

Short communication

# Ternary composite electrodes based on poly(3,4-ethylenedioxythiophene)/carbon nanotubes-carboxyl graphene for improved electrochemical capacitive performances



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## ABSTRACT

Co-electrodeposited poly(3,4-ethylenedioxythiophene)/carbon nanotubes-carboxyl graphene (PEDOT/CNT-CG) ternary composite is reported herein. Thereinto, the CG is prepared from graphene oxide (GO) by carboxylation treatment, during which the hydroxyl and epoxide groups on the basal plane of GO nanosheets are converted into carboxyl groups. Compared to PEDOT/CNT-GO composite, PEDOT/CNT-CG composite shows markedly improved electrochemical capacitive performances, because the latter composite takes full advantage of carboxyl groups distributed on both edges and basal planes of CG sheets to combine with PEDOT coating, unlike only utilizing the edged carboxyl groups on GO sheets for the former composite. This study provides a new platform to construct CG based composite electrodes for high performance supercapacitor applications.

## 1. Introduction

As one kind of electrochemical energy storage devices, supercapacitors (SCs) have their unique properties including high power density, fast charging-discharging, and long cycle life [1–4]. Among various supercapacitor electrode materials, poly(3,4-ethylenedioxythiophene) (PEDOT), one of conducting polymers, has been extensively investigated due to its high electrical conductivity, fast charge/discharge kinetics, wide potential window, and environmental friendliness [5,6]. However, the poor cycle life is an obvious drawback that restricts its applications in SCs. It is related with the swelling and shrinkage during charging-discharging caused by the doping/dedoping of counter anions. In addition, PEDOT commonly shows a compact morphology because of its dense growth, limiting the access of electrolyte to interior sites of the polymer [7–9]. Graphene oxide (GO), a single sheet of graphite oxide, has become the most common starting material for graphene based applications, because it can be directly prepared in large quantities from graphite. Especially GO possesses abundant oxygen-containing functional groups such as epoxide, hydroxyl, carbonyl, and carboxyl groups, featuring negative charge surface, large specific surface area, and high dispersibility in water [10–12].

In recent years, PEDOT-GO composites have attracted great research interest owing to their enhanced supercapacitive performances

relative to PEDOT [13–17]. This can be ascribed to the three factors: (1) The GO nanosheets increase the specific surface area of composites and promote the dispersion of PEDOT as coating; (2) The GO improves the wettability of composites due to its good hydrophilicity; (3) The GO sheets provide extra mechanical support and allow room for volume swelling and shrinkage of PEDOT, consequently resulting in longer cycle life. Although PEDOT-GO composites show good capacitive properties, the insulating GO in the composites still hinders their electrochemical capacitive performances. We have thus developed PEDOT/CNT-GO ternary composite in a recent work by one-step electrochemical co-deposition [18], during which the anionic GO and carboxylated CNT simultaneously acted as not only charge carriers in deposition solution, but also the counter ions for charge balancing of the PEDOT. Note that carboxylated CNT still has a high electrical conductivity [19]. As a consequence, the introduced CNT obviously enhanced the electrochemical capacitive properties of PEDOT-GO composite. Now the question is that GO sheets have quantities of hydroxyl and epoxy groups on the basal planes, in addition to lesser carboxyl groups located at the edges [20]. In other words, GO as counter anions in the PEDOT/CNT-GO composite only utilizes the edged carboxyl groups to bond PEDOT, leaving the ample basal oxygenated groups intact.

To further improve the supercapacitive performances of PEDOT/CNT-GO composite, we propose in this contribution to convert

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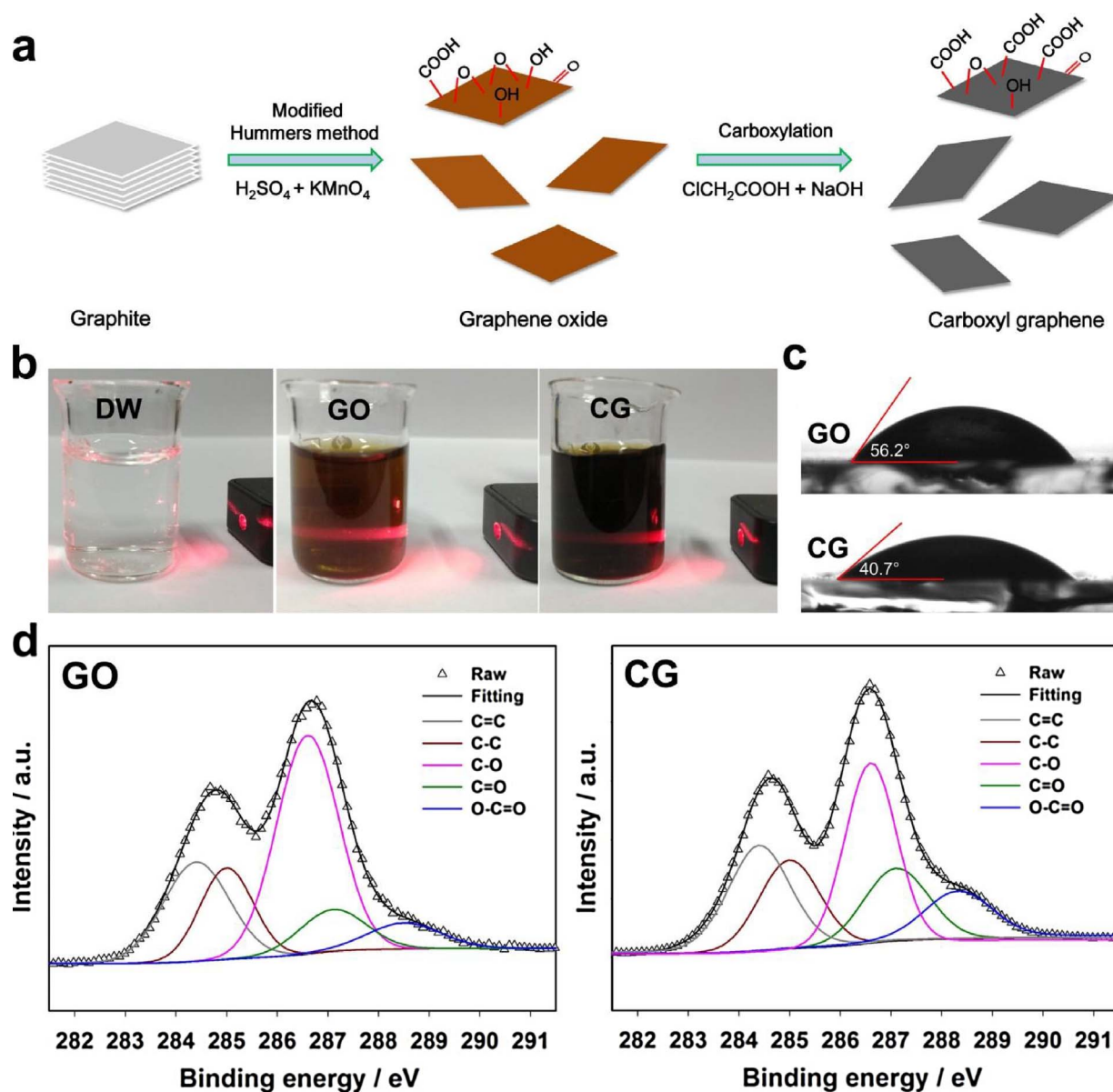


Fig. 1. (a) Schematic representation of the preparation procedures of GO and CG. (b) Tyndall scattering effect of  $1 \text{ mg mL}^{-1}$  of GO and CG dispersed in deionized water. (c) Water contact angle of the GO and CG films spread evenly on glasses. (d) High-resolution C 1s XPS spectra of GO and CG.

hydroxyl and epoxy groups on the basal planes of GO sheets to carboxyl groups through the treatment of carboxylation. The obtained carboxyl graphene (CG) can provide more active sites for the dispersion and polymerization of PEDOT with superior pseudocapacitance. Correspondingly, PEDOT/CNT-GO and PEDOT/CNT-CG ternary composite electrodes are prepared with the same co-electrodeposited procedure. Electrochemical measurements indicate that PEDOT/CNT-CG composite has markedly improved supercapacitive performances compared with PEDOT/CNT-GO composite.

## 2. Experimental

### 2.1. Carboxylation treatment

As shown in Fig. 1a, GO was synthesized by the oxidation of graphite powder on the basis of a modified Hummers method [21]. Subsequently, CG was prepared by performing carboxylation treatment to GO. For carboxylation of GO [22], 5.0 g of chloroacetic acid and 6.0 g of NaOH were added to the 50 mL of GO aqueous suspension at a

concentration of  $2 \text{ mg mL}^{-1}$  and reacted under ultrasonication for 3 h. The resulting CG suspension was neutralized and purified by repeated rinse with deionized water (DW) and filtration to remove excess reactant, followed by drying at  $50^\circ\text{C}$  in vacuum oven for 24 h. For carboxylation of CNTs, pristine CNTs were pretreated in 3 M  $\text{HNO}_3$  at  $140^\circ\text{C}$  under magnetic stirring by refluxing for 72 h. Subsequently, they were transferred into a mixture of concentrated  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  (volume ratio 3:1) and functionalized with carboxyl groups under bath-sonication at  $40^\circ\text{C}$  for 2 h. Finally, the resultant carboxylated CNTs were rinsed with abundant DW until the pH reached about 6.0 and dried at  $50^\circ\text{C}$  for 24 h.

### 2.2. Fabrication of electrodes

PEDOT/CNT-CG electrodes were prepared via one-step co-electrodeposition in the aqueous deposition bath containing 0.01 M EDOT monomer,  $1 \text{ mg mL}^{-1}$  CG, and  $1 \text{ mg mL}^{-1}$  carboxylated CNTs, using a constant and low current density of  $1 \text{ mA cm}^{-2}$  for 30 min. A three-electrode system was used to perform the electrodeposition,

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