



# Synthesis of polypyrrole wrapped graphene hydrogels composites as supercapacitor electrodes



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## ABSTRACT

Different mass ratios of polypyrrole (PPy) to graphene hydrogel (GH) nanocomposites were synthesized by hydrothermal reduction of graphene oxide and chemically oxidative polymerization of pyrrole, forming a three-dimensional framework of PPy wrapped on the surface of GH without adding any toxic reductive agents. Electrochemical tests show that PPy/GH<sub>15</sub> nanocomposite exhibits unique electrochemical properties, such as enhanced electrolytic permeability and high electric capacity. Thanks to the synergistic effect of the pseudo-capacitance of PPy and the electric double layer capacitance of GH, PPy/GH<sub>15</sub> exhibits a high specific capacitance of 375 Fg<sup>-1</sup> at a scan rate of 10 mVs<sup>-1</sup>. In addition, the PPy/GH<sub>15</sub> electrode shows good cycling stability, and its specific capacitance retention is 87% even after 4000 charge–discharge cycles in the potential window of –0.1 to 0.6V, suggesting it an ideal electrode material for supercapacitor.

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## 1. Introduction

The increasing demand in energy and the decreasing availability of fossil fuels as well as the concern about global warming have stimulated great research efforts on sustainable and environmental-friendly technologies for energy conversion and storage. Supercapacitors (SCs) are the promising power source and have attracted much attention in view of a number of important features including higher power density, faster charging/discharging rate and longer cycling stability compared to conventional capacitors or batteries [1–4], which make them promising in a wide range of applications from hybrid vehicles and portable electronics to military devices [5]. Carbon-based materials that store the charge electrostatically using reversible adsorption of electrolytic ions onto active materials on the electrode are primarily used as active electrode materials for SC application [6]. Among various carbon materials, graphene, a single layer of sp<sup>2</sup> bonded carbon atoms patterned in a hexagonal lattice, is a hotspot and frontier of materials research and has aroused great interest in those involved in sensors [7,8], catalysis [9], energy-storage devices [10,11] and environmental fields [12]. It has been found that graphene or graphene oxide (GO) sheets can be assembled

into graphene hydrogel (GH) with low mass density, thermal stability, mechanical stiffness combined with high specific surface and exceptional electrical conductivity [13]. The unique 3D porous structure of graphene hydrogel allows most of the graphene sheets to be exposed to electrolyte, and provides open channels for unobstructed transportation of electrolyte which make them promising as high performance electrode materials for SCs application [14]. However, graphene-based electric double-layer capacitors (EDLC) with aqueous electrolytes usually exhibited low specific capacitance (normally less than 200 Fg<sup>-1</sup>), high self-discharge rate and poor wetting capability in electrolyte, which imposed significant challenges in employing them as primary power sources to replace batteries.

Recent success in fabricating pseudocapacitive material modified GH leads to the formation of a new type of nanohybrid GH, which exhibited improved capacitive properties and enhanced ion transportation in comparison with the pristine GH. The optimal nanohybrid electrode materials for SC applications are expected to consist of multiple components such as conductive graphene-based materials with EDLC, and redox active materials of conductive polymers [15] or transition metal [16,17] and metal oxides [18]. For example, Yang et al. prepared the deformable electrode materials based on polypyrrole-mediated GH and found that the combination of polymer and graphene-based hydrogel resulted in excellent mechanical properties, which can be used for highly compression-tolerant SCs [15]. Lee et al. reported a facile and template-free hydrothermal synthesis of Mn<sub>3</sub>O<sub>4</sub> nanorods on

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graphene sheets, for supercapacitor electrodes, the combination of metal oxide and graphene resulted in the excellent capacitance activity and long cycling stability [18]. Xing et al. demonstrated the environmentally friendly hydrothermal synthesis of nickel sulfides nanospheres/reduced graphene oxide (nickel sulphides/RGO) nanocomposites using L-cysteine as a reducing agent, the resulting nanocomposites exhibited high capacitance of  $1169 \text{ F g}^{-1}$  at current rates of  $5 \text{ A g}^{-1}$  and good cycling stability, making it a potential candidate for energy storage devices [19].

In this work, we adopted a new strategy for the green synthesis of PPy/GH through one-pot hydrothermal reaction and explore its application as high-performance electrode material for supercapacitor application. For the preparation of 3D structured pyrrole/graphene hydrogel nanocomposite, hydrothermal method played an important role in achieving a uniform coating of the PPy on GH. The polypyrrole/graphene hydrogel (PPy/GH) was synthesized through a sequential hydrothermal reduction and in situ chemically oxidative polymerization. This method can effectively avoid the disadvantages of electrochemical method for the synthesis of Py/GH such as more steps, time consuming, and poor dispersion of GH in water. Furthermore, the effect of different mass ratios of Py/GO and various potential windows on the electrochemical supercapacitive properties and cycling stability of the electrode materials has also been studied in details. Our results showed that as electrode material for supercapacitor, the PPy/GH<sub>15</sub> nanocomposite electrode exhibited higher specific capacitance and better cycling stability than those of PPy, which was attributed to the synergistic effect between the graphene material and PPy. Moreover, this synthesis method presents a promising green route for the large-scale production of PPy/GH composites as energy storage materials.

## 2. Experimental

### 2.1. Chemicals and apparatus

Pyrrole (99%, Aldrich Chemical Co.) was distilled under reduced pressure and then stored at  $-10^\circ\text{C}$  in a nitrogen atmosphere before use. Other reagents were in analytical grade and used without further purification.

Scanning electron microscope (SEM) images were taken using a Sirion 200 field scanning electron microscopy operated at 10 kV. Fourier transform infrared spectrometry (FTIR, Equinox 55, Bruker) was employed to analyze the chemical compositions of composites. Raman spectroscopy was recorded using a micro-Raman DXR laser spectrometer (Thermo scientific, USA). The spectra were excited by 532 nm laser light from a 35 mW air-cooled He-Ne laser and power of the laser was 2 mW. The laser beam was focused on the sample by a  $\times 80$  lens to give a spot size of ca. 1 mm. X-ray diffraction pattern measurements were performed with an X'Pert PRO X-ray diffract meter with Cu-K ( $\lambda = 1.5406 \text{ \AA}$ ), using an operation voltage and current of 40 kV and 40 mA, respectively.

### 2.2. Preparation of PPy/GH

Graphene oxide was synthesized from natural flake graphite by a modified Hummers method [20,21]. A certain amount of GO was firstly dissolved in 20 ml deionized water to form GO suspension. Pyrrole (1 ml, 0.014 mol) was then slowly added and dispersed ultrasonically to form a homogeneous solution. The mixture were poured into a 50 ml Teflon-lined auto-clave and then deoxygenized by  $\text{N}_2$  gas flow, it was finally heated at  $180^\circ\text{C}$  for 5 h to synthesize Py/GHs. The PPy/GH nanocomposite was then prepared by in situ chemical polymerization.  $\text{FeCl}_3$  acted as oxidant with the molar ratio of pyrrole monomer/ $\text{FeCl}_3$ /p-toluenesulfonic acid (p-TSA) at

1:1:1. Firstly, p-TSA (2.408 g, 0.014 mol) and Py/GH composites were dispersed ultrasonically in 50 ml deionized water to form a homogeneous solution.  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (3.892 g, 0.014 mol) was dissolved in 30 ml deionized water, and then dropwise added into the Py/GH-TSA mixture at  $0^\circ\text{C}$ . The in-situ polymerization reaction was conducted statically at  $0^\circ\text{C}$  in an ice bath for 24 h. Secondly, the composite was filtered and washed with plenty of methanol and deionized water thoroughly to remove the impurities. The precipitate was finally dried under vacuum at  $65^\circ\text{C}$  for 24 h. For comparison, the pure polypyrrole was prepared without adding GO by the similar procedure. PPy/GH nanocomposite with different mass ratios of PPy/GH were obtained based on their weight feed ratios of GO:pyrrole (1:35, 1:25, 1:15, 1:5), and named as PPy/GH<sub>35</sub>, PPy/GH<sub>25</sub>, PPy/GH<sub>15</sub>, and PPy/GH<sub>5</sub>, respectively, (superscript representing the weight percentage of pyrrole to graphene oxide).

### 2.3. Electrochemical measurements

Electrochemical workstation CS 350 (Corrtest, China) was employed for the electrochemical measurement of the samples at ambient temperature ( $\sim 22^\circ\text{C}$ ). The working electrodes were prepared by mixing the synthesized electrode materials, acetylene black, and poly (tetrafluoroethylene) (PTFE) with a mass ratio of 85:10:5. A small amount of ethanol was added to obtain a homogeneous slurry, which was subsequently pressed on a stainless steel net (316 L, 500 mesh) and allowed to dry at  $65^\circ\text{C}$  in vacuum for 24 h. The mass loading in the working electrode was about  $1.5 \text{ mg/cm}^2$  (the active material is  $\sim 1.0 \text{ mg/cm}^2$ ).

The electrochemical performances were evaluated by cyclic voltammetry (CV), galvanostatic charge-discharge (GV) and electrochemical impedance spectrum (EIS) in a conventional three-electrode electrolytic cell with a platinum plate (1 cm  $\times$  2 cm), a saturated calomel electrode (SCE) and the composite electrode as the counter electrode (CE), reference electrode (RE) and working electrode (WE), respectively. The electrolyte was 0.5 mol/L  $\text{H}_2\text{SO}_4$  aqueous solution. EIS measurements were performed around open circuit potential in the frequency range of  $10^5$ – $10^{-2}$  Hz with ac amplitude of 5 mV. CVs were carried out at the scan rates ranging from 10 to  $200 \text{ mV s}^{-1}$  within the potential range of  $-0.1 \text{ V}$  to  $0.7 \text{ V}$  (vs. SCE). Galvanostatic charge-discharge test was recorded at current densities ranging from  $5 \text{ A g}^{-1}$  to  $50 \text{ A g}^{-1}$  with the same potential range.

A symmetric dual-working-electrode cell system was used to investigate the capacitive properties of PPy/GH composites as capacitor electrode material. The two working electrodes facing each other were separated by a glass-fiber separator and assembled in a button type cell. CV and galvanostatic charge-discharge tests were carried out at the same condition as the three-electrode system except for a new potential range of  $-0.8$  to  $0.8 \text{ V}$ .

## 3. Results and discussion

### 3.1. Structure and morphology studies

The surface morphologies of as-synthesized GH, PPy, and PPy/GH with different mass ratios composites were investigated by SEM. GH exhibits typical cross-linked 3D network feature with interconnected pores of submicrometers to several micrometers (Fig. 1A), the walls of the pores consist flexible graphene nanosheets (Fig. 1A, inset). PPy/GH nanocomposite was prepared by one-pot hydrothermal reaction. When the mass ratio of Py to graphene oxide is 25:1, the PPy tend to grow on the graphene nanosheets to form a thick-layered structure (Fig. 1B, inset), and the cross-linked 3D network feature of GH and the density packed of PPy are still visible in this case (Fig. 1B). When the mass ratio of Py to graphene

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