



Polypyrrole nanosphere embedded in wrinkled graphene layers to obtain cross-linking network for high performance supercapacitors



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ABSTRACT

Polypyrrole nanospheres were embedded in graphene layers (rGCP) to successfully form three-dimensional hierarchical cross-linking structure through simple hydrothermal method. The structure of rGCP composite mainly resulted from the synergistic effect of cetyltrimethyl ammonium bromide and crumpled graphene layers, which was beneficial for achieving large surface area, short ion diffusion pathway, excellent rate performance and cycling stability. As a result, the hybrid rGCP composite exhibited excellent electrochemical performance with a specific capacitance of almost 400 F g^{-1} at the scan rate of 1 mV s^{-1} . Furthermore, even at the high current density of 10 A g^{-1} , it still retained the capacitance of 243.2 F g^{-1} , and excellent cycling stability (91.8% capacitance retention even after 5000 cycles). The as-prepared hierarchical hybrid composite has promising potential in electrochemical energy storage.

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1. Introduction

With the rapid consumption of fossil fuel and the aggravated environmental pollution, renewable clean energy sources and advanced energy storage systems have become the mainstream of the energy storage [1–6]. Therefore, supercapacitors (SCs), based on the traditional electrochemical charges of the electric double layer (EDLC) and the pseudocapacitance of Faradaic reactions, have drawn great concerns in past decades [7]. Porous carbon materials [8–14], transition metal oxides [15–18] or hydroxides [19–22], and conducting polymers [23–26] are fundamental candidates used as SCs electrode materials.

Among these electrode materials, conducting polymers are more capable to meet the ever-growing need for peak-power assistance in the hybrid electric vehicles, because it can simultaneously store charges via both the EDLC and the pseudocapacitance ways. As an important class of conducting polymers, polypyrrole (PPY) has attracted more and more interests due to their merits (such as low cost, environmentally friendly availability, and easy synthesis). Zhang et al. designed the granular-like PPY composite with the hard template of

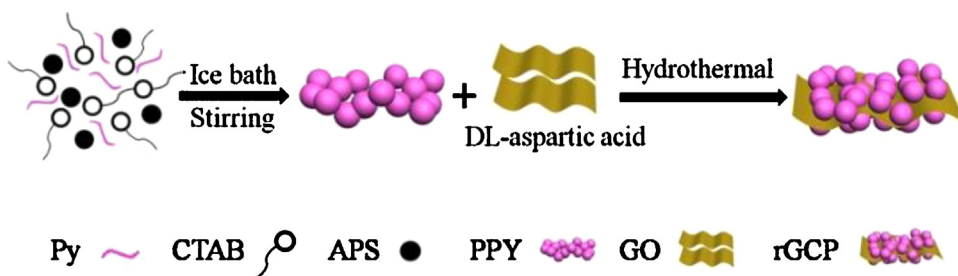
manganese dioxide sphere, which showed the specific capacitance of 352.8 F g^{-1} at a constant current of 8 mA cm^{-2} [27]. Liu and Zhang et al. made efforts to fabricate different morphologies of hollow sphere or nanotubular PPY, which exhibited the specific capacitance of around 120 F g^{-1} at low scan rate of 5 mV s^{-1} for original PPY nanotubes [28,29]. Although people have obtained some achievements, the relatively low specific capacitance and poor cycle life still restrict their practical application. Because polymer backbone are not sufficiently stable during many charge-discharge processes as well as irreversible redox reactions. Therefore, numerous efforts have been devoted to fabricate hybrid composites such as graphene/carbon nanotube-based PPY hybrid, metal oxide doped-PPY [30,31] to enhance cycling stability and rate performance [32–38]. Compared to the complicated synthetic processes, high cost and the environmental problems of sacrificing hard templates, soft template (e.g., surfactant) is more suitable for preparing materials with porous structures. In addition, conducting polymers with three dimensional (3D) ordered or aperiodic porous texture containing macropores or micro-mesoporous pores are strongly recommended for the advanced SCs [39,40], which is beneficial for ion or electron transfer by providing low resistances, short diffusion pathways, and a relatively stable structure.

Herein, we developed a straightforward approach to synthesize 3D hierarchical micro-mesoporous graphene-polypyrrole (rGCP, in Scheme 1) hybrid material with decent electrochemical properties through simple hydrothermal method. The synergistic effect of

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Scheme 1. Schematic illustration for the fabrication process of the rGCP hybrid composite.

graphene and the cationic surfactant cetyltrimethyl ammonium bromide (CTAB) resulted in the formation of the cross-linking micro-mesoporous structure. Moreover, the strong π - π and electrostatic interactions in rGCP composite contributed to the excellent electrochemical stabilities. When working as the electrodes for SCs, rGCP exhibited high specific capacitance of almost 400 F g^{-1} , good rate performance (even at a current density of 10 A g^{-1} , the capacitance still retained 70.3% of the capacitance at 1 A g^{-1}), and outstanding cycle stability, which was superior to the pure PPY and the graphene-polypyrrole without CTAB (rGP).

2. Experimental

2.1. Materials

Pyrrole (Py, 99.9%, Aladdin) was purified through distillation under reduced pressure and stored in the refrigerator before use. All the other solvents and raw materials were purchased from Aladdin and used as received without further purification unless noted.

2.2. Preparation of PPY

Py (2.0 mL) monomer was added in 1 M HCl (30.0 mL) under an ice bath. Pre-cooled ammonium persulfate (APS, 1.6506 g) dissolved in 1 M HCl (30.0 mL) was dropwise added into the above solution under magnetic stirring. The reaction was maintained for 6 h. The obtained black precipitate was washed with deionized water.

2.3. Preparation of rGCP

A certain amount of CTAB was dissolved in 1 M HCl (30.0 mL) and then 2.0 mL Py was added under an ice bath. After stirring for 30 min, 1.6506 g APS dissolved in 1 M HCl (30.0 mL) was dropwise added into the above Py solution under magnetic stirring. The reaction was maintained under an ice bath for 6 h. Then a black

precipitate was washed with deionized water until neutral. Graphite oxide was prepared from flake graphite by an improved Hummers' method [41]. A uniform GO suspension (2.0 mg mL^{-1} , 20.0 mL) was first prepared through ultra-sonication for 1 h, and pre-weighted PPY (40.0 mg) was dispersed in above suspensions with ultra-sonication for another 4 h followed by vigorously stirring overnight. Then, 100.0 mg of DL-aspartic acid was dissolved in the as formed solution. The mixture was stirred for 10 min, and then was transferred to a Teflon-lined autoclave for hydrothermal treatment at 160°C for 3 h [42]. After that, the autoclave was naturally cooled to room temperature and the received black precipitate (rGCP) was washed with deionized water to neutral. The preparation of rGP was similar to the rGCP composite, only without the addition of CTAB.

2.4. Characterization and Tests

Typical X-ray diffraction (XRD, Rigaku P/max 2200VPC) patterns were recorded with $\text{Cu K}\alpha$ radiation. Fourier transform infrared spectroscopy (FT-IR) was recorded from a KBr window on a Nicolet AVATAR 360 FT-IR spectrophotometer. Resonant Raman scattering spectra were recorded at room temperature with a JY HR-800 Lab Ram confocal Raman microscope in a backscattering configuration with an excitation wavelength of 633 nm. X-ray photoelectron spectroscopy (XPS, ThermalFisher ESCALab 250 X-ray photoelectron spectrometer with Al $\text{K}\alpha$ radiation). The morphologies were characterized by field-emission scanning electron microscopy (FESEM, XL 30 ESEM-FEG, FEI Company) and transmission electron microscope (TEM, JEM-2010F). To confirm the existence of hierarchical pores in the hybrid composites, nitrogen adsorption isotherms were carried out at -196°C using a micromeritics ASAP 2020 analyzer. Prior to adsorption, the samples were degassed at 150°C for 10 h.

2.5. Electrochemical measurements

Electrochemical analyses were performed using a conventional three-electrode system equipped with a saturated calomel

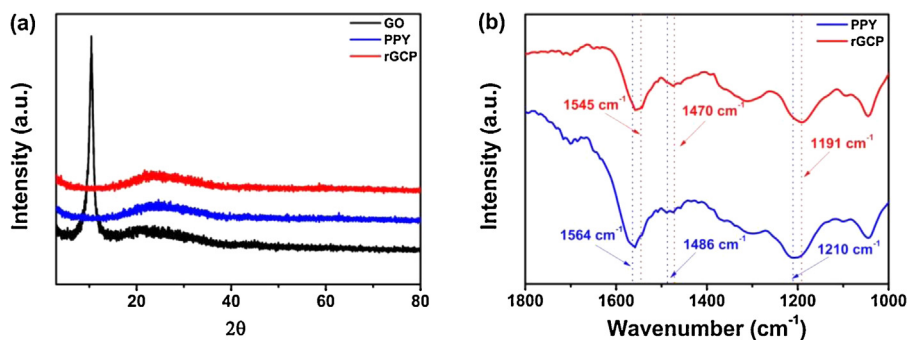


Fig. 1. (a) XRD spectra of the as-synthesized GO, pure PPY, and rGCP; (b) The enlarged FT-IR spectra of pure PPY and rGCP.

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