Doctoral Thesis

Multifunctional Carbon-Based Composites for Different Applications

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Abstract

Carbon materials such as hollow carbon spheres (HCSs) and nanoporous carbon (NPC) have excellent mechanical and electrical properties and show great application prospects in energy storage, catalysis, adsorption, gas storage, and other fields.

In this thesis, we firstly introduced HCSs prepared from core-shell silica templates. Due to their low density, good surface permeability, large specific surface area (SSA), high porosity, and big inner cavities, HCSs can be used to encapsulate metal oxides like Fe_3O_4 and Mn_3O_4, and the composites (HCS-Fe_3O_4 and HCS-Mn_3O_4) can be used as electrode materials for symmetric supercapacitors. HCS-Fe_3O_4 presents the highest specific capacitance of 193 F g^{-1} at a scan rate of 1 mV s^{-1} and retains 94.75% up to 10000 cycles. The highest specific capacitance of HCS-Mn_3O_4 is 430 F g^{-1} at a scanning rate of 1 mV s^{-1} with 93.15% retention after 10,000 cycles, and the largest energy density is 22.6 Wh kg^{-1}.

Different from the brittle shell of HCS-Fe_3O_4 and HCS-Mn_3O_4, NiO@HCS we prepared has a harder carbon shell, which can limit volume expansion, protect the core from aggregating and allow selectively ion diffusion. Based on these, NiO@HCS possesses the high capacity of 598 mA h g^{-1} at 0.1 A g^{-1} and superior rate capability, as well as good cycle stability at a high current density when investigated as anode materials for a lithium-ion battery.

We also presented interconnected NPC materials synthesized from direct carbonization of Al-based metal-organic frameworks (MOFs). We have investigated NPC in both environmental and energy storage applications. Without chemical activation, the NPC material shows specific capacitances of 298 F g^{-1} at a scanning rate of 1 mV s^{-1} and retention of 97 % after 5,000 cycles in a symmetrical supercapacitor. Besides, NPC presents an excellent adsorption capacity for MB with a maximum adsorption capacity of 415 mg/g. The adsorption process was found to proceed via physical process and presents spontaneous and endothermic properties.

In order to improve the mechanical, hydrophilicity, chemical and electric properties of NPC, N-doped NPC (N-NPC) was fabricated and obtained improved

performance in CO_2 storage and Li-ion battery. N-NPC showed high CO_2 capture of 10 mmol g^{-1} at 45 bar at 40 °C and still maintains the adsorption of 7.2 mmol g^{-1}at 100 °C. Besides, N-NPC exhibited a high initial discharge capacity of 820 mA h g^{-1} and reversible charge capacities of 762 mA h g^{-1}at a rate of 0.1 A g^{-1}. Moreover, N-NPC exhibited a good rate capability and long cycle stability.

Furthermore, since the interconnected NPC has been proved to give a strong contribution to good electron and ion transport, making it a good candidate as an electrode material for supercapacitor. NPC-based composites (NPC-MnOOH) are synthesized and the pseudocapacitive properties with symmetrical configurations are determined. NPC-MnOOH//NPC-MnOOH supercapacitor device with 26.7 wt% of MnOOH has the highest specific capacitance of 410 F g^{-1} at a scanning rate of 1 mV s^{-1}. More interestingly, this symmetrical device can be scanned with a wide voltage window from 0~1.6 V with 1 M Li_2SO_4 achieving a high energy density of 33.5 Wh kg^{-1}.

The carbon materials and carbon-based composites we prepared were found to have great potential in both environmental and energy storage applications. The electrochemical performance of HCS-based composites can be further optimized via tuning shell thickness and core size. Moreover, such structures are also fit for other transition metal oxides, sulfur, or silicon, providing further applications. NPC and NPC-based composites can be further modified with other heteroatoms (B, P, S, etc.) doping and other transition metal oxides for improved performance and further applications.

Keywords: hollow carbon spheres, nanoporous carbon, composites, heteroatoms doping, symmetric supercapacitors, lithium-ion battery, dye adsorption, CO_2 capture

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