RAPID COMMUNICATION

Elucidating surface redox charge storage of phosphorus-incorporated graphenes with hierarchical architectures

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Abstract
The incorporation of heteroatoms into carbon nanomaterials is extremely crucial for tuning their electronic and surface properties, but phosphorus (P) incorporation into hierarchical structure remains challenging and its charge storage mechanism is obscure. Herein, we investigate surface redox charge storage of hierarchically structured, P-incorporated graphene architectures (hpGAs). As probed by *in-situ* and *ex-situ* spectroscopic techniques and density functional theory, the P=O site of C–P=O bonding with the most favorable proton binding energy is identified and associated with highly reversible and fast pseudocapacitive behavior. As a consequence of synergistic effects arising from compositional and structural features, the hpGAs show dramatic improvements in capacitance, rate capability, and cyclic stability. This work broadens our knowledge about the unique surface charge storage phenomenon originating from the controlled heteroatom chemistry using combined spectroscopic and computational methods.
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Introduction

The incorporation of heteroatoms into carbon nanomaterials is a fundamental chemical process that can tailor the electronic structures and improve the surface properties [1,2]. Boron-, oxygen-, sulfur-, and nitrogen-containing functional groups have been incorporated into the surface and lattice of carbon nanomaterials [3-7] for a wide range of electrochemical applications [2-8]. Motivated by the additional capacitance (i.e. pseudocapacitance) that is generated by fast surface or near-surface redox reactions through faradaic means [9], carbon nanomaterials have been chemically modified by various heteroatoms to improve electrochemical capacitive behaviors [10-12]. Moreover, the ionic resistance at the electrode/electrolyte interface can be reduced by means of the favorable interactions of heteroatoms with ions [12], and the wettability can increase for maximum utilization of the accessible area [13]. Compared to other heteroatoms, the synthesis and application of phosphorus (P)-incorporated carbon nanomaterials is in a more primitive stage of investigation [2], but their potential has already been demonstrated for (electro) catalysis [14,15]. The chemical modification of conjugated structure by the P incorporation is expected to enhance the capacitive performances; the charge and spin densities can be changed due to lower electronegativity of P than that of carbon and the structural defects can be generated because of bigger size of P atoms than that of carbon [2,14,16]. For instance, Hulicova-Jurcakova and Lu et al. first presented the highly stable capacitive performance of P-enriched carbons [17].

Recently, in- and ex-situ spectroscopic and computational analyses of electrochemical energy storage systems have been extensively demonstrated [18-22]. Despite these important works about the redox charge storage of inorganic oxides and double layer capacitance of carbon nanomaterials [23-25], the surface redox charge storage mechanism of P-containing groups occurring in graphenes and other carbon nanomaterials has yet to be explored. The surface dominating electrochemistry relative to the bulk becomes more influential on the overall electrochemical property, when materials are scaled to a nanometer. Accordingly, a deep understanding of the surface redox charge storage behavior and the interplay of charge carriers with redox-active sites of heteroatom-incorporated graphene surfaces may offer significant insights into energy storage mechanism. In particular, chemical approach to control the chemical identity, bonding configuration and composition of P-containing group should be elaborated in order to elucidate the surface redox chemistry coupled with the structural change.

>Herein, we report a highly reversible and fast pseudocapacitive mechanism of hierarchically structured, P-incorporated graphene architectures (hpGAs). Our synthetic approach is (1) to incorporate P-containing moieties into the three-dimensional (3D) graphene frameworks for a controlled chemical composition and bonding configuration and (2) to construct hierarchical structures (combining structures at different scales) for enhanced capacitive performances. The in-situ and ex-situ spectroelectrochemical and theoretical interpretations are first highlighted to understand the charge storage mechanism of P-incorporated grapheme.

Material and methods

Synthesis of GAs electrodes

16 mL of homogeneous graphene oxide (GO) aqueous solution (Supporting information S1) with GO concentration of 1, 1.5, 2, 2.5, 3 mg mL^{-1} was ultrasonicated at room temperature for 1 h. And then the GO solution was sealed in a 20 mL Teflon-lined autoclave at 180 °C for 10 h. The GO was converted to the reduced graphene oxide (RGO) by reduction during the hydrothermal process as previously reported [26]. After the autoclave was cooled down to room temperature, the black cylinder gel product was formed and it was washed by ethanol/water (1:1) solution until the solvent was neutral to get the graphene hydrogel. The wet gel was freeze-dried in three days by liquid nitrogen to get the areogel GAs.

Synthesis of hierarchical structure hpGAs electrodes

A 16 mL homogeneous mixture solution with 48 mg GO and 0.96 mg phytic acid was ultrasonicated at room temperature for 1 h. And then the mixture was sealed in a 20-mL Teflon-lined autoclave at 180 °C for 10 h. After the autoclave was cooled down to room temperature, the black cylinder gel product was formed and it was washed by ethanol/water (1:1) solution until the solvent was neutral to get the phytic acid functionlized RGO hydrogel. The wet gel was freeze-dried in three days by liquid nitrogen to get the un-hpGAs. In order to incorporate P into the un-hpGAs, they are thermally activated. The un-hpGAs were placed in the center of the furnace tube and then, heated from room temperature to 900 °C in inert nitrogen atmosphere (the flow rate of 200 cm^3 min^{-1}, the heating rate of 10 °C min^{-1}, and holding time of 1 h). After heating, the system was cooled down to room temperature under the same flow rate of nitrogen to get the hpGAs.

In-situ and ex-situ spectroelectrochemical methods

In-situ Raman spectra were measured in the charge/discharge process using two-electrode system. The as-prepared hpGAs was cut into small slices with a thickness of about 2 mm and diameter of about 8–10 mm. The 3D monolithic material was glued with Pt wire by silver paste, and then inmmersed in the hot solution of PVA/H$_2$SO$_4$ electrolyte solution for 5 min. The solid-state PVA/H$_2$SO$_4$ was used as separator and electrolyte. Finally, the electrodes were solidified for 12 h at room temperature. The two electrodes were intergrated symmetrically into a solid-state supercapacitor. Ex-situ XPS spectra were measured after the electrode was charged in 1 M H$_2$SO$_4$ electrolyte at potential from −0.3 to +0.3 V for 30 min using the three-electrode system. The sample was fully discharged for 40 min and then, directly used to check the XPS