



# Synthesis and electrochemical properties of poly (2-ethynylpyridine) functionalized graphene nanosheets



Niranjanmurthi Lingappan<sup>a</sup>, Dong Woo Kim<sup>a</sup>, Xuan Thang Cao<sup>a</sup>, Yeong-Soon Gal<sup>b</sup>, Kwon Taek Lim<sup>a,\*</sup>

<sup>a</sup> Department of Imaging System Engineering, Pukyong National University, Busan 608-737, Republic of Korea

<sup>b</sup> Chemistry Laboratory, College of Engineering, Kyungil University, Hayang 712-701, Republic of Korea

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## ABSTRACT

A straightforward and efficient approach was demonstrated for the synthesis of an ionic conjugated, reduced graphene oxide/poly (2-ethynylpyridinium) (RGO/P2EP) hybrid *via* covalent bond chemistry. Graphene oxide (GO) were treated with thionyl chloride to yield acylated GO (GO–COCl), which was subsequently used to activate the polymerization of 2-ethynylpyridine (2-EPy). FTIR and XPS results revealed that 2-EPy was successful polymerized in the presence of GO–COCl and covalently attached onto the surfaces of GO sheets. The XRD and FESEM results indicated that GO sheets were encapsulated in the P2EP matrix. The as-obtained hybrid exhibited an excellent dispersion in water. When evaluated as an electrode material for supercapacitors, the RGO/P2EP hybrid exhibited a high specific capacitance of 225 F g<sup>-1</sup> at the current density of 0.5 A g<sup>-1</sup>, remarkable rate capability, and excellent cycling performance with the capacitance retention of ~94% after 1000 cycles. The enhanced electrochemical property can be attributed to the synergetic effect and strong interfacial interaction at the interface of RGO/P2EP.

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## 1. Introduction

The ever-growing global energy consumption has greatly stimulated extensive research on exploiting high-performance energy harvesting and conversion devices for various applications such as portable electronics and hybrid vehicles [1]. Of notable devices, supercapacitors, known as electrochemical capacitors or ultracapacitors have attracted vast attention because of their higher power density and longer cycle life than batteries, and higher energy density than conventional dielectric capacitors [2]. A variety of materials including, carbon nanostructures, transition metal oxides/hydroxides and conjugated polymers (CPs) have been extensively studied as electrode materials for supercapacitors [3]. Carbon-based materials store charge electrostatically from the reversible adsorption of ions onto their surfaces, leading to high power density at the cost of low energy density. In contrast, metal oxides/hydroxides and conducting polymers store charge in a faradaic or redox-type process similar to batteries, which enables high energy density [4].

Graphene, a single layer of graphite which is a two-dimensional honeycomb nanostructure, has attracted tremendous attention because of its large surface area, high carrier mobility, excellent chemical and mechanical properties [5]. These intriguing

properties make graphene as an advanced material in a variety of research areas such as nanoelectronics, energy storage devices and biosensors [6–8]. A potential member of graphene family, graphene oxide (GO) has been studied because of its low-cost and large-scale production [9]. GO is the oxidized form of graphene, which consists of various oxygen functional groups (e.g. hydroxyl, epoxide, and carbonyl groups) on their basal planes and edges. Therefore, GO is hydrophilic and can be readily dispersed in water and organic solvents to form stable colloidal suspensions [10]. Meanwhile, these oxygen-containing groups were further utilized to graft polar small molecules or polymers to form graphene based functional materials [11,12].

On the other hand, hybrid materials based on conducting polymers (CPs) and graphene are highly attractive for various potential applications [13–15]. In particular, CPs are the another class of novel materials due to their remarkable psychochemical and optical properties [16]. Among various CPs, polyaniline, polypyrrole and polythiophene have been well studied as electrode materials for supercapacitors as well as other applications [17–19]. Although the aforementioned CPs have demonstrated huge potential, it is also equally important to investigate the synthesis and properties of other related analogous or new type of conducting polymers not only for energy storage devices but also for other prospective applications. In this regard, polyacetylene, a one-dimensional traditional macromolecule with alternating single and double bonds, is the best-known CP because of its metallic

\* Corresponding author. Tel.: +82 51 629 6409; fax: +82 51 629 6408.

E-mail address: [ktlim@pknu.ac.kr](mailto:ktlim@pknu.ac.kr) (K.T. Lim).

conductivity upon doping as well as its bandgap of  $\sim 1.5$  eV [20]. Besides, it also exhibits excellent fluorescent and opto-electronic properties, thus considered to be a most promising candidate for future electronic applications. Despite these intriguing properties, the practical application of polyacetylene is impeded by its low environmental stability and poor solubility [21]. To overcome these limitations, mono and di substituted polyacetylene derivatives have been prepared [22]. Unlike polyacetylene, the substituted polyacetylene is highly soluble in aqueous or organic solvents and stable in air for a long period of time. Furthermore, the substituted polyacetylene has both ionic and electrical conductivity owing to the extensive conjugation and ionic nature [23]. Thus, substituted polyacetylene has attracted growing interest in recent years [24–26]. In general, polyacetylene derivatives have been prepared by the linear polymerization of the corresponding monomer by various catalyst systems [27]. It has been reported that that quaternization of pyridine nitrogen in 2-ethynylpyridine using alkyl halides in polar solvents led to the spontaneous polymerization of the monomer, resulting in a substituted polyacetylene, poly (2-ethynylpyridinium) (P2EP) salts [28]. However, the electrical conductivity of the resulting polymers is still far from the requirements, which further limits their practical applications. Thus, improving the functional properties such as electrical conductivity and mechanical property of pristine P2EP is highly desirable for various applications. We have previously demonstrated the green synthesis and electrochemical property of the carbon nanotube/P2EP (CNT/P2EP) hybrid [29]. However, the possibility for the P2EP based hybrid to be used as an electrode for energy storage devices has not been exploited.

Herein we report the synthesis of ionic conjugated reduced graphene oxide covalently bonded poly (2-ethynylpyridine) (RGO/P2EP) hybrids via the activated polymerization of 2-ethynylpyridine using acylated graphene oxide as an activator. As an electrode for supercapacitors, the ionic RGO/P2EP hybrid exhibits an excellent electrochemical performance with high specific capacitance, good cycling stability and remarkable rate capability.

## 2. Experimental

### 2.1. Materials

Graphite powder was purchased from Sigma-Aldrich (Korea). 2-Ethynylpyridine (2-EPy) was obtained from Sigma-Aldrich and vacuum distilled before use. Concentrated sulfuric acid (98%), sodium nitrate, potassium permanganate, 30%  $\text{H}_2\text{O}_2$  solution, hydrochloric acid, diethylether, N,N'-dimethyl formamide (DMF) were supplied from Junsei Chemicals (Japan) and used as received without further treatment.

### 2.2. Preparation of acylated graphene oxide (GO-COCl)

The oxidized graphite powder was first prepared from natural graphite flake using Hummer's method [30]. 1 g of graphite powder and 0.5 g of  $\text{NaNO}_3$  were added into a 500 mL beaker containing 25 mL of 98%  $\text{H}_2\text{SO}_4$ , and the resultant dispersion was stirred in an ice-bath at  $0^\circ\text{C}$  for 30 min. 3 g of  $\text{KMnO}_4$  was slowly added into the above dispersion at the temperature below  $5^\circ\text{C}$ . The temperature of the reaction mixture was raised to  $40^\circ\text{C}$  and maintained for 30 min. After completion of the reaction, 90 mL of deionized (DI) water was gradually added into the solution. The suspension was reacted further by adding a mixture of  $\text{H}_2\text{O}_2$  (30 mL, 30%) and water (250 mL). The as-obtained powder was separated from the reaction mixture by filtration, washed three times with warm diluted HCl (3%, 150 mL), and then dried under a vacuum at  $40^\circ\text{C}$  for 24 h. The oxidized graphite powder was dispersed in DMF and ultrasonicated for 1 h to yield exfoliated GO. To the above dispersion, an excess amount of  $\text{SOCl}_2$  was added and the mixture was refluxed at  $80^\circ\text{C}$  for 24 h under argon atmosphere. After reaction, the excess  $\text{SOCl}_2$  and solvent were removed under reduced pressure.

### 2.3. Synthesis of RGO/P2EP hybrid

0.34 g of GO-COCl was dispersed in 10 mL of DMF and ultrasonicated for 30 min to create a homogeneous dispersion. Afterward, 1 g of 2-EPy was added slowly into the dispersion. The reaction was stirred at  $80^\circ\text{C}$  for 24 h under nitrogen

atmosphere. As the reaction proceeded, the color of the reaction mixture was changed from black into red. After the polymerization, the resulting product was precipitated into a large excess amount of ethyl ether, filtered and dried under vacuum at  $40^\circ\text{C}$  for 24 h (yield = 95%). The as-obtained GO/P2EP hybrid was chemically reduced as follows. 0.1 g of GO/P2EP hybrid was dispersed in 100 mL of DI water, and 2 mL of hydrazine monohydrate was added and the solution was heated in an oil bath at  $95^\circ\text{C}$  for 24 h. The RGO/P2EP was filtered, washed with DI water and dried under vacuum at  $50^\circ\text{C}$  for 24 h.

### 2.4. Characterization

Fourier transform infrared (FTIR) spectra were recorded with a Perkin Elmer FTIR spectrometer in the range from 4000 to  $400\text{ cm}^{-1}$ . The specimens were dispersed into KBr powder by mortar, and compressed into disks. Raman spectra were recorded on a confocal micro Raman spectrometer with an excitation wavelength of 514 nm. X-ray photoelectron spectroscopy (XPS) measurements were carried on a Kratos AXIS HSi spectrometer with a monochromatized Al K $\alpha$  X-ray source (1486.6 eV photons) at a constant dwell time of 100 ms and the pass energy of 40 eV. X-ray diffraction (XRD) patterns were recorded on a Rigaku X-ray diffractometer with Cu K $\alpha$  ( $\lambda = 1.5418 \text{ \AA}$ ), and the data were collected in the  $2\theta$  of  $5\text{--}80^\circ$  at a scanning rate of  $2^\circ\text{C min}^{-1}$ . Thermogravimetric analysis (TGA) was carried out using a Perkin Elmer Pyris 1 TGA with a heating rate of  $10^\circ\text{C min}^{-1}$  under nitrogen atmosphere. High resolution transmission electron microscopy (HRTEM) images were obtained using a JEM-2010 (JEOL). The TEM samples were dispersed in THF and deposited on a carbon TEM sample grid and imaged at an accelerating voltage of 200 kV. The surface morphology of samples was studied by field-emission scanning electron microscopy (FESEM) (Hitachi; JSM6300, Japan), and elemental analysis was performed with energy dispersive X-ray (EDX) spectroscopy.

### 2.5. Electrochemical measurement

The cyclic voltammetry and galvanostatic charge/discharge measurements were performed in a three-electrode electrochemical cell with a solution of 1 M tetraethylammonium tetrafluoroborate in acetonitrile (TEABF $_4$ /AN) as the electrolyte. A platinum plate and saturated calomel electrode were used as counter and reference electrodes, respectively. The working electrode was fabricated by mixing RGO/P2EP (80%), carbon black (10%) and polyvinylidene fluoride (10%) and dispersed in N-methyl-2-pyrrolidinone to form homogeneous slurry. The resulting slurry was then coated on a FTO substrate that served as a current collector. The working electrode was then dried at  $80^\circ\text{C}$  for 12 h under high vacuum. The typical mass of the active materials was calculated to be  $0.6\text{ mg cm}^{-2}$ . All electrochemical analyses were performed on electrochemical workstation, CHI 605B at ambient conditions.

## 3. Results and discussion

The RGO/P2EP hybrid was synthesized via the spontaneous polymerization of 2-EPy using GO-COCl as an activator as illustrated in Fig. 1. In this process, the freshly distilled monomer was added to the GO-COCl dispersion in DMF, and the color of the reaction mixture was monitored. The black color dispersion was turned into red<sup>1</sup> color within a few minutes, indicating the activated polymerization of 2-EPy. The possible reaction mechanism for the synthesis of the GO/P2EP hybrid is schematically shown in Fig. 2. First, the electron lone pair of the nitrogen atom on the pyridine ring were reacted with -COCl species, and then the polymerization was initiated spontaneously by the activation of the acetylenic bond of the monomer [29,31], which resulted in the formation of covalently bonded GO/P2EP hybrids. For comparison, the polymerization of 2-EPy was also carried out in the presence of pristine graphite or GO, but no polymerization was observed even at elevated temperature, indicating that the 2-EPy monomer was activated and polymerized only in the presence of GO-COCl species. The dispersion stability of GO and RGO/P2EP in DI water is shown in Fig. 3. After few days GO tends to aggregate, as can be seen in Fig. 3a. In a stark contrast, the RGO/P2EP produces a homogeneous dispersion which is stable for several months owing to the ionic nature of the hybrid. The structure of the RGO/P2EP was confirmed by FTIR analyses.

The FTIR spectrum of GO (Fig. 4a) displays a broad and intense peak centered at  $\sim 3400\text{ cm}^{-1}$  attributed to the -OH stretching

<sup>1</sup> For interpretation of color in Fig. 1, the reader is referred to the web version of this article.

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