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Preparation of graphene /poly (diallyldimethylammonium chloride) – poly (styrene sulfonate) polyelectrolyte composites and their electrochemical performance

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Abstract. Here, we successfully prepare graphene /poly (diallyldimethylammonium chloride) – poly (styrene sulfonate) (G/PDADMAC-PSS) polyelectrolyte composites by simple mixing method. The effect of NaCl adding at 2, 4, 6, 8 and 10 % wt. on the sizing of polyelectrolyte composites (PECs) is investigated. The concentration of NaCl ion plays an important role in size control by the formation of the primary polyelectrolyte composites and following by the agglomeration itself. The electrochemical properties are evaluated by cyclic voltammetry demonstrating that G/PDADMAC-PSS PECs at 8 %wt. can yield the highest specific capacitance of 68 m F.cm^{-2} at 10 mV sec^{-1}

1. Introduction

Polyelectrolyte complexes are formed by the association of oppositely charged polymers, *assembling* electrostatic interaction between polycations and polyanions. The direct mixing of dispersed aqueous solutions of oppositely charged PECs can formed a dense phase of the nano-polymer molecule that is separated from the medium [1]. Moreover, the modulating of ionic interaction by salt ion addition can customize the shrinking/extending of the PECs molecule. This class of PECs polymer is practically utilized for reproducible preparation and controllable sizing. These unique characteristics are key requirements to improve the nanoparticle features, especially addressing for biomedical and pharmaceutical application. One of interesting that still has not been sufficiently addressed is to introduce the other substances such as carbon nanomaterials in PECs. The nanoparticles in the core shell surrounding with PECs can offer the charge surface with controlling sizing the nanoparticles. [2] Graphene is a form of nanosheet carbon which has a single layer of hexagonal lattice structure, high electrical, thermal conductivity and high surface area. Principally, graphene is known as the forefront materials for energy-storage research and widely used for EDLC owing to its excellent electrical conductivity and high surface area [3,4]. However, the agglomeration of graphene during fabrication causing the decrease in surface area is critical issue to obtain the high electrochemical performance.[5] Therefore, the aim of this work is to study the characteristics of the introduce of graphene into poly (diallyldimethylammonium chloride) - poly (styrene sulfonate) polyelectrolyte complex systems. The

effect of salt ion concentration on the customizing size of G/PDADMAC-PSS PECs is purposed. Additionally, the efficiency of electric charge of PECs on graphene is evaluated by cyclic voltammetry [6]. This G/PEC material is expected to fulfill the novel class material electrodes composites, utilizing on the surface materials of any shape.

2. Experimental

2.1. Materials
Graphite powder (> 99% purity, Aldrich), Poly (diallyldimethylammoniumchloride) (20 %wt., MW 200,000 - 350,000 g/mole, Aldrich) and Poly (sodium 4-styrenesulfonate) (MW 70,000 g/mole, > 99% purity Aldrich) were used as received. Other the reagents were of analytical grade and used as received without any further purification.

2.2. Preparation of graphene
GO was synthesized by the modified Hummers' our modified method. Briefly, 6.0 g of graphite and 3.0 g of $NaNO_3$ was added into 150 ml of H_2SO_4, followed by adding the first portion of 18.0 g $KMnO_4$. The reaction was kept stirring at 35 ℃ for 7 h. After that, the second portion of $KMnO_4$ (18.0 g) was added and employed at 50 ℃ for 7 h. Then, the reaction mixture was poured into ice water, followed by adding H_2O_2. The slug products were washed with dilute HCl and further neutralized with deionized water. Graphite powder was obtained after dry at 60 ℃. Graphite powder was further dispersed in distilled water by aiding of ultrasonic and chemically reduced with sodium ascorbate at 60 ℃ for 12 h. The obtained reduced graphene was further washed with deionized water several times and freeze dry overnight.

2.3. Preparation of graphene/Poly(diallyldimethylammonium chloride) - Poly(styrene sulfonate) Polyelectrolyte composites
6.0 mg of graphene was dispersed in 60 ml of 0.1 M PSS aqueous solution by aiding of ultrasonic irradiation for 3 h. Then, the solution was mixed with 30 ml of 0.1 M PDADMAC solution at 25 ℃ for 30 minutes. The various of NaCl content (2, 4, 6, 8 and 10 %wt.) was added into the mixture and then kept stirring at 25 ℃ for 30 minutes to obtain the polyelectrolyte composites.

2.4. Characterizations
The characteristic functional groups of the graphene oxide and graphene were examined by Fourier transform infrared spectroscopy (FT-IR) with a Thermo scientific Nicolet 6700 (Tokyo, Japan). The laser diffraction particle size analyzer (SALD-7101) was utilized to determine the size distribution of the G/PDADMAC/PSS samples in different NaCl concentration.

2.5. Electrochemical measurements
The electrode samples were prepared by direct pasting the G/PDADMAC/PSS samples onto carbon fiber paper without the additional of binder. This paste active material can easily apply on any surface materials. The electrochemical performance was determined with three electrode consisting of the as-prepared samples as working electrode, platinum as the counter electrode and Ag/AgCl as the reference electrode by using cyclic voltammetry, employing in 50 ml of 1 M NaCl between 0 to 1 V from 10 to 100 mV/sec.

3. Results and discussion
FTIR spectra of graphite, synthesized GO and G are exhibited as seen in Fig. 1a. There is no significant signal for graphite spectrum due to non functional group of graphite. For GO, the oxidized structure of graphite is examined. The broad center peak at 3400 cm^{-1} attributes to OH stretching vibration of adsorbed water and -OH group functional. The peaks at 1728, 1628 and 1388 cm^{-1} are assigned to C=O, C=C and C-O stretching vibrations, respectively. In contrast, G reveals the dramatic

decrease in oxygen functional groups of GO which occurs from redox reaction, mainly consisting of decrease at the intensities peaks of 1728 (C=O) and 1388 (C-O) cm^{-1}.

XRD spectra is used to confirm the planar characteristic of the graphite, synthesized GO and G (Fig. 1b). Graphite exhibits the typical crystal structure of graphite at 26.5°. The calculated intercellular space by Bragg's Law is 3.36 Å. After oxidation process, GO displays the shift of (002) position to the sharp peak at 10.8°, implying that the space between layer is increased to 8.16 Å. The reduced graphene oxide shows the board peak at 25.8° with the disappearance of the sharp peak, confirming the exfoliation of layered structures of graphene.
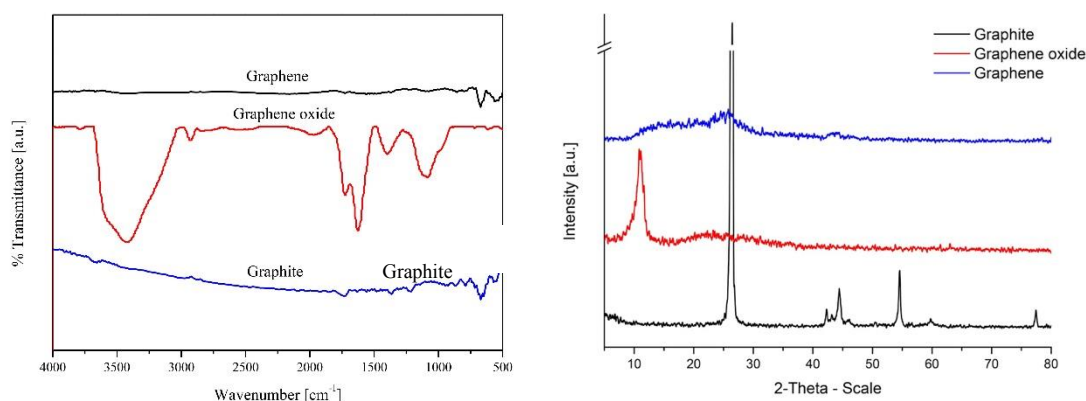

Figure 1. (a) FT-IR spectra of GO and (b) XRD spectra of GO and G

In this work, the polyelectrolyte complexes is formed by the direct mixing of the G/PDADMAC and PSS solution at different NaCl concentrations. As evident in Fig. 2a, the formation of the aggerated G/PDADMAC-PSS PEC manifestly reveals the size dependence on NaCl concentration. The formation of the aggregated PEC particles in molecular level is arose from the result of the agglomeration of the primary colloid particles, when the PEL charge is disturbed by changing of Na$^+$ and Cl$^-$ concentration in Fig. 2b [1]. The PSD of the primary G/PEC particle molecule from mixed PEL solutions is examined by laser diffraction particle size analyzer. The aggregated G/PEC particles is diluted and centrifuged to separate the G/primary colloid particles from mixed PEL solution. PSD result in Fig. 3 demonstrating that the primary G/PEC at 2 %wt. NaCl in aqueous medium exhibits a wide size distribution with an effective particle size of 50 μm, which is almost nearly to the graphene size (33 μm), indicating the high efficiency of PEC surrounding on graphene surface in nano to submicrometer level. Principally, the addition of NaCl after mixing PEC affects rather outer particle surface than the inner particle. The adding NaCl up to 6 %wt. leads to swell in primary PEC particles size on graphene surface (average particle size of 600 μm). At 8 %wt. of NaCl adding, the primary PEC on G surface starts to shrink with the major average size of 80 μm and minor average size of 600 μm. This results might be explained by the changing of the conformation of PECs molecules at the critical salt concentration. The rapid aggregation process is initiated and the large aggregated PEC is formed, resulting that the residual primary PEC portion reveals less agglomeration in system [2].
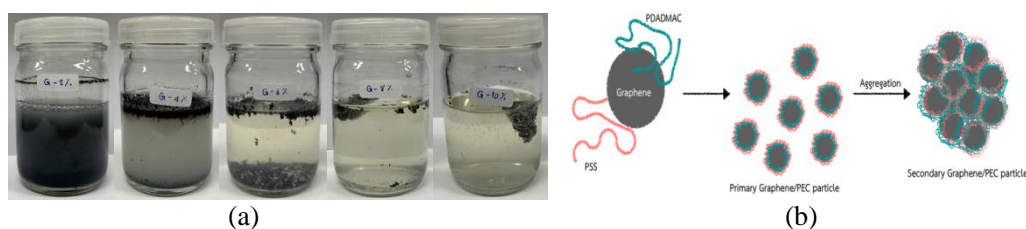

(a)   (b)

Figure 2. (a) G/PDADMAC-PSS PECs at different NaCl concentrations (2, 4, 6, 8 and 10 %wt.) and (b) The mechanism of the formation of G/PECs
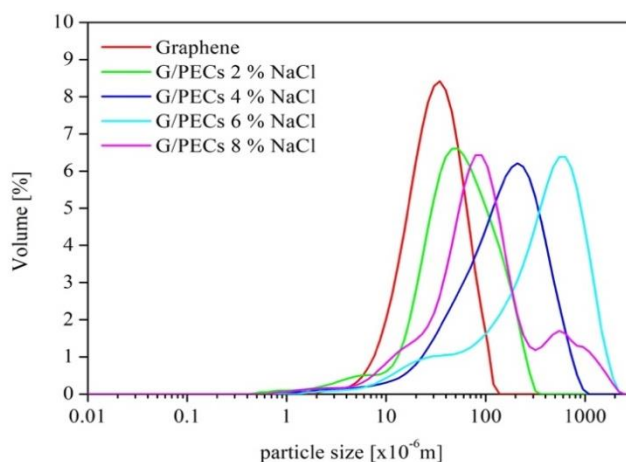
Figure 3. PSD curves of graphene and G/PDADMAC-PSS at different NaCl concentration
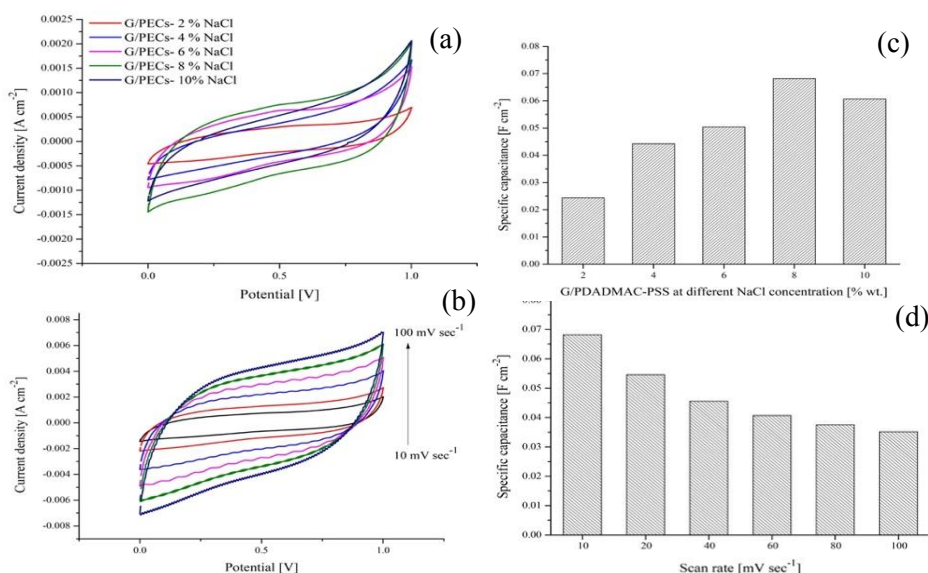

Figure 4. CV results in 1 M NaCl for (a) G/PDADMAC-PSS with different NaCl concentration**s** at 10 mV sec^{-1} (b) G/PDADMAC-PSS with 8 %wt**.** NaCl at different scan rate; The calculated specific capacitance values for (c) G/PDADMAC-PSS with different NaCl concentration at 10 mV sec^{-1} (d) G/PDADMAC-PSS with 8 %wt**.** NaCl at different scan rate

The comparative study of the CV plots is used to evaluate the electrochemical properties of the G/PDADMAC-PSS at different NaCl concentrations. Fig. 4a displays the CV curves for all those of G/PDADMAC-PSS on CFP electrodes at 10mV sec^{-1}, demonstrating the nearly idealized rectangular and symmetric shape implying a good electrical double layer capacitance behavior. The increasing of NaCl adding up to 8 %wt. affects the CV area by enhancing the electrochemical characteristics. This result might be arisen from the effect of more inserted Na^+ and Cl^- ion, inducing ion conductivity for capacitive properties. The slight decrease in CV area at 10 %wt. NaCl is due to the fact that the large aggregated G/PDADMAC-PSS is formed at high NaCl content, affecting to reduce in ion transportation.

The calculated the area specific capacitance values of G/PDADMAC-PSS at different NaCl concentration of 2, 4, 6, 8 and 10 %wt. are 24, 44, 50, 68 and 61 mF cm^{-1} at 10 mV sec^{-1}, respectively (see Fig. 4c). The capacitance preservations of G/PDADMAC-PSS at 8 %wt. NaCl is tested by

increasing scan rates from 10 to 100 mVsec^{-1} as seen in Fig. 4b and 4d. The rectangularity of CV curve is deteriorated at very high scan rate, implying the development of electrochemical irreversibility. G/PDADMAC-PSS at 8%wt. NaCl electrode exhibits the capacitance preservations around 48 %.

4. Summary

G/PDADMAC-PSS PECs exhibit the size dependence at different NaCl concentrations by changing of the conformation of PEL molecules and the agglomeration process. This PDADMAC-PSS PECs at appropriate NaCl concentration can form the aggregated molecule which can apply on any shape surface. G/PDADMAC-PSS at adding 8 %wt. NaCl electrode can yield the highest specific capacitance of 68 mF cm^{-1} at 10 mV sec^{-1} with the capacitance preservations around 48 % which is good enough for practical capacitive electrode.

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