



Prussian blue-nitrogen-doped graphene nanocomposite as hybrid electrode for energy storage applications



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ABSTRACT

Water-soluble Prussian blue nanoparticles (PB NPs) supported on nitrogen-doped graphene (N-graphene) with high dispersion was fabricated for high performance energy storage hybrid electrodes. An efficient loading of the PB NPs and nitrogen doping of graphene were achieved. The structure and morphology of the composite was determined by X-ray diffraction, transmission electron microscopy, Raman spectrometry and X-ray photoelectron spectrometry. The energy storage performance was assessed by cyclic voltammetry and galvanostatic charge/discharge techniques. The nanocomposite was fabricated as a hybrid battery-supercapacitor electrode and exhibited excellent performance with the highest capacity of 660 C g^{-1} at 1 A g^{-1} , which was higher than pure PB NPs and N-graphene electrodes. Moreover, the synergistic effect of N-graphene and the PB NPs prevented the N-graphene from shrinking and swelling and increased the cycle stability to 84.7% retention after 1500 cycles at 6 A g^{-1} , compared to the pure N-graphene.

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1. Introduction

In recent years, supercapacitors are excellent energy storage devices due to their long-term cycling stability, high power densities and high charge/discharge rates. Supercapacitors are promising storage devices for a wide range of applications, such as hybrid electric vehicles, cordless electric tools, portable electronic equipment and backup power sources [1]. The energy stored in supercapacitors arises from individual electrostatic interactions [electrical double layer capacitor (EDLC)] and charge transfer process across the electrode–electrolyte interface (pseudocapacitance) [2], or a combination of both EDLC and pseudocapacitance in hybrid supercapacitors. The energy stored in EDLC devices is significantly lower than in pseudocapacitors due to the shrinking and swelling of the electroactive materials, which leads to a significant decrease in the cycle life during the charge/discharge

process. Therefore, to overcome this problem, it is extremely necessary to combine both types of capacitive materials with high capacitance and long cycle life to develop a new generation of hybrid supercapacitors.

To date, various carbon polymorphs, such as carbon nanotubes, activated carbon, carbon onions, carbon fibers and graphene [2,3] have been widely utilized as EDLC electrodes to enhance supercapacitor performance further. Notably, graphene, a new member of the carbon family with a high surface area, rapid charge carrier mobility and excellent thermal conductivity [2], is suitable as EDLC or as the support material in pseudocapacitor electrodes. However, the aggregation of graphene during the fabrication of the supercapacitor nanostructures, could dramatically decrease the surface area [4–7], and thereby lead to a significant decrease in capacitance. Therefore, the functionalization or doping of the graphene lattice with elements such as sulfur, phosphorous boron and nitrogen is an effective step to modulate the surface chemistry and the electronic properties of graphene [8,9]. Among these heteroatoms, nitrogen is best dopant in the graphene lattice due to its similar atomic radius and valence electrons [8]. Furthermore, the graphene π -electronic system and the lone pair of the nitrogen atoms can form strong valence bonds. This will lead to a significant

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improvement in the electronic conductivity, charge distribution and spin density of the doped graphene, which promotes a uniform dispersion and fast nucleation growth kinetics of the nanostructures [8]. Therefore, nitrogen doping not only increases the pseudocapacitance and double-layer capacitance of graphene [10], but also enhances its ability to bind with guest molecules to improve the electrochemical performance of the nanocomposites. However, nitrogen-doped graphene (N-graphene) still shows unsatisfactory performance due to its insufficient charge capability; in addition, the shrinking and swelling of an N-graphene electrode leads to a significant reduction in the capacitance and cycle life of the supercapacitor electrode. Therefore, it has been suggested that inorganic materials such as metal oxides [10], or organic compounds such as conductive polymers [11] with fast Faradaic reaction rate, should be incorporated into the N-graphene system to improve the capacitance and cycle life of the hybrid supercapacitor electrode.

Prussian blue (PB) is an inorganic compound with a cubic framework, where the Fe(III) and Fe(II) are located on the alternating corners of a cube. The corner-shared octahedral in the Prussian blue framework is bridged by the linear $(\text{CN})^-$ anions; the high-spin Fe(II) ($S=5/2$) bonds with the N atoms, while the low-spin Fe(III) ($S=0$) bonds with the C atoms [12]. Due to its high specific surface area, controllable structure, adjustable pore size and high thermal stability, PB has been widely used as an outstanding candidate in clean energy applications such as electrocatalysts, sensors and batteries, as well as electrochromic, spintronic and hydrogen storage devices [13–17]. The redox process of the Fe ions in PB could provide an electron transfer pathway. Alternatively, the crystal structure of PB promotes the reversible intercalation and extraction of ions, in organic and aqueous electrolytes [13], which is largely suitable for electrocatalytic and energy storage applications of the hybrid composite. In addition, the presence of N-graphene in the Prussian blue-N-graphene composites (PB-NGs) not only provides a platform for the formation of PB nanoparticles (NPs) to decrease the agglomeration of graphene layers, but it also promotes rapid electron transfer, which enhances the energy storage of the hybrid battery-supercapacitor electrode.

In this work, we have developed a simple process for the synthesis of a highly water-soluble PB-NG nanocomposite with excellent energy storage performance. There are no previous reports on the synthesis and energy storage performance of N-graphene in the presence of PB NPs. Although both materials are energy storage electrodes, there is a fundamental difference between a supercapacitor material such as N-graphene and PB which is a battery material, in the charge storage/release mechanism. Thus the combination of these two materials can be referred as a hybrid battery-supercapacitor electrode. The loading of PB NPs in the nanocomposites leads to the enhancement of the energy storage and cycling stability of the hybrid battery-supercapacitor electrode, compared to the pure N-graphene and pure PB NPs.

2. Experimental methods

2.1. Chemical reagents

Analytical grade chemicals were procured from Sigma Aldrich and dissolved in double-distilled water (resistance = 18.3 M Ω).

2.2. Synthesis of Prussian blue nanoparticles

In a typical procedure, 20 ml of 1.5 M $\text{Fe}(\text{NO}_3)_3$ solution were added into 40 ml of 0.5 M $\text{K}_4\text{Fe}(\text{CN})_6$ with continuous stirring for 30 min at 70 °C to produce a dark blue PB pigment suspension. The

mixture was centrifuged three times with doubly distilled water and the PB precipitate was collected and dried in air overnight. Next, 600 mg of PB pigment were dispersed in 40 ml doubly distilled water, and followed by the addition of 10 ml of a fresh solution of 50 mM $\text{K}_4\text{Fe}(\text{CN})_6$. With vigorous stirring for 6 h, the pigment was completely dissolved, and the suspension turned a transparent blue. The purification of the PB NPs was achieved by a stirred ultrafiltration cell and membrane with a cut-off of molecular weight 3000 to remove the residual salts. This process was repeated at least five times by adding fresh doubly distilled water until the filtrate became colorless.

2.3. Synthesis of nitrogen-doped graphene

Graphite powder (1–2 μm , Aldrich) was the precursor for the graphene oxide (GO) synthesis according to the modified Hummers method [18]. The synthesis of N-graphene is described according to our previous work [19]. Briefly, 50 mL of a GO suspension in ethanol (1 mg/mL) was added with 100 mg of urea. The dispersion was heated to 80 °C with stirring until it dried. The powders were then placed in an Al_2O_3 crucible in a tube furnace and flushed with Ar gas to remove the oxygen. After the flow of Ar gas (100 sccm), the temperature was increased to 600 °C at 3 °C min^{-1} for an hour. Then, the temperature was increased to 900 °C at 5 °C min^{-1} . The temperature was held at 900 °C for 4 hours. Finally it was cooled to room temperature, to collect the as-synthesized N-graphene.

2.4. Synthesis of Prussian blue-nitrogen-doped graphene hybrids

To prepare the PB-NG hybrids, PB NPs and an N-graphene solution were mixed with a mass ratio of 2:1 with continuous stirring for 10 h to produce a dark green dispersion. The PB-NG dispersion was centrifuged three times with doubly distilled water to remove the supernatant and collect the PB-NG sediment.

2.5. Instrument characterizations

A X-ray powder diffractometer (XRD, PANalytical's Empyrean) with CuK α radiation ($\lambda = 1.54056 \text{ \AA}$) was used to characterize the powders. A transmission electron microscope (500 kV, TEM-FEIG-4020) was utilized to examine the particle sizes and the morphology of the electrodes. The electrodes were ultrasonicated in distilled water prior to the characterization. The spectroscopic measurements were performed with an ESCALAB MK II X-ray photoelectron spectrometer (Mg excitation source) for the X-ray photoelectron spectroscopy (XPS) analysis, while a Renishaw Invia Raman Microscope instrument (laser excitation, $\lambda = 514 \text{ nm}$) was utilized for the Raman spectroscopy analysis. The electrochemical experiments were performed with a potentiostat/galvanostat (Autolab PGSTAT30, Ecochemie Netherlands).

2.6. Electrochemical measurements

All electrochemical measurements such as galvanostatic charge/discharge (GCD), electrochemical impedance spectroscopy (EIS), and cyclic voltammetry (CV) were conducted in a three-electrode cell system with 1 M H_2SO_4 aqueous solution as the electrolyte. A platinum wire and $\text{Hg}/\text{Hg}_2\text{SO}_4/\text{K}_2\text{SO}_4$ electrode were the counter and reference electrode, respectively. The working electrode was a glassy carbon disc with a diameter of 3 mm. The electrodes of pure PB NPs, pure N-graphene and PB-NG hybrids, were prepared by casting onto the glassy carbon surface. Typically, 5 mg of the electroactive material was dispersed in 5 ml doubly distilled water for 1 h by ultrasonication. Then, 10 μl of the suspension and 5 μl of Nafion solution (0.05% Nafion in ethyl

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