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Fluorescent modified graphene oxide/polyaniline nanowhiskers composites as smart electrode material for supercapacitors

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ABSTRACT

Fluorescent modified Graphene oxide/Polyaniline (Xn-GO/PANI, or Xn-GP) composites with ordered PANI nanowhiskers were successfully fabricated through a facile *in situ* chemical oxidation polymerization doping the fluorescent agents, Fluorescein (F), Rhodamine B (R) and Coumarin (C), respectively. The ordered PANI nanowhiskers (~25 nm) were uniformly grown onto the surface and edge of GO sheets. TEM and SEM images demonstrated a quasi-two-dimensional (2D) architecture of Xn-GP nanocomposites. FT–IR, UV–vis, and Fluorescence emission analysis further verified the Xn-GP composites. As electrode materials for supercapacitors, the electrochemical results confirmed that the Fn-GP, Rn-GP and Cn-GP nanocomposites possessed the high electrochemical specific capacitance (555.6 F/g, 473.5 F/g and 459.5 F/g, respectively) at 0.5 A/g, the low charge transfer resistance, and excellent electrochemical stability by CV, GCD, EIS and cycle stability. The superior electrochemical performance of the Xn-GP ternary composites are principally ascribed to the fine synergistic effects of Xn, GO and PANI, which offered a quasi-2D conductive matrix for effective electron transfer, suitable channels for ion diffusion, good π–π interactions, and valid buffer for volume expansion of the PANI nanowhiskers during charge/discharge process. Especially, the novel Xn-GP composites with fluorescence property have the promising applications as smart electrode materials for supercapacitors.

1. Introduction

The efficient utilization of energy is of crucial importance for energy storage technologies. As a state-of-the art energy storage devices, electrochemical supercapacitors (ECs) has drawn meaningful attention due to safe handling, high power densities, long cycle life, low maintenance cost, and fast charging/discharging rates, which makes them attractive in widespread applications, such as portable electronic devices, power grids, electric vehicles, and aerospace applications [1-5]. According to the energy storage mechanism, supercapacitors can be divided into two types: pseudocapacitors coming from the reversible and fast redox reactions at electrochemically active sites of the surface of electrode, and electrical double-layer capacitors (EDLC) based on the electrostatic charge accumulation in the electrode/electrolyte interface. Generally speaking, electrochemical properties of supercapacitors are enormously influenced by the slow electrode kinetics and/or mass transport of electrode materials [1]. In order to match with the ever-increasing developments in supercapacitors, the critical target is to exploit the optimal electrode materials with outstanding electrochemical properties simultaneously, such as large specific capacitance, good cycling stability, and high power delivery [6].

Polyaniline (PANI) is a promising electroactive electrode materials for supercapacitors [7,8], which has been extensively researched because of its low cost, low environmental impact, unique doping/dedoping chemistry, high pseudocapacitance derived from multiple redox states, and ease of fabrication for large-scale devices [9,10]. Nevertheless, similar to the other conducting polymers (CPs), PANI suffers from poor cycling stability and bad mechanical stability resulting from a large volumetric shrinking and swelling during charge/discharge cycling upon the ion doping/dedoping process [11,12]. Moreover, the above-mentioned problems usually bring about the structural pulverization of polymers skeleton and thus fast capacitance decay of CPs [10]. Particularly, most PANI based electrode materials retain less than 50% of their initial capacitance and have fast electrochemical performance capacitance decay after cycling for 1000 times [11], which are a great challenge for practical applications of PANI-based electrodes in supercapacitors. On the contrary, composite structures

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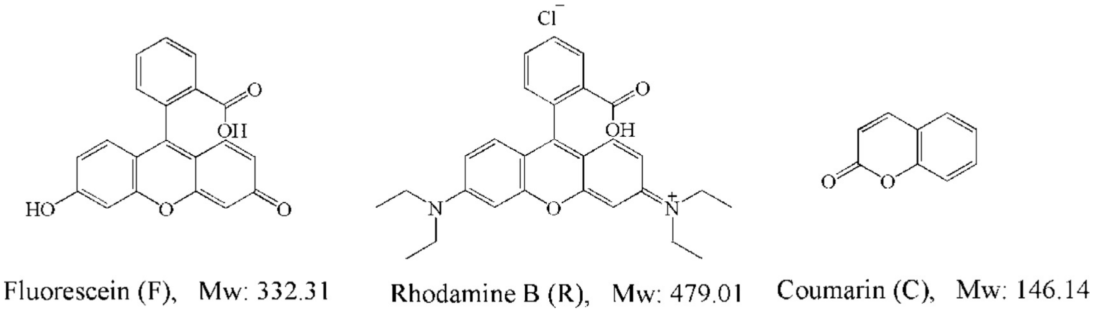

Scheme 1. Structure of fluorescein (F), Rhodamine B (R), Coumarin (C).

with the suitable stuffing material could effectively prevent the structural breakdown and buffer the electrochemical performance degradation of PANI [13,14].

On the other hand, graphene and/or graphene oxide (GO), which has 2D layered structures with a monolayer or a few atomic layers, is extensively studied widely used to improve the reliability and electrochemical performance of PANI-based composites, owing to the superior mechanical strength, a low fabrication cost, high electrical conductivity, and high theoretical specific area of graphene [15]. However, the irreversible agglomerates of the nanostructures between PANI and graphene (or GO) through van der Waals interactions [16] usually obstruct the optimal use of the nanostructures and the positive reinforcement of electrochemical performance of synergistic GO/PANI nanocomposites. To overcome this limitation, a lot of PANI nanostructures such as nanocones [17], nanofibers [18], nanowires [19], nanowhisker [20], and nanocomposites with GO have been studied. Meanwhile, the electrochemical performance of GO/PANI nanocomposites can be increased by means of enhanced specific surface area of the nanostructures and heightened ion transport at the electrolyte/electrode interface, which could be attributed to the excellent synergistic effect between them [21]. Therefore, the GO/PANI composites with nanowhiskers structures are proven to be of significant advantages. First, the quasi-2D architecture with nanowhiskers can obtain greater synergetic improvements from intrinsic properties of different components such as better mechanical stability, shorter ionic transport, greater electrochemical reversibility and cycling stability. Second, its ordered nanowhiskers can effectively reduce the aggregation possibilities of active materials, increase the specific surface area, and facilitate electrode/electrolyte contact [22].

Here, we suggest a conceptually new pathway to design and synthesize the fluorescent modified Xn-GP composites with ordered PANI nanowhiskers via a facile *in situ* chemical oxidation polymerization. Fluorescent agents (F, R and C) with strong fluorescence (Scheme 1), which have the large π-conjugated systems, were used as the dopants for the fluorescent Xn-GP composites. FT-IR, UV–vis, photoluminescence (PL), SEM and TEM analysis were used to investigate the structure and composition of the Xn-GP nanocomposites. The electrochemical performances of this composites with large polyaromatic molecule structure were characterized by cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), electrochemical impedance spectroscopy (EIS), and cycle stability. By taking advantage of the favorable fluorescence property of F, R and C, good mechanical properties of GO, and excellent electrochemical activity of PANI, the Xn-GP ternary composites with ordered PANI nanowhiskers aimed to improve the specific capacitance, decrease the charge transfer resistance, and promote the cycling stability of the Xn-GP nanocomposites. Noticeable enhancements in the fluorescent Xn-GP composites with ordered nanowhiskers allow its promising application as smart electrode material for supercapacitors.

Table 1
The chemical oxidative polymerizing conditions of Xn-GP nanocomposites (for Fn-GP) in ice-water bath.

Fn-GO/PANI Sample	An (mL)/GO (g)	F (g)	APS (g)	F feeding ratio with An (mol%)
F1-GP	0.5/0.05	0.0083	1.14	5
F2-GP	0.5/0.05	0.0166	1.14	10
F3-GP	0.5/0.05	0.0332	1.14	20
F4-GP	0.5/0.05	0.0831	1.14	50
F5-GP	0.5/0.05	0.1162	1.14	70

2. Experimental

2.1. Materials and reagents

Fluorescein (F), Rhodamine B (R) and Coumarin (C) were purchased from Sinopharm Chemical Reagent Co. Ltd, Shanghai, China. Aniline monomer (An, Tianjin Chemical Reagent Co., Tianjin, China) was distilled under reduced pressure and stored below 0 °C before use. Ammonium persulfate (APS, Tianjin Guangfu Fine Chemical Industry Research Institute, Tianjin, China), as well as all other reagents, were purchased from the Tianjin Chemical Reagent Co. and used without further purification. All other chemical reagents were in analytical grade. The double-distilled water was used throughout.

2.2. Preparation of Xn-GO/PANI nanocomposites

GO was synthesized using a modified Hummer's method, and the details of the procedure developed by our previous study were described elsewhere [23]. The polymerization method of Xn-GP ternary composites was as follows (the conditions of polymerizing were summarized in Table 1, it was illustrated by Fn-GP nanocomposites): GO (0.05 g) was dispersed in 60.0 mL 1.0 M HCl aqueous solution, by ultrasonication for 30 min. Then, a certain amount of fluorescein and 0.5 mL An was introduced and vigorously stirred for 1 h, respectively. 1.14 g APS dissolved in 20 mL of 1.0 M HCl aqueous solution was added drop by drop into the reaction system to start the polymerization, and kept stirring in the ice bath for 24 h. The deep green product was washed with ethanol and water for three times, and dried in a vacuum oven at 60 °C for 24 h. The Fluorescein-GO/PANI nanocomposites (Fn-GO/PANI, Fn-GP) were obtained. Meanwhile, Rhodamine B-GO/PANI (Rn-GO/PANI, Rn-GP) and Coumarin-GO/PANI (Cn-GO/PANI, Cn-GP) were also synthesized by the same condition. The preparation process and electrochemical mechanisms of Fn-GP nanocomposites was shown in Scheme 2.

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