

Abstract

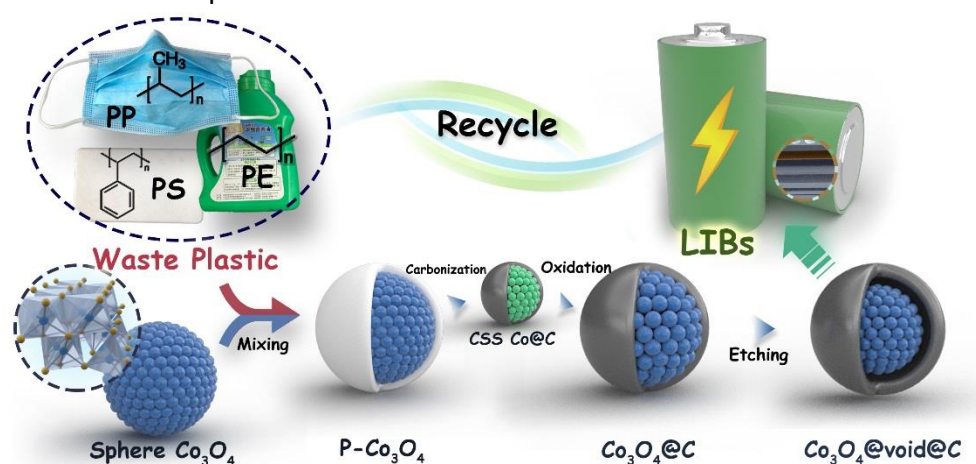
PhD thesis

Carbon-based Materials for High Performance Energy Storage Devices

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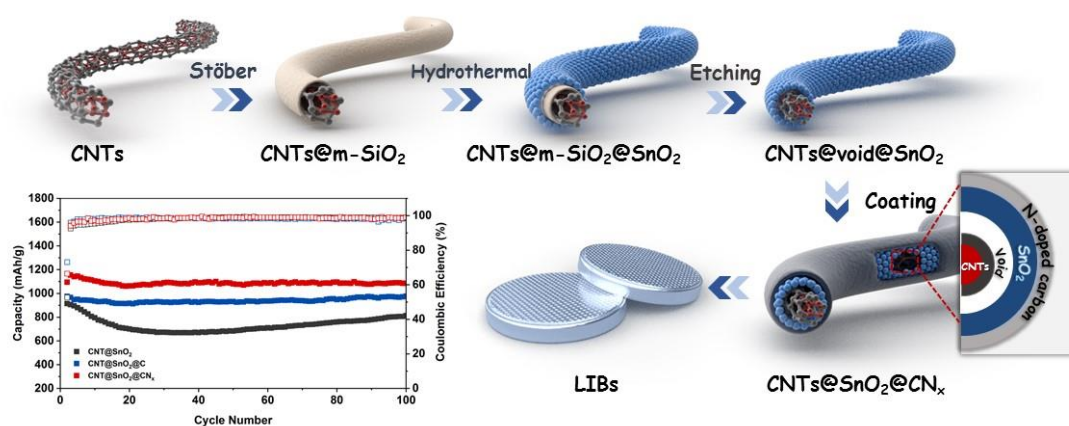
For the past several decades, the fossil fuels have contributed the energy sources for the modern economic society. However, consumption of the fossil fuels leads to the negative environmental impacts. Meanwhile, the development of the renewable energy, such as solar energy and wind electricity is extremely limited by their intermittent production and inefficiency for energy storage. Therefore, it is essential to develop the cost-effective and safe electrochemical energy storage devices (EES) to accumulate the electrical energy boost from renewable resources before applying it into grid-power system. Recently, steady progress has been made by developing new electrode materials to achieve this goal, especially the high-energy lithium-ion batteries (LIBs) and high-power capacitors. Nanoscience has led the significant improvement in the performance of EES via optimal material and structural design of the electrodes. In particular, carbon-based nanomaterials have been considered to be the enabling electrode materials for creating high-performance EES. In this thesis, various carbon-based nanomaterials from different carbonaceous precursors with nanostructures were prepared through rational strategies and applied in electrochemical energy storage devices. The graphical abstract of the fabrication and a conclusive description of each carbon-based nanomaterials were summarized.



Graphical abstract 1). The schematic illustration of the recycle the real-world waste plastics into Co₃O₄@void@C composites for lithium-ion batteries (LIBs).

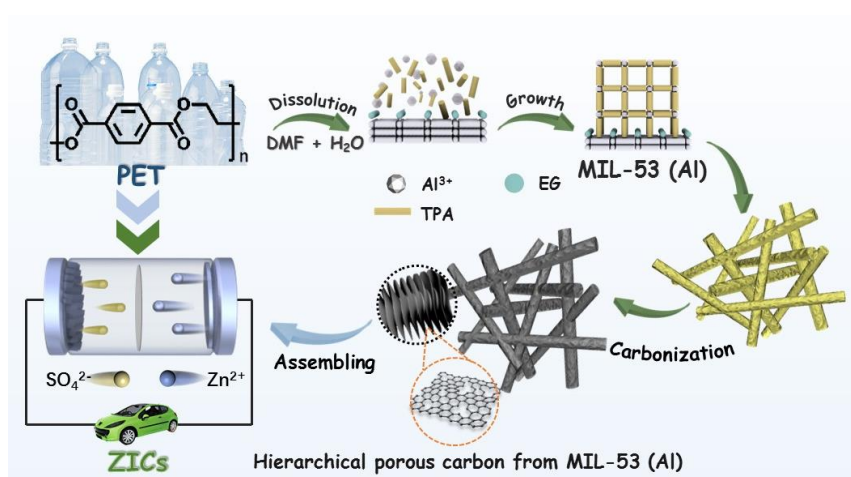
- 1) Recycling real-world waste plastic (waste face mask-PP, plastic jar-PE and foam sheets-PS) into cobalt oxide@void@carbon (Co₃O₄@void@C) nanomaterials by using Co₃O₄

nanoparticles as the catalysis at high-temperature carbonization (800 °C), followed partially etching of the Co_3O_4 . The obtained $\text{Co}_3\text{O}_4@\text{void}@\text{C}$ possessed a void space between inner Co_3O_4 and outer protective carbon layer, which can release the stress from the repeated lithiation/delithiation cycles and improve the electrochemical performance. The $\text{Co}_3\text{O}_4@\text{void}@\text{C}$ showed a high specific capacity of 1190 mAh g^{-1} and still remained a capacitance of 1066 mAh g^{-1} at 0.1 A g^{-1} after 100 cycles. This work not only guides an effective strategy to prepare electrode nanomaterials high performance for LIBs but also proposes a practical way to recycle the waste polymers.



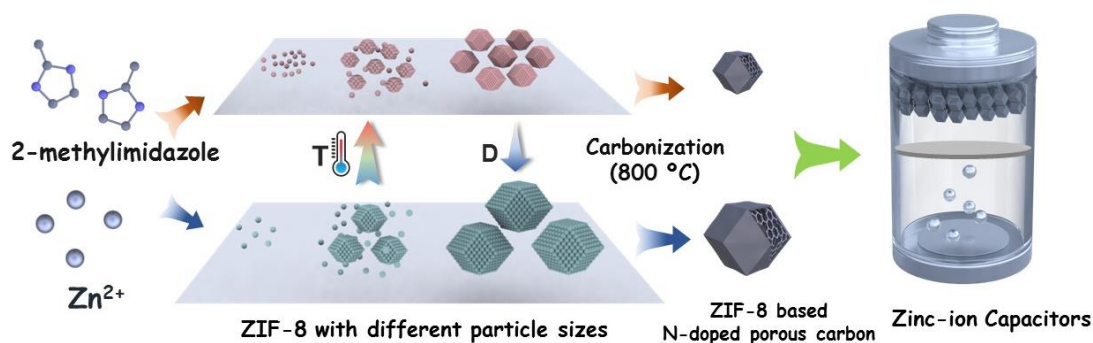
Graphical abstract 2). The fabrication scheme of N-doped carbon coated CNT@SnO₂ sword-sheath structures for lithium-ion batteries (LIBs).

- 2) A unique sword-sheath structures nanostructure composites with a void space between carbon nanotubes (CNTs) and tin oxide (SnO₂) were fabricated via a step-by-step method. The unique nanostructure combined with electrochemical features allow greatly improved lithium battery performance. When assembled as the anode for LIBs, CNT@SnO₂@CN_x showed excellent cycle stability and rate performance, delivering specific capacity of $1087.5 \text{ mAh g}^{-1}$ at a 0.1 A g^{-1} after 100 cycles and 533.6 mAh g^{-1} at 5 A g^{-1} . Note that, it is believed that the smart architectures design for CNT@SnO₂@CN_x nanocomposites can provide a practical guidance for preparing high-performance electrochemical energy storage.



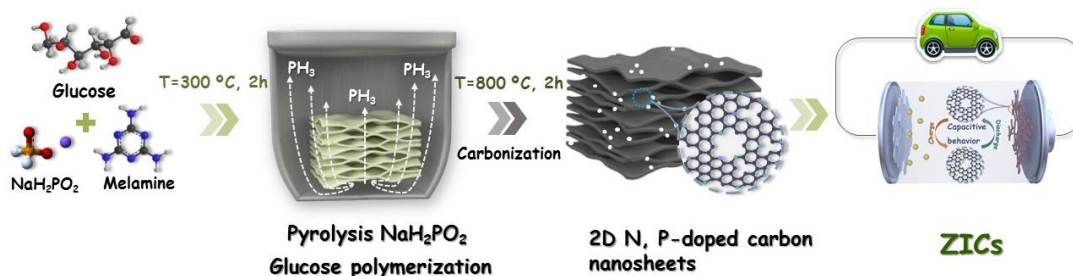
Graphical abstract 3). The schematic illustrating the directly recycling waste Polyethylene terephthalate (PET) bottles into MIL-53(Al) for the synthesis of accordion-like porous carbon and its application as high-performance zinc-ion capacitor (ZICs).

- 3) Accordion-like nanostructure porous carbon was produced by directly carbonized the metal organic framework (MOF), which was derived from the waste PET by a hydrothermal method with 100% conversion. The results indicated that the as-synthesized carbon exhibited a high SSA of $1712 \text{ m}^2 \text{ g}^{-1}$ and a unique accordion-like structure with hierarchical porosity. Benefiting from these advantageous characteristics, the assembled three-electrode supercapacitor and ZICs showed an excellent performance. The assembled three-electrode supercapacitor displayed a specific capacitance of 391 F g^{-1} at the current density of 0.5 A g^{-1} and an improved rate capability of 73.6% retention at 20 A g^{-1} in 6M potassium hydroxide (KOH) electrolyte. A high capacitance of 335 F g^{-1} at 0.1 A g^{-1} , excellent cycling retention of 92.2% after 10 000th cycles and superior energy density of 150.3 Wh kg^{-1} were obtained in ZICs. This work provides a practical method to recycle waste plastic into carbon materials for ZICs.



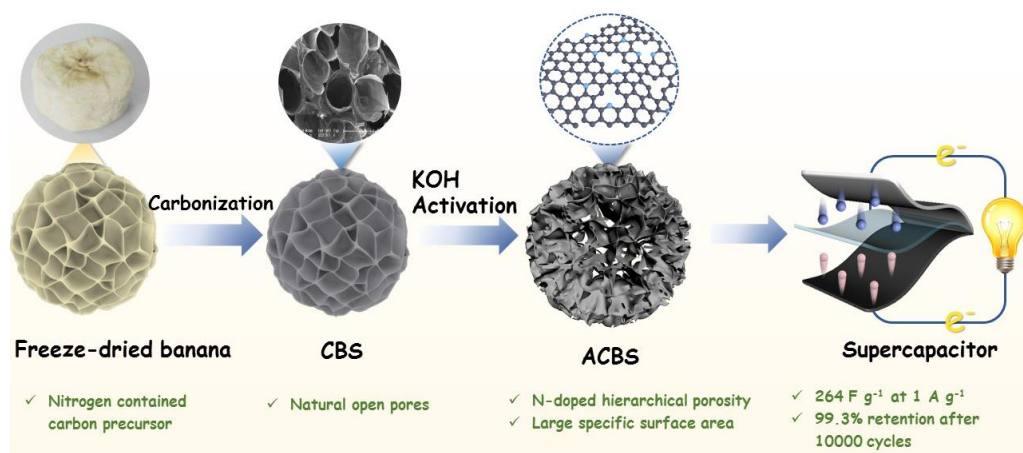
Graphical abstract 4). A schematic illustration of the size dependent effect of ZIF-8 in nanocarbon based zinc-ion capacitor (ZICs).

- 4) A series of monodisperse N-doped hierarchical porous carbon (CZ-Y) was obtained from narrow particle size distribution of zeolitic imidazolate framework-8 (ZIF-8), which was synthesized by a temperature-control process. The porosity characteristic and the contents of N dopants were significantly affected by its particle size. The resulting carbon materials possessed the optimal particle size that can effectively increase the ion diffusion coefficient for fast electrolyte ion transport caused by the short ion transport distance and fast ion diffusion rate. When assembled as the symmetric supercapacitor, the optimal electrodes delivered a capacitance of 137 F g^{-1} and 15.4 Wh kg^{-1} . A gravimetric capacity of 291 F g^{-1} at 0.2 A g^{-1} was obtained, with 100% capacity retention after 10 000 cycles at 5 A g^{-1} in ZICs.



Graphical abstract 5). Schematic diagram for the N, P co-doped 2D carbon nanosheets by a gas-steamed method for high performance zinc-ion capacitor.

- 5) The N, P co-doped 2D nanosheets porous carbon matrix is designed and achieved by a gas-steamed process. The well-designed hierarchical porous showed a large specific surface area and effective channels for fast electrolyte transport, and the introducing N, P dopants favor the chemical adsorption electrolyte ions, leading an improved performance on supercapacitor and ZICs. A specific capacitance of 167 F g^{-1} was achieved in symmetric supercapacitor in 1M lithium sulfate (Li_2SO_4). The assembled ZICs exhibited a specific capacity of 401 F g^{-1} , a high energy density of 180 Wh kg^{-1} under power density of 85 W kg^{-1} at 0.1 A g^{-1} . Furthermore, the capacity retention of 95% over 10 000 cycles at a current density of 5 A g^{-1} . The present work boosts a practical way to synthesize the N, P co-doped 2D porous nanosheets from biomass materials for high energy density supercapacitor and ZICs.



Graphical abstract 6). The preparation process for the synthesis route of 3D N-doped porous carbon materials for supercapacitor.

- 6) The hierarchical N-doped porous carbon derived from freeze-dried banana flesh via the low carbonization temperature and followed by KOH activation. As expected, the N-doped porous carbon materials delivers a high SSA of 2335 m² g⁻¹ and a pore size distribution in the range of 0.9-1.2 nm. The high capacitance of 264 F g⁻¹ was achieved at a current density of 1 A g⁻¹ in a three-electrode supercapacitor system with 3M KOH. More important, a maximum specific capacitance of 155 F g⁻¹ and energy density of 49 Wh kg⁻¹ was obtained in two-electrode system with 1M EMIMBF₄ electrolytes. These results showed an example to prepare the carbon materials from biomass materials for supercapacitors.

Keywords: porous carbons; nanomaterials; MOF; waste polymers; biomass; organic molecule; lithium-ion batteries; supercapacitors; zinc-ion capacitors

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