

# Electrochemical synthesis of graphene/polypyrrole nanotube composites for multifunctional applications



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## ABSTRACT

A conducting composite film has been fabricated using graphene oxide (GO) and pre-prepared one-dimensional polypyrrole (PPy) nanotube as the feedstock. GO with various oxygen-containing groups effectively promotes the dispersion of well-defined PPy nanotubes to obtain a stable and homogeneous GO/PPy complex solution. By a one-step and large-scale electrochemical reduction, the graphene/PPy nanotube composite film is successfully synthesized. Graphene nanosheets uniformly cover the surface of the electrode and PPy nanotubes act as spacers and conducting bridges to prevent the restacking of graphene sheets and connect the isolated graphene nanosheets. Electrochemical experiments indicate that the composite films have high performances due to the combination of the advantages of graphene and PPy nanotube. When the graphene/PPy nanotube composite is directly used as the supercapacitor electrode, it shows high specific capacitance and good cycling stability during 1000 charge/discharge cycles. Furthermore, an electrochemical biosensor is constructed through the entrapment of horseradish peroxidase (HRP) onto the composite film-modified glassy carbon electrode (GCE). The immobilized HRP showed high catalytic activity for the reduction of H<sub>2</sub>O<sub>2</sub>, which may be ascribed to high conductivity, great surface coverage, and good biocompatibility of the prepared graphene/PPy nanotube composite film. This method may be extended to prepare other conducting composite films with structure-controllable nanostructures in large scale for the application of electrochemical fields.

## 1. Introduction

As a kind of unique two-dimensional material of sp<sup>2</sup>-hybridized carbon, graphene and its derivatives have gained much attention due to their huge specific surface area, high thermal, electronic, and mechanical properties [1–4]. They have been proposed for potential applications in the field of nanoelectronics, such as supercapacitors and biosensors. However, graphene-based electrochemical devices exhibit unsatisfactory performance owing to the unavoidable aggregation of graphene nanosheets. Therefore, the hybridization between graphene and other components is currently considered to be a feasible route to obtain an ideal material [5–12].

Polypyrrole (PPy) have been extensively studied because of their low cost, easy production, good conductivity and controlled doping/dedoping properties as well as extensive applications in various areas such as energy storage, sensors, and electronic devices [13–16].

Especially, some nanostructures of PPy, including nanorods, nanospheres, nanowires, and nanofibers [17–20], have been developed in order to further enhance the electrochemical activity of PPy. It is known that one-dimensional nanotubes have their advantages of facile electron transportation and the larger surface area compared with the nanorods or nanowires. Thus, PPy nanotubes have been applied for dye-sensitized solar cells [21], gas sensors [22] and energy storage devices [23].

Considering the interaction between  $\pi$ -conjugated PPy chains and graphene nanosheets, the previous works about graphene/PPy composites in the form of powder, paper, and three-dimensional hydrogel or aerogel have been reported [24–30]. Generally, these composites are prepared through the polymerization of pyrrole monomers pre-adsorbed on the graphene nanosheets. But it is difficult to design and control the structure of PPy, which significantly influences the properties of the resulting composites, especially impacts their electrochemical performance. Recently, the synthesis of graphene/PPy with struc-

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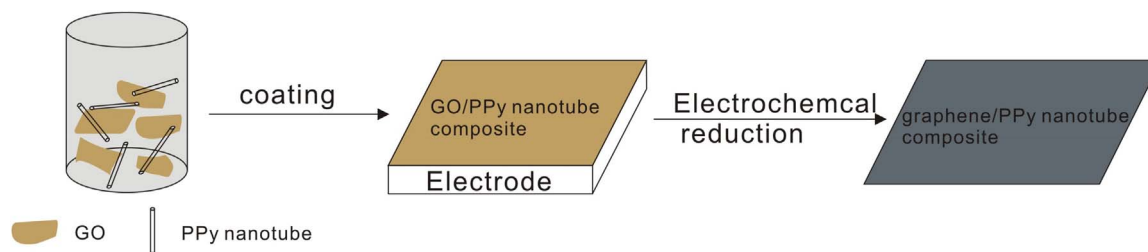
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Scheme 1. Schematic diagram for the synthesis of G/PNT composite.

ture-controlled PPY has been achieved. Graphene/PPy nanotube composites have been synthesized through the mixing of GO and PPY nanotubes followed by the treatment of hydrazine solution at 95 °C [31]. Three-dimensional graphene/PPy nanotube aerogels were also prepared by a hydrothermal self-assembly method with the aid of ethylenediamine [32]. Therefore, it is still a big challenge to develop a simple and controlled route to prepare graphene/PPy composite with precise nanostructures.

In this work, the electrochemical synthesis of graphene/PPy composite film using graphene oxide (GO) and PPY nanotube as the starting materials is reported. This method is very simple and fast; no toxic reductive agents are added. It can be used in bulk synthesis and the centrifugation or filtration does not need for the purification of the products. In this composite film, two-dimensional graphene nanosheets are beneficial for improving the surface coverage of the one-dimensional PPY nanotubes on the electrode, while PPY nanotubes can minimize the aggregation of graphene nanosheets and enhance the charge transport between the isolated graphene nanosheets. The above interactions endow graphene/PPy nanotube composite film good electrochemical performance as supercapacitor electrode and biosensor.

## 2. Experimental

### 2.1. Synthesis of graphene/PPy nanotube composite films

PPy nanotubes were prepared with the reactive template of  $\text{Fe}^{3+}$  ions and methyl orange according to our previous work [15]. GO was obtained using a modified Hummers' method [33,34]. GO solution was first ultrasonicated for 2 h. Then, PPY nanotubes with the same weight were added and mixed in the GO solution under vigorous stirring. The electrochemical synthesis of graphene/PPy nanotube composite films was conducted in a three-electrode system on CHI 660 C electrochemical workstation (Shanghai Chenhua). Pt wire and Ag/AgCl electrode were used as the counter electrode and reference electrode, respectively. Glass carbon electrode (GCE) or indium tin oxide (ITO) glass was used as the working electrode. GCE was polished using aluminum powder and then rinsed thoroughly with deionized water and ethanol. ITO was cleaned sequentially with acetone, ethanol and deionized water. GCE or ITO electrode was coated uniformly with the dispersion of GO/PPy and dried in a vacuum oven. Electrochemical synthesis was carried out by scanning in the potential range of  $-1.2$  and  $0$  V in  $0.2$  mol L $^{-1}$  phosphate buffer solution (PBS) solution. The size of the composite film could be controlled by the area of electrode. For comparison, PPY nanoparticles were prepared without the addition of methyl orange and the corresponding graphene/PPy nanoparticle composite films were electrochemically synthesized with the same procedure. The resulting graphene/PPy nanotube composite film and graphene/PPy nanoparticle composite film were designated as G/PNT and G/PNP, respectively.

### 2.2. Characterization

The morphology of the film was observed using scanning electron

microscopy (SEM, JSM-5510LV). Raman spectra were recorded on a Thermo Scientific Raman Microscope. G/PNT or G/PNP synthesized at ITO was directly used for supercapacitor electrode. The loading amount for supercapacitor was  $1.1$  mg cm $^{-2}$ . Electrochemical performances of the supercapacitor electrodes were measured by cyclic voltammetry (CV) and galvanostatic charge/discharge on CHI 660 C electrochemical workstation using  $1.0$  mol L $^{-1}$   $\text{H}_2\text{SO}_4$  aqueous solution as the electrolyte. For the fabrication of sensor electrode, the prepared G/PNT-modified GCE was dipped into horseradish peroxidase (HRP) solution overnight and then immersed into  $0.1$  mol L $^{-1}$  PBS solution to wash away the loosely adsorbed HRP. The modified electrode was stored at  $4$  °C under dry condition prior to use. Amperometric experiments were also conducted with CHI 660C electrochemical workstation using HRP/G/PNT-modified GCE as the working electrode in  $0.1$  mol L $^{-1}$  PBS solution. The electrochemical cell was purged with high-purity nitrogen for at least 30 min and the nitrogen atmosphere was kept over the solution for each amperometric experiment (Scheme 1).

## 3. Results and discussion

It is well-known that the hydrophilic GO, as the precursor of graphene, has abundant epoxy, carboxyl and hydroxyl functional groups on the nanosheets. During the dispersion process of PPY nanotubes in GO solution, the interaction including  $\pi$ - $\pi$  interaction or hydrogen bonding between GO nanosheets with aromatic structures and conjugated PPY nanotubes prevent the precipitation of the insoluble PPY nanotubes and guarantee the homogeneous distribution of PPY nanotubes in GO solution. Subsequently, when the electrode coated with the suspension of GO/PPy nanotubes was subjected to potential scanning between  $-1.2$  and  $0$  V, the G/PNT composite film was successfully synthesized. Fig. 1 presented the cyclic voltammograms for the synthesis of G/PNT composite film. It could be observed that there was an obvious cathodic current in the first scan. This reduction

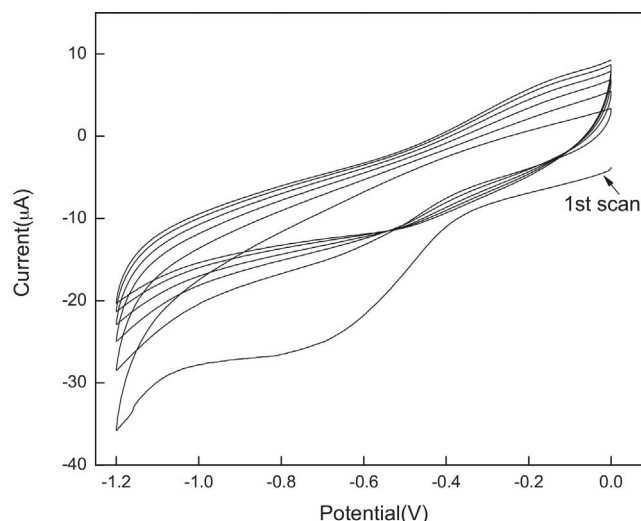


Fig. 1. CV curves for the synthesis of G/PNT composite film. scan rate:  $50$  mV s $^{-1}$ .

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