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RESEARCH PAPER

Hydrothermal synthesis of porous phosphorus-doped carbon nanotubes and their use in the oxygen reduction reaction and lithium-sulfur batteries

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Abstract: The many uses of carbon nanotubes (CNTs) depend not only on their intrinsic physical properties, but also on their tunable chemical components. Exploring a low-temperature method for the incorporation of phosphorus atoms in the carbon framework is expected to change the chemical properties of CNTs. Here, phosphorus-functionalized CNTs (PCNTs) were prepared by the direct hydrothermal treatment of a CNT-H_3PO_4 mixture at 170 °C. The PCNTs had a high phosphorus content of 1.66 at %, a specific surface area of 132 m^2•g^{-1}, and an improved thermal stability with a weight loss peak at 694 °C during oxidation in pure oxygen. They showed good electrocatalytic activity for the oxygen reduction reaction with an onset potential of -0.20 V *vs* Hg/Hg_2Cl_2, an electron transfer number of 2.60, and a larger current density as well as improved cyclic stability compared with pristine CNTs. PCNTs were also used as conductive scaffolds for the cathode in lithium-sulfur batteries. The cathode delivered an initial discharge capacity of 1106 mAh•g^{-1}, a capacity retention of 80 % from 0.1 to 1.0 C, and a low decay rate of 0.25 % per cycle during 100 cycles..

Key Words: Carbon nanotube; Oxygen reduction reaction; Lithium sulfur batteries; Phosphorous-doped carbon

1 Introduction

The broad applications of sp^2 carbon (such as carbon nanotubes (CNTs) and graphene) in the area of supercapacitors, batteries, fuel cells, heterogeneous catalysis, drug delivery, sensors, water treatment, as well as composites strongly depend not only on their intrinsic physical properties derived from sp^2 bonding structure, but also on their tunable chemical components through heteroatom doping and surface modification. The incorporation of heteroatoms brings tunable electronic properties and therefore offers tunable chemical reactivities. Recently, the heteroatom-incorporated nanocarbon is widely considered as a potential platform for diverse applications in heterogeneous catalysis (e.g. selective oxidation of cyclohexane and H_2S, oxidative dehydrogenation, and hydrohalogenation) [1], electrocatalysis (e.g. oxygen reduction reaction (ORR) [2-4] and oxygen evolution reaction [5]), energy storage (e.g. supercapacitors [6], lithium ion batteries [7], and lithium-sulfur batteries [8]), as well as gas adsorption (e.g. CO_2 capture [9]).

Phosphorus is a nonmetallic chemical element that is essential for life. Vast majority of P-containing compounds are employed as fertilizers. Similar to N atoms, P atoms can serve as electron donors for carbon to induce a shift in the Fermi level to the conducting band. However, the size of P atom is much larger than that of N atom and thus it is difficult to substitute into graphitic honeycomb lattice. Therefore, P atoms are always bonding with O and/or C in the heteroatom incorporated frameworks. The introduction of P-containing functional groups into carbon matrix significantly improves the thermal stability of the carbon matrix [10-12]. Therefore, P doped graphene are employed as n-type semiconductor in an air-stable field effect transistors [13]. The electrical conductivity of the carbon based material are enhanced by several orders of magnitude with the P-doping. Furthermore, P-containing functional groups in carbon frameworks also bring pseudo-capacitance when it served as the electrodes for supercapacitors. With the content of pyrophosphates decreasing and the heterogeneity of phosphorus containing species increasing, the capacitance increases and the retention ratio of the capacitor is increased. Recently, it was also reported that a small amount of P doping may greatly improve

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the selectivity by suppressing the combustion of hydrocarbons in oxidative dehydrogenation with P-functionalized CNTs as catalyst. The P-doped carbon catalyst also afford excellent reactivity in the electrochemical reduction of oxygen in an alkaline medium [2-4, 7, 14, 15]. The well combination of P with N atoms in the nanocarbon framework also rendered the synergy effect, which further promoted the catalytic activity for ORR [16, 17]. Therefore, exploring the material chemistry and their potential applications of P incorporated carbon nanomaterials with controllable doping manner is highly required.

In most cases, the P-incorporated carbon was synthesized by the decomposition of triphenylphosphine [2-4, 7, 17], phosphorus oxychloride [11], and 1-butyl-3-methylimidazolium hexafluorophosphate [14]. In addition, the chemical activation of carbon precursors with H_3PO_4 at a high temperature of 500 to 1000 °C is also an efficient route to incorporate P into the framework of nanocarbon materials [6, 15, 16, 18-25]. However, the reduced P was exhausted as by products or wastes. A low temperature route for direct P-doping in carbon matrix is more favorable and environmental friendly to tune the surface chemistry of carbon materials towards unique properties and diverse applications.

In this contribution, a moderate hydrothermal modification strategy was proposed to synthesize phosphorous-functionalized carbon nanotubes (PCNTs). CNTs were selected as nanocarbon platform in this work because of their extraordinary intrinsic properties, easiness for structural characterization, as well as their broad applications. The CNTs have been mass produced through fluidized bed chemical vapor deposition at a low cost and have been commercialized as conductive agents for lithium-ion batteries and additives for tires or plastics. We employed the idea of hydrothermal modification of CNTs at a low temperature of 170 °C. The as-obtained PCNTs were with a P content of 1.66 at%. The electrochemical performance was evaluated as the electrocatalyst for ORR and conductive scaffolds for lithium-sulfur batteries.

2 Experimental

2.1 Synthesis of CNTs and PCNTs

The CNTs were synthesized in a 50 mm fluidized bed reactor on layered double hydroxide derived catalysts. The raw CNTs were routinely purified by HCl (3.0 $mol\cdot L^{-1}$) and subsequent NaOH (15.0 $mol\cdot L^{-1}$) aqueous solution to remove the catalyst residual. The PCNTs were fabricated by hydrothermal functionalization with H_3PO_4 as the phosphorus source. H_3PO_4 (85%) and CNTs were well mixed in a Teflon-lined stainless steel autoclave with a mass ratio of 6.78, corresponding to the mass ratio of the P element to CNTs of 2.0:1.0. The H_3PO_4/CNT mixture was sealed and heated to 170 °C at a ramp rate of 0.5 $^{\circ}C\cdot min^{-1}$. The hydrothermal treatment was kept at 170 °C for 12.0 h and then the autoclave was cooled down to room temperature naturally. The solid products were further rinsed by deionized water to pH = 7.0 and then dried at 110 °C for 6.0 h. Finally, the PCNTs were collected for further structure characterization and performance evaluation.

2.2 Structure characterization

The nanostructures of CNTs and PCNTs were characterized by a JSM 7401F scanning electron microscope (SEM) and a JEM 2010 transmission electron microscope (TEM). The Raman spectra were collected with a Horiba Jobin Yvon LabRAM HR800 Raman spectrometer with a He-Ne laser excited at 633 nm. The N_2 sorption isotherms of CNTs and PCNTs were collected by the Autosorb-IQ2-MP-C system. Before measurements the sample was degassed at 200 °C until a manifold pressure of 2 mmHg was reached. The specific surface areas (SSAs) of the CNT samples were calculated from the isotherm by the Brunauer-Emmett-Teller (BET) equation. The pore size distribution was determined by the non-linear density functional theory model. The thermogravimetric (TG) analysis of the CNT samples was performed by the Mettler Toledo TGA/DSC-1 under O_2 atmosphere at a ramping rate of 20 $^{\circ}C\cdot min^{-1}$. The P and O-containing functional groups were characterized by X-ray photoelectron spectroscopy (XPS) on an Escalab 250xi system. The XPS spectra were calibrated with a reference binding energy at 284.4 eV of C1s peak. A Shirley background was subtracted prior to fitting. The peak areas were normalized with theoretical cross-sections to obtain the relative surface elemental compositions.

2.3 ORR performance of the CNTs and PCNTs

To evaluate the ORR performance, the CNTs and PCNTs were dispersed in ethanol (5.0 $mg\cdot mL^{-1}$) as catalyst ink. The CNT sample was then transferred onto the glass carbon electrode via a routine drop casting with an areal loading amount of 0.25 $mg\cdot cm^{-2}$. After the evaporation of ethanol at room temperature, a drop of Nafion solution (1.0 wt%) was cast onto the surface of the electrode to form a thin layer and then dried in an oven at 60 °C for 30 min to serve as the working electrode. The ORR measurements were performed in a three-electrode setup in a 0.10 $mol\cdot L^{-1}$ KOH aqueous electrolyte. The saturated calomel electrode was used as the reference electrode, and Pt foil was employed as the counter electrode. The cyclic voltammogram (CV) profiles were collected at a scan rate of 100.0 $mV\cdot s^{-1}$ on the CHI 760D electrochemical workstation.

The electron transfer number (n) of ORR per oxygen molecule is calculated from the Koutechy-Levich equation described as below [3, 5].

$$\frac{1}{J} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_K} \qquad (1)$$