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Understanding the impact of nitrogen doping and/or amine functionalization of reduced graphene oxide via hydrothermal routes for supercapacitor applications

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ABSTRACT

Nitrogen doping and amine-functionalization have previously been used to improve the capacitance of graphene-based materials, however there is a lack of understanding on the mechanisms by which these modifications impact the electrochemical behavior and electrochemical supercapacitor performance, or if these approaches can be combined to achieve synergistic benefits. Herein, we investigate this by synthesizing reduced graphene oxide (HtrGO) with varying degrees of nitrogen-doping (N-HtrGO), amine-functionalization (NH_3^+-HtrGO), and a hybrid amine-functionalization and nitrogen-doping (N-NH_3^+-HtrGO). Synthesized materials were systemically investigated to show the effect of nitrogen-doping and amine-functionalization using electrochemical characterization and rigorous physico-chemical analysis. The capacitance performance was increased in the order of NH_3^+-HtrGO < HtrGO < N-NH_3^+-HtrGO < N-HtrGO. The highest capacitance of 244 F/g was observed at 50 mV/s for N-HtrGO. The specific capacitances of NH_3^+-HtrGO was limited to 179 F/g at 50 mV/s, indicating graphene sheet restacking likely due to interactions between positively charged amine species and oxygen functional groups. Interestingly, the capacitance of N-NH_3^+-HtrGO was significantly higher as compared to that of NH_3^+-HtrGO, which was attributed to less agglomeration of GO due to deoxygenation through nitrogen-doping. This work provides fundamental understanding towards nitrogen-based modification of graphene materials and the impact on electrochemical properties that will guide the design of new materials for supercapacitor applications.
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1. Introduction

Supercapacitors store energy through either electrical double layer capacitance (rapid ion adsorption/desorption) or by reversible Faradaic charge transfer mechanisms (pseudocapacitance). Graphene is one of the most promising carbon-based materials for supercapacitor applications due to the high surface area (theoretical surface area of 2630 m^2g^{-1}), excellent electrical conductivity, and good mechanical properties [1–4]. Although the theoretical capacitance of graphene is as high as 550 F/g, experimentally measured capacitance values for graphene in aqueous electrolytes are generally limited in the range of 100–200 F/g [4]. This is mainly due to the π-π interaction that causes restacking and agglomeration of graphene sheets, thereby decreasing the electrochemically accessible surface area as well as the hydrophobicity of graphene in the absence of functional groups that hinders electrolyte wettability.

Over the past decade, the introduction of heteroatom (e.g., boron, nitrogen, oxygen, phosphorous, and sulfur) dopants into the carbon lattice of graphene has been extensively studied to tailor the properties of graphene materials, including sheet-to-sheet separation, conductivity, wettability, and pseudocapacitance that is derived from Faradaic charge transfer reactions between the heteroatoms and the electrolyte [5–13]. Particularly, nitrogen is considered a compatible dopant for graphene materials due to its comparable atomic radius with carbon and high electronegativity, and has been investigated for numerous applications including supercapacitors, electrocatalysis, energy conversion and sensors. Many research efforts have explored the effect of nitrogen doping levels and nitrogen bonding configurations using various synthesis methods that are generally classified into either bottom-up or post-treatment approaches. For bottom-up methods, nitrogen doped graphene materials are fabricated from nitrogen and carbon containing materials using chemical vapor deposition (CVD)

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