

Carboxyl-Functionalized Graphene Oxide/Polyaniline Composite as a Promising Supercapacitor Material

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Graphene, a 2D sheet of sp^2 -bonded carbon atoms arranged in a honeycomb lattice, has attracted increasing attention since it was firstly isolated from 3D graphite by mechanical exfoliation¹. The high specific surface area and the fast electron transportation specially endow graphene with natural merits as the ideal supercapacitor materials. However, the pure graphene based supercapacitor materials actually exhibited unsatisfactory capacitance because of inevitable aggregation of graphene sheets. At the present, a great number of papers have reported graphene/polyaniline (PANI) composites using different synthetic methods. But most previous researches on graphene/PANI composites only utilized the edged carboxyl groups to bond aniline and remained the ample basal oxygenated groups intact, which means the graphene sheets freely dangled by the edges from the PANI, not orderly fixed by the basal planes². Herein, we try to make the best use of the basal oxygenated groups to create orderly constructed graphene oxide/polyaniline (GO/PANI) composites by in situ polymerization. Considering the differences for the naturally existed oxygenated groups, we intend to further develop them into carboxyl groups on the GO sheets. The epoxide groups ($-O-$) on the basal plane of GO sheets were converted into hydroxyl groups ($-OH$) via a ring-opening reaction catalyzed by concentrated hydrobromic acid (HBr). An esterification reaction was then followed by the introduced oxalic acid ($HOOC-COOH$) interacting with $-OH$ groups to realize carboxylation of GO sheets. The all-round (including edged and basal oxygen-containing sites) carboxyl-covered graphene sheets (CFGO) provide highly consistent affinity to the amine nitrogens of the polymerized PANI chain, thus facilitate formation of stable, orderly composite structure. The as-assembled carboxyl-functionalized graphene oxide/polyaniline (CFGO/PANI) composite as supercapacitor electrode material demonstrated excellent capacitive capability thanks to its high-efficiency charge-transfer tissue architecture.

CFGO/PANI were synthesized using aniline (2.76ml) and ammonium persulfate (1.71mg) as monomer and as initiator respectively by in situ polymerization in CFGO aqueous solution ($2.0 \text{ mg}\cdot\text{mL}^{-1}$, 30.0 mL) under ultrasonication. For comparison, GO/PANI was synthesized in the similar method using GO ($2.50 \text{ mg}\cdot\text{mL}^{-1}$, 30.0 mL) which was prepared by modified Hummers method without functionalization. Besides, the carboxyl-functionalized graphene/polyaniline (CFG/PANI) was also synthesized. Specifically, CFGO/PANI was subjected to a solvothermal reaction at 95°C for 1 h employing 0.1 mL of hydrazine hydrate as reductant. And then the precipitates were filtrated and repeatedly washed with deionized water, ethanol, and hexane, and dried at 50°C in vacuum for 24 h.

The electrochemical behaviors of the as-prepared

electrode materials shown in Fig.1 were compared via cyclic voltammetry (CV), galvanostatic charge-discharge (GCD). Obviously, in Fig.1a the CFGO/PANI exhibits the largest capacity, whereas the CFG/PANI only has the minimal capacitance. The representative GCD plots in Fig.6b have consistent outcomes.

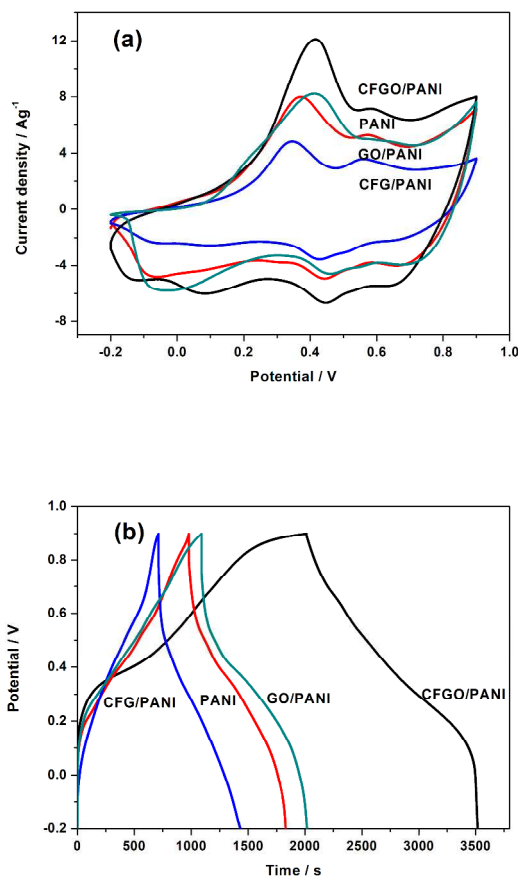


Fig.6 Electrochemical behaviors of PANI, GO/PANI, CFG/PANI, and CFGO/PANI electrodes in $1.0 \text{ mol}\cdot\text{L}^{-1}$ H_2SO_4 solution. (a) CV with scan rate $10 \text{ mV}\cdot\text{s}^{-1}$, (b) GCD with current density $0.3 \text{ A}\cdot\text{g}^{-1}$

In summary, the CFGO/PANI composite shows a sound architecture for fast charge transfer. Meanwhile, effective utilization of the electroactive PANI is markedly enhanced due to eliminative entanglement as well as compact assembly. The as-synthesized CFGO/PANI electrode material demonstrates enhanced capacitance capability and is highly expected to be a promising supercapacitor material.

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