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# Graphene improved electrochemical property in self-healing multilayer polyelectrolyte film

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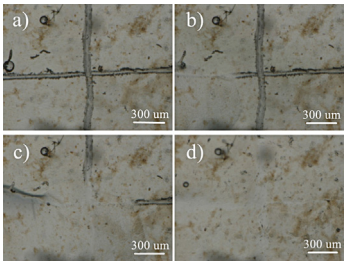
## HIGHLIGHTS

- bPEI/(PAA-GE) self-healing multilayer polyelectrolyte film was prepared by poly(acrylic acid) (PAA), graphene(GE) and branched poly(ethyleneimine) (bPEI) based on LBL self-assembly technique.
- The bPEI/(PAA-GE) self-healing multilayer polyelectrolyte film shows excellent self-healing ability.
- The bPEI/(PAA-GE) film has an improved conductive than bPEI/PAA multilayer polyelectrolyte film.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Mimicking the nature to confer synthetic materials with self-healing property in order to expand their lifespan is highly desirable and has attracted much more attention from the scientific community. But poor electrochemical property of the fabricated self-healing materials limit the current and future application. Here, self-healing multilayer polyelectrolyte film based on branched poly(ethyleneimine) (bPEI), poly(acrylic acid) (PAA) and graphene(GE) (bPEI/(PAA-GE)) was prepared by layer-by-layer (LBL) self-assembly technique. The bPEI/(PAA-GE) self-healing multilayer polyelectrolyte film not only shows excellent self-healing ability at high humidity, but also possesses good electrical conductivity. It is promised to be applied in battery, supercapacitor or hydrogen fuel cell to improve their cyclic stability and lifetime.



## 1. Introduction

The self-healing phenomenon, refers to the damage parts can repair or mend themselves and restore their previous properties after impair, which can be found on the skin in animals and the branch grafted onto the tree, is an amazing occurrence in nature [1]. Mimicking the nature to confer synthetic materials with self-healing property to expand their lifespan is highly desirable and has attracted much more attention from the scientific community. After decades of study, two kinds of artificial polymeric self-healing materials: extrinsic self-healing materials and intrinsic self-healing materials have been reported [2], the initial example of self-healing polymers is extrinsic self-healing materials that employed microcapsules or microvascular networks to release healing agents after crack propagation and achieve self-healing process [3,4]. As extrinsic self-healing materials require incorporation of healing agents and cannot repeated repair, in addition to that there is a critical need for more efficient self-healing materials, hence the ensuing research begin to seek and reveal intrinsic self-healing materials that exhibit a desired repeatable self-healing

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property [5]. These materials use reversible covalent bonds (e.g., based on the Diels–Alder reaction) [6], weaker non-covalent interactions (e.g., hydrogen bonding [7], ionic interactions [8], π–π interactions [9], or host–guest interactions) [10,11] to achieve a repeatable healing response [12].

The purpose of developing new and advance materials is to facilitate our lives or improve our quality of life. Hence, through efforts of many research workers, self-healing materials moved toward application stage from the theoretical stage. Artificial skin, which mimics the functions of natural skin, is a typical application of self-healing materials [13]. Employ self-healing materials to enable the spontaneous repair of mechanical damage of electrode thus increase the lifetime of the battery is another sample. All these applications need self-healing materials possess good mechanical properties and certain electroconductivity. However, self-healing materials are generally insulators. Therefore, there is an urgent demand for designing and synthesizing intrinsic self-healing materials with good electrical conductivity.

Graphene materials are identified as beneficial additive or effective responding component, and have been widely used to fabricate composite materials due to its good compatibility with polymeric materials. Furthermore, graphene materials also have super chemical stability, outstanding electrical conductivity and mechanical properties [14] which prompt us to believe that integrating graphene materials with appropriate polymeric materials might generate some novel self-healing materials. These materials may not only have enhanced mechanical properties but also have increased conductivity. Huang and coworkers [15] reported a novel self-healing material fabricated with few-layer graphene (FG) and thermoplastic polyurethane (TPU). This FG-TPU self-healing material has enhanced mechanical property and can be healed repeatedly via different methods including infrared (IR) light, electricity and electromagnetic wave. Cong and coworkers [16] expand the intertwined double-network mechanism to fabricate a novel kind of graphene oxide (GO)/poly(N-acryloyl-6-aminocaproic acid) hydrogel endowed with enhanced mechanical properties and self-healing capability.

The LBL self-assembly technique is a versatile approach to fabricate nanostructure thin films and is typically accomplished by alternating the adsorption of mutually interacting polymers on surfaces. This method is based on non-covalent intermolecular interactions among charged or hydrogen-bonding moieties. The LBL technique has been used as a new approach to produce multilayered thin films. Recently, Sun et al. [17] used multiwall carbon nanotube and PEI multilayered films to modify a carbon paper electrode based on LBL self-assembly technique. In our previous work [18], we also successfully used functional graphene and poly(allylamine hydrochloride) (PAH) to modify the MFCs electrode by this method.

Inspired by the previous work, the self-healing multilayer polyelectrolyte film with good conductivity was prepared based on LBL self-assembly technique.

However, GE without any treatment was hydrophobic and electrically neutral nanomaterial which is not conducive to doping in the copolymer. To conquer this problem, treating GE with mixed acids is necessary [19–21]. By pre-treatment, various different oxygen functional groups have been grafted onto the surface of GE.

## 2. Experimental

### 2.1. Chemicals and materials

GE was obtained from Nanjing XFNano Materials Tech Co., Ltd., (Nanjing, China). Ethanol was obtained from Sinopharm Chemical Reagent Shanghai Co. Ltd. Poly(acrylic acid) (PAA) ($M_w \approx 450{,}000$) and branched poly(ethyleneimine) (bPEI) ($M_w \approx 750{,}000$) were obtained from Sigma-Aldrich Co. Ltd. All other reagents were used as received. The glass substrates were soaked in the mixture of 98% $H_2SO_4$/30% $H_2O_2$ (volumetric ratio 3:1) for 24 h, then, the glass substrates were rinsed with ethyl alcohol and ultrapure water several times, and finally dried with $N_2$ stream. In that order, the glass substrates were negatively charged after the treatments.

### 2.2. Synthesis and preparation of the self-healing multilayer polyelectrolyte film

First, to make GE can be better used for self-assembly, it was partly acidified to obtain oxygen-containing functional groups and electric. GE was sonicated in concentrated nitric acid and sulfuric acid (v/v, 1:3) mixed solution for 24 h, then, large particles of GE were filtered to remove. By pre-treatment, various different oxygen functional groups have been grafted onto the surface of GE.bPEI and PAA solution, whose concentrations were 4 mg/mL, pH was 10.5 and 3, respectively, were prepared. Then, 24 mg GE was dissolved into 100 mL PAA solution to prepare (PAA-GE) solution.

Preparation of the bPEI/(PAA-GE) self-healing multilayer polyelectrolyte film: first, the prepared glass substrate was immersed in bPEI solution for 15 min, then, the glass was soaked in ultrapure water for 5 min to remove the bPEI that did not adsorbed on glass. Second, to obtain bPEI/(PAA-GE), the bPEI-glass was immersed in (PAA-GE) solution for 15 min. Then the bPEI/(PAA-GE) was soaked in ultrapure water for 5 min to remove the (PAA-GE) that did not adsorbed on bPEI-glass. Third, repeated 30 times, the bPEI/(PAA-GE) was obtained.

The bPEI/PAA self-healing multilayer polyelectrolyte film was also prepared through above steps with bPEI and PAA solution.

### 2.3. Characterization

Raman spectrum of the prepared samples was obtained on a Smart Raman Spectrometer (Voyage). The surface morphology of the prepared samples was characterized by field emission scanning electron microscopy (FESEM, Ultra Plus Zeiss). The water contact angle of the prepared samples was analyzed using inductively coupled plasma atomic emission spectroscopy (ICP-AES, Shanghai Zhongchen Digital Technology Equipment Co., Ltd., Shanghai, China). The self-healing process and surface behavior of the samples were observed by Stereo Microscope (MVX10 OLYMPUS). Electrochemical impedance spectroscopy (EIS) measurement was carried out using the electrochemical workstation (chi660d CHI instruments Inc., Shanghai, PR China) at open circuit potential with a superimposed 5 mV sinusoidal voltage in the frequency range from $10^5$ Hz to $10^{-3}$ Hz. The prepared self-healing multilayer polyelectrolyte film was used as working electrode. The counter electrode was a piece of platinum sheet and the reference electrode was an Ag/AgCl electrode. A 2 m $MC_6FeK_3N_6$ aqueous solution was used as electrolyte.

## 3. Results and discussions

Raman spectroscopy has been used to characterize GE, and several review articles have been published discussing the Raman spectrum of GE [22]. In this article, we employed Raman spectrum to detect the GE in bPEI/(PAA-GE) multilayer polyelectrolyte film and the results are shown in Fig. 1. From the results we can find that bPEI/PAA and bPEI/(PAA-GE) multilayer polyelectrolyte film both present characteristic bands at 2120 $cm^{-1}$ and 1095 $cm^{-1}$. The sharp band at about 2120 $cm^{-1}$ corresponds to stretching vibrations of CN bond [23]. The weaker bands at about 1095 $cm^{-1}$ are due to flexural vibrations of $NH_2$ bond [24]. It is generally known that Raman spectra of GE include the G peak located at ~1580 $cm^{-1}$