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High volumetric supercapacitor with a long life span based on polymer dots and graphene sheets

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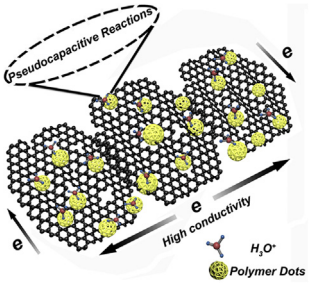
HIGHLIGHTS

- Abundant functional groups from polymer dots (PDs) take part in faradic reactions.
- PDs can bind onto graphene sheets tightly through chemical bonds.
- PDs can effectively increase the surface areas and pore volumes of the composites.

GRAPHICAL ABSTRACT



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ABSTRACT

A series of polymer dots/graphene sheets composites with high densities are prepared and tested for supercapacitors. Polymer dots (PDs) are synthesized by one-step method at room temperature. They can effectively increase surface areas of the composites (almost 10 times), and the functional groups from PDs produce high pseudocapacitance, so that the samples exhibit high specific capacitances (e. g., 364.2 F cm^{-3} at 1 A g^{-1}) and high cycling stability (e. g., more than 95% of the initial capacity retention over 10 000 cycles at different current densities). The optimal sample is employed to fabricate a symmetric supercapacitor, which exhibits an energy density up to 8 Wh L^{-1} and a power density up to 11 800 W L^{-1}, respectively.

1. Introduction

The concerns of electronic hazards and high cost of metallic materials let researchers keep on developing metal-free electrode for greener and more sustainable energy storage systems [1]. In a variety of nonmetallic materials, graphene has become a focus in the fundamental research of supercapacitors electrode materials regarding its unique properties in chemical stability, tunable structure, excellent electrical conductivity and high surface area [2]. However, capacitive performance of related nanomaterials like 2D graphene nanosheets (GS) tend to degrade after chemical processing, which mainly arises from fewer functional groups on the surface, nonporous structures and lower surface areas caused by aggregation [3]. And as for electrical double layer capacitance (EDLC), a key parameter of supercapacitor, specific surface areas

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(SSA) and pore size distributions (PSDs) of the electrode materials play the main roles in the influence of it [4]. In order to increase the SSA and pore volume of GS, hard templates, self-assembly and chemical activation agents (like KOH) have been employed to achieve above objectives [5,6]. Nevertheless, such methods mean complex processes or harsh conditions, which do not fit the concepts of green chemistry. On the other side, some other researchers have tried to introduce more functional groups through compositing graphene with pseudocapacitive materials like conducting polymer [7]. Polyaniline (PANI), as a typical example, has been widely studied as a supercapacitor material for its high capacitance, good conductivity in the doped state and fast redox reactions [7]. Although such composite could exhibit an outstanding specific capacitance, its cycle life was influenced heavily by the PANI dissolution from graphene layers during charge-discharge cycles. Therefore, it is still a challenge to find a better material, which can offer abundant organic groups for faradaic reactions, increase the surface area of graphene for electrical double layer capacitance and bind onto graphene layers tightly for stable combination.

In view of this, polymer dots (PDs) will be a better choice to meet above requirements. Typically, PDs are cross-linked polymers prepared from linear polymers (lower molecular weight) or monomers [8]. Similar to carbon quantum dots (CQDs) or graphene quantum dots (GQDs), PDs have advantages in small size (around 10 nm), good dispersion in many solvents, abundant surface groups and low production cost [8,9]. Yet due to these natural merits of PDs, they will have better prospects when taken as supercapacitors electrode materials. First, the functional groups on PDs are not only able to produce high pseudocapacitance, but also able to bind PDs onto graphene tightly through chemical bonds [10,11]. Thus, PDs could play their significant role continuously during the long cycle life. Moreover, quantum sizes make PDs an excellent filler for the graphene-based materials, which means it is possible to make full use of the limited space between layers. Therefore, the dense structure of GS will be protected and volumetric capacitance can be greatly improved accordingly. Finally, according to our and other previous works [12], such nano dots would have a positive effect on the morphologies, SSA and PSDs of matrix materials. Accordingly, it will provide some considerable benefits for the electrochemical performance. But so far, PDs were merely studied for fluorescence sensors and bioimaging probes [8,9], while their applications in the electrode materials have never been reported.

In the present research, we synthesized PDs from polyethylene imine (PEI) and prepared PDs/GS composites at room temperature in facile ways. Mild conditions enable the preservation of a large number of amino groups from PDs, which have a great contribution to pseudocapacitance. The introduction of PDs can improve the SSA of graphene sheets and contribute to a diversified distribution of pore sizes. More than that, reactions between surface groups from both PDs and GS will make such composites very stable. The optimal sample had a density of about 1.4 g cm^{-3} (compaction density, including binder), with its specific volumetric capacitances of 364.2 F cm^{-3}. In comparison to graphene sheets, whose specific capacitance is only 193 F cm^{-3}, the optimal result is nearly twice as much. The corresponding symmetric supercapacitor showed a volumetric energy density of 8 Wh L^{-1} and a volumetric power density of 11 800 W L^{-1}. Furthermore, almost 100% retention rates were observed at different current densities during long term cycling tests.

2. Experiment section

2.1. Synthesis of PDs

PEI (0.5 g, Aldrich) was dissolved in DI water (20 mL) and then hydroquinone solution (0.5 mL, 1 mg mL^{-1}) was also added. After standing at room temperature for one day, the color of the mixed solution changed from colorless to clear yellow. Solid PDs were obtained by adding *N*,*N*-Dimethylformamide (DMF) into the solution and collecting the precipitate after centrifugation. The precipitate was washed by DMF and further dried in a vacuum oven at 40 °C for 48 h.

2.2. Preparation of GS and PDs/GS composites

GS colloidal suspension (5 mg mL^{-1}) was prepared by sonication of graphite oxide powder which has been synthesized from nano graphite powder (Aladdin) by a modified Hummers method. After that, PDs was added in the suspension with different mass ratios (1:10, 1:5, 1:2 and 1:1). After standing at room temperature for 12 h, the as-prepared hydrogels (PDs/GS composites) were freeze dried to remove adsorbed water for following experiments.

2.3. Characterizations

The data of X-ray diffraction (XRD) were collected at room temperature using a Bruker D4 Endeavor X-ray diffractometer with Cu Kα radiation (λ = 0.1541 nm, 40 kV). Fourier transform infrared (FT-IR) spectra were recorded on a Thermo Fisher Nicolet 6700 FTIR spectrometer in a range of 4000–500 cm^{-1}, using the KBr pellet method. The UV-vis absorption spectra were measured on the Unico UV-2802 PC spectrometer. The fluorescence spectra were recorded using a Horiba Jobin Yvon FluoroMax-4 spectrofluorometer. Nitrogen adsorption-desorption measurements were performed at 77.3 K with a Quantachrome Autosorb IQ surface area analyzer to obtain the SSA. X-ray photoelectron spectroscopy (XPS) data were obtained by a Thermo ESCALAB 250 electron spectrometer using an Al Kα X-ray source (1486.6 eV). The morphologies of the samples were characterized via a fieldemission scanning electron microscopy (FESEM) under a JSM-6390 microscope (Zeiss, German), while the transmission electron microscopy (TEM) images of the samples were obtained by a high resolution transmission electron microscope (JEM-2010) at 200 kV.

2.4. Electrochemical measurements

The electrochemical performance was determined using a three-electrode or two-electrode system (symmetric capacitor) in 1 mol L^{-1} H_2SO_4 aqueous solutions. For three-electrode system, cyclic voltammetry (CV) was recorded on a CH Instruments 660E electrochemical workstation at the potential range of −0.6 to +0.4 V vs. Hg/Hg_2SO_4 and the scan rate was set from 2 to 100 mV s^{-1}. Galvanostatic charge-discharge (GCD) tests were performed by a CT2001A Land cell tester at the same potential ranges, while the current densities varied from 1 to 30 A g^{-1}. Electrochemical impedance spectroscopy (EIS) measurements were also conducted on the electrochemical workstation and frequency limits were set at 100 kHz to 0.01 Hz with 5 mV of voltage amplitude at the open-circuit potential. In this system, the working electrode was prepared by pressing a mixture of the sample (95 wt %) and poly(tetrafluoroethylene) (PTFE) binder (5 wt %) onto a stainless steel grid with an area of 1 cm^2, followed by drying at 80 °C for 24 h, and the active material loading for each electrode was about 1.2 mg cm^{-2}. The counter electrode was prepared with activated carbon (commercial, surface area >1200 m^2 g^{-1}) and PTFE binder in the same proportion, but the area of the counter electrode was about 3 cm^2 (about 5 mg cm^{-2}) in order to reduce the interference to working electrode.

Symmetric supercapacitors (two-electrode system) were assembled by using the optimal sample (PDs/GS-0.5) as positive