

# GRAPHENE-OXIDE-POLYMER COMPOSITES AS HIGH-PERFORMANCE SUPERCAPACITOR ELECTRODES

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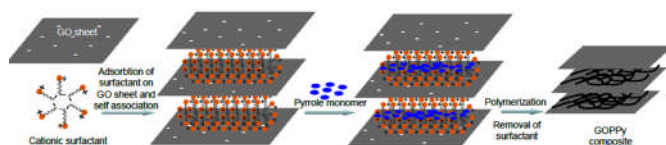
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## Introduction

Graphene oxide (GO) is a promising precursor for making composite materials because of its rich surface chemistry and unique two dimensional layered structure [1,2]. In this work, GO produced by chemical exfoliation of graphite was modified with polymers using an one-step method. Conducting polymers with different morphologies were sandwiched between two layers of GO sheets. The GO-polymer composite materials were used as supercapacitor electrodes. Electrochemical data showed that the composite electrode exhibited an energy density as high as 70 Wh/kg at a power density of 200 W/kg with a good rate performance, showing that such composites are very promising electrode materials for supercapacitors and other energy storage and conversion devices. The facial method for the preparation of GO-polymer composites demonstrated in this work opens up a generalized route to making a wide range of GO-based composite materials for various applications.

## Experimental

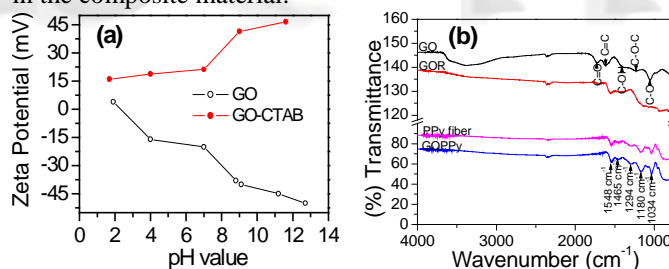
The preparation of GO-polypyrrole fiber composite (GOPPy) is schematically illustrated in Scheme 1, where cetyltrimethyl ammonium bromide (CTAB) and pyrrole were used as the surfactant and conducting polymer monomer, respectively. GO solution was obtained from chemical exfoliation of graphite by a modified Hummers method [3]. By controlling the surfactant concentration, rodlike micelle assembled on the GO surface. The pyrrole monomer predominantly resided in the micelle core and polymerization began upon adding ammonium persulfate (APS). After repeated washing to remove excess ingredients, PPy fibers sandwiched between GO sheets forming a layered composite structure was obtained. Pure PPy fiber was obtained under the same experimental conditions except for without the presence of GO. A reduced graphene sample (denoted as GOR) was prepared by hydrazine reduction of GO.



**Scheme 1.** Schematic illustration of the formation process of GOPPy composite.

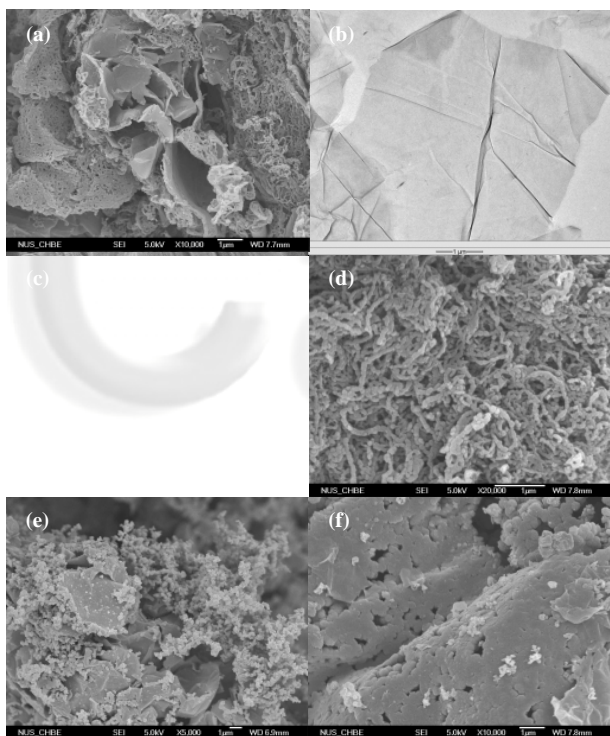
## Results and Discussion

The GO sample was characterized using zeta-potential analysis and Fourier-transform infrared (FTIR) spectroscopy shown in **Fig. 1**. The zeta potential profiles (**Fig. 1a**) reveals that the GO dispersion was negatively charged over a wide range of pH. This is known to be due to the ionization of surface functional groups, such as carboxylic acid and phenolic hydroxyl groups [4]. After adding surfactant CTAB, the surface charge of the GO sheets reversed, showing the adsorption of the surfactant on the GO surface. The FTIR spectrum of the GOPPy composite shown in **Fig. 1b** displays characteristic peaks of PPy [5], indicating the presence of PPy in the composite material.



**Fig. 1** (a) Zeta potential profiles of GO and CTAB modified GO in aqueous dispersion as a function of pH value, (b) FTIR spectrum for GO, GOR, GOPPy composite and PPy fiber.

The morphological information of the samples was obtained using field-emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). The layered structure of the GO sheets can be seen from the FESEM image shown in **Fig. 2a**. The TEM image (**Fig. 2b**) showed a typical single layer GO sheet with lateral dimensions of several micrometers. As for the GOPPy composite, a flat and layered structure can be readily seen from **Fig. 2c** with PPy fibers sandwiched between GO sheets and/or on the GO surface. On contrast, only random PPy were obtained for a pure PPy sample (**Fig. 2d**), which was prepared in the absence of GO. The role of surfactant was investigated. Without adding CTAB, no layered or flat composite structure was obtained. Instead, only separate PPy particles and GO sheets were obtained as shown in **Fig. 2e**, implying that the surfactant played a critical role in the formation of the GO-conducting polymer composite materials. In addition, the morphology of the PPy can be controlled by varying the surfactant concentration and/or adding a coadsorbing molecule [6]. We have succeeded in synthesizing PPy spheres sandwiched between two GO sheets, designated as GOPPy-S, with surfactant dodecyltrimethylammonium bromide (DTAB) and cosurfactant 1-decanol using the ultrasonication polymerization method [7]. In this case, spherical micelle aggregates formed to direct the formation of PPy spheres. The use of the cosurfactant was to avoid the diffusion of pyrrole monomers through the aqueous phase to enhance the size uniformity and stability of micelles [7]. Indeed, the FESEM image (**Fig. 2f**) revealed PPy spheres instead of PPy fibers on the GO sheets of a flat and layered structure.



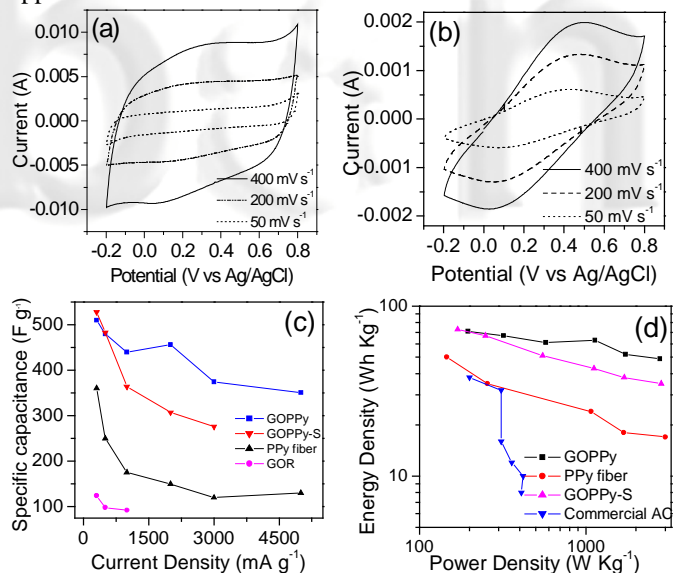
**Fig. 2** FESEM and TEM images of (a,b) GO, FESEM images of (c) GOPPy, (d) pure PPy fiber, (e) GO-PPy composite without surfactant and (f) GOPPy-S.

The electrochemical performance of the samples is presented in **Fig. 3**. The cyclic voltammetry (CV) profiles of GOPPy exhibited a rectangular shape at sweep rates ranging from 50 to 400  $\text{mV s}^{-1}$ , whereas the CV curves for PPy fiber (fig. 3b) are distorted, demonstrating a better charge propagation behavior and ion response of GOPPy than pure PPy fiber. The excellent rate performance of the composite can be clearly seen from fig. 3c. Although the pure PPy fiber sample exhibited a capacitance value of 360  $\text{F g}^{-1}$ , its rate performance was poor as the capacitance was below 150  $\text{F g}^{-1}$  when the current density was increased to 5  $\text{A g}^{-1}$ . On contrast, a very high specific capacitance of 510  $\text{F g}^{-1}$  was obtained from the GOPPy composite electrode and a high capacitance retention ratio (about 70 %) was obtained when the current density was increased by 17 times. The Ragone plot shown in fig. 3d clearly demonstrated that over a wide range of power density, the GOPPy electrode significantly out-performed other electrode materials. The highest energy density of the GOPPy electrode reached 70  $\text{Wh kg}^{-1}$ , showing a very promising electrode material for high-performance supercapacitors.

## Conclusions

We have demonstrated the preparation of graphene oxide conducting polymer composites and their superior electrochemical performance as supercapacitor electrodes. Such composite materials with a layered structure embrace the unique properties of graphene oxide and conducting polymers. The polymer-pillared graphene oxide structure with an

opened-pore system effectively reduces the dynamic resistance of electrolyte ions. Considering the simple method and wide applications of the composite structures, the concept introduced in this work can be extended for making other graphene oxide- and graphene-based architectures for various applications.



**Fig. 3** (a) CV profiles of GOPPy and (b) pure PPy measured at sweep rates. (c) Specific capacitance as a function of current density. (d) Ragone plot comparing the capacitive performance of GOPPy with pure PPy and a commercial electrode (Maxsorb).

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## References

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