicates that the capacitive reversibility is high, attributed by the high-quality contact at the interface of active layer/current collector. For example, the field aligned m-rGO exhibited

up to ~300% higher specific capacitance at 100 mV/s and a specific capacitance of 240±7 F/g at 10 mV/s, compared to those without an external field. Aligning deposited graphene nanosheets via external field could be a novel versatile fabrication technique to tailor microscopic architecture of graphene coatings for high performance supercapacitor.

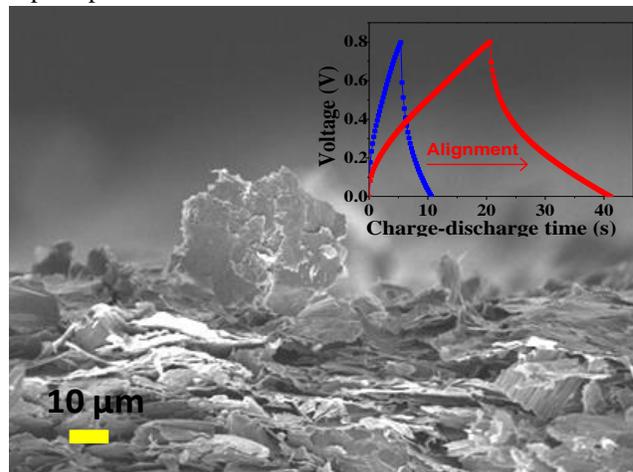


Figure 4. Vertically aligned graphenes via external field deposition

4 CONCLUSION

In summary, this work has demonstrated that molecular ligand grafting of graphene flakes/sheets could serve as a molecular engineering approach to control the nanoscale interspacing of restacked graphene in the form of a dried powder or film deposit. Furthermore, external field-induced favorable alignment of m-rGO graphene sheets/flakes expects a new engineering approach to tailoring the microscopic architecture of the deposited films, resulting better electrode film performance

REFERENCES

- [1] Zhang, K.; Mao, L.; Zhang, L.L.; Chan, H.S.O.; Zhao, X.S.; Wu, J. *J. Mater. Chem.* **2011**, *21*, 7302-7307.
- [2] Yoon, Y.; Lee, K.; Kwon, S.; Seo, S.; Yoo, H.; Kim, S.; Shin, Y.; Park, Y.; Kim, D.; Choi, J.; Lee, H. *ACS Nano* **2014**, *8*, 4580-4590.
- [3] Lu, X.; Li, L.; Song, B.; Moon, K. S.; Hu, N.; Liao, G.; Shi, T.; Wong, C. P. *Nano Energy* **2015**, *17*, 160-170.

ACKNOWLEDGEMENT

This research work was supported by the Advanced Research Project Agency-Engergu (ARPA-E) Program DE-AR0000303. Part of this research was conducted at the Center for Nanophase Materials Sciences, which is sponsored by DOE Office of Basic Research Sciences.

* huml@ornl.gov