Abstract of doctoral thesis of mgr Xiaoguang Liu entitled: „Biomass derived porous carbon materials for electrochemical energy storage”

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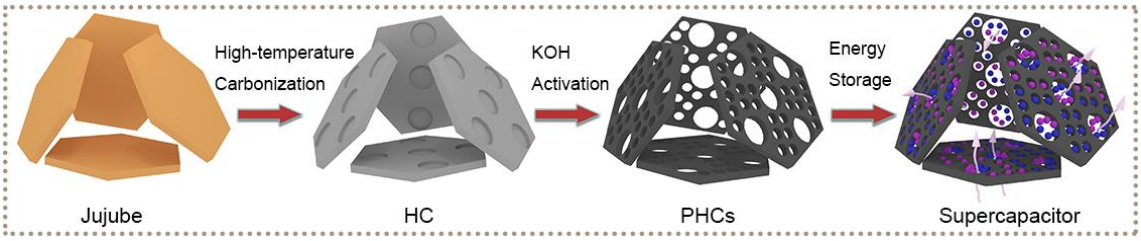
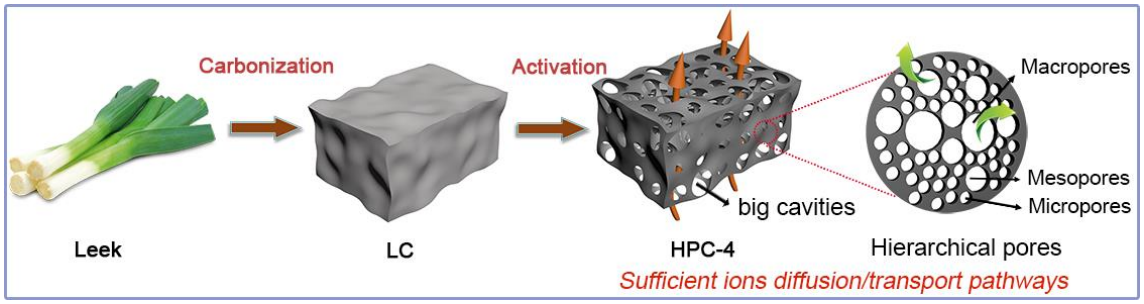
As an important energy storage device, the carbon-based supercapacitor has already been used in various applications, such as uninterruptible power supplies, hybrid vehicles, and energy harvesting because of its superior power density, fast charge-discharge capacity, and ultralong life span. The electrode material used in carbon-based supercapacitors is porous carbons due to their low manufacturing cost, high electric conductivity, and electrochemical stability. However, the commercial porous carbons, typically activated carbons, exhibit inferior electrochemical performance with low charge storage capacity and poor rate capability. Since the electrochemical performance of carbon-based supercapacitor is determined by the physicochemical properties of porous carbons, encompassing morphology, particle density, ion-accessible specific surface area (SSA), pores architecture, and surface functional groups, producing novel porous carbons with optimized physicochemical properties is highly urgent and necessary to meet the requirements of the next-generation supercapacitor. In this thesis, various porous carbons derived from different carbon precursors (biomass, small organic molecule, and polymer) were synthesized via facile methods and their physicochemical properties/electrochemical performance were investigated. The graphical abstract of the synthesis process and a short description of each porous carbon were listed as follows:



Graphical abstract 1). Preparation of robust 3D porous high-temperature carbons (PHCs) from jujube and further supercapacitor applications. The spheres indicate the electrolyte ions and the arrows represent the transport pathways of electrolyte ions.

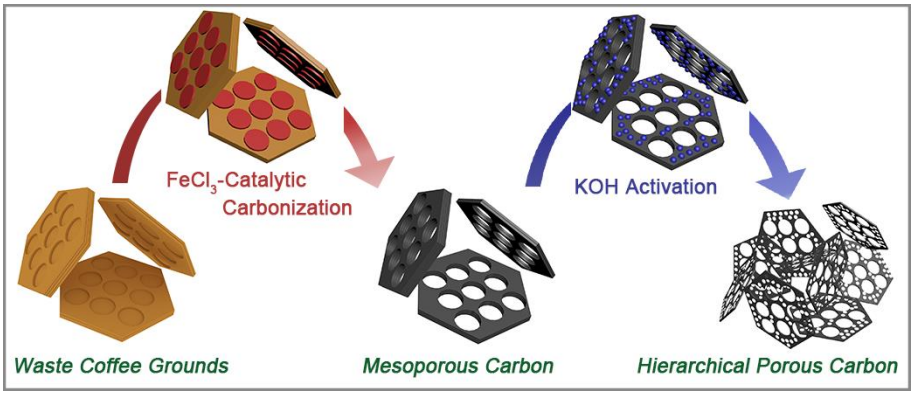
1) Using jujube as the carbon precursor, high-temperature carbonization (800 °C) followed by KOH activation was conducted to synthesize the robust 3D porous high-temperature carbons (PHCs). The obtained PHCs possessed a high particle density (1.06 g cm^{-3}), abundant micropores, and some meso-/macropores. The effect of different carbonization temperatures on particle densities of activated samples was studied in detail. In a two-electrode system, PHCs based electrode showed a remarkable rate capability (75% capacitance retention at 20 A g^{-1}) and good cycling life in aqueous 1M H_2SO_4 electrolyte. The PHCs based symmetric supercapacitor manifested a high volumetric energy density of 13 Wh L^{-1} at a volumetric power density of 477 W L^{-1}

in 1M Li_2SO_4 electrolyte. This work could be used to guide the synthesis of porous carbon with high particle density for high volumetric-performance supercapacitor.



Graphical abstract 2). Preparation of hierarchical porous leek-derived carbons.

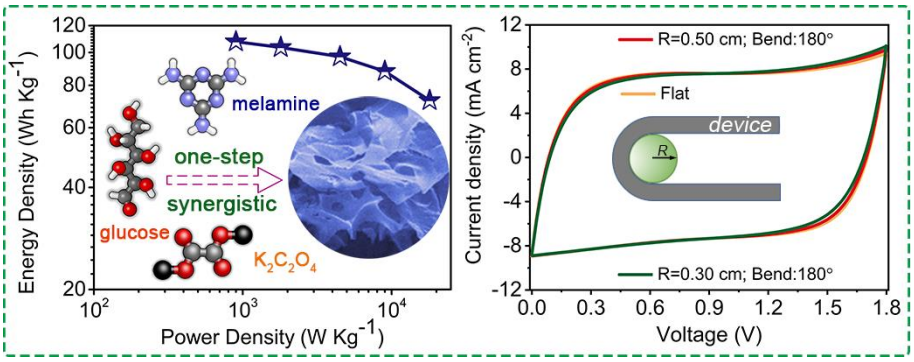
2) Hierarchical porous carbons (HPCs) derived from leek were synthesized via the low-temperature carbonization and KOH activation. The HPCs possessed a three-dimensional (3D) highly porous structure with big cavities, high SSA (2512 m^2 g^{-1}), and well-defined hierarchical pores. In a three-electrode system, HPCs based electrode exhibited a high capacitance of 349 F g^{-1} at 0.5 A g^{-1} in 6M KOH electrolyte. The assembled symmetric supercapacitor revealed a capacitance as high as 191 F g^{-1} at 0.5 A g^{-1} with an excellent rate capability (77% capacitance retention at 10 A g^{-1}) in 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMIMBF_4$) ionic liquid electrolyte, better than those of many biomass-derived carbons. The present work showed a facile method to synthesize porous carbon for high-performance supercapacitors.



Graphical abstract 3). Illustration of the synthesis of hierarchical porous carbon from waste coffee grounds.

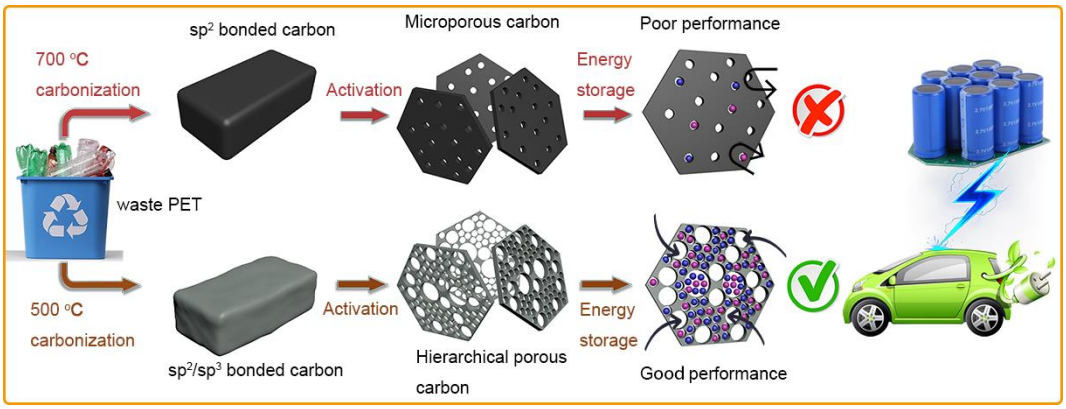
3) The hierarchical porous carbons (HPCs) were fabricated via the catalytic-carbonization combined with alkali activation. The well-defined mesoporous carbon was derived from the catalytic-carbonization of waste coffee grounds (CGs). Subsequently, the alkali activation was applied to produce HPCs with high SSA (3549 m^2 g^{-1}) and large meso-/macropores volume (1.64 cm^3 g^{-1}). The HPCs based electrode exhibited a maximum capacitance of 440 F g^{-1} in a three-electrode system using 6M KOH electrolyte. In a two-electrode system, the HPCs based electrode showed a capacitance as high as 319 F g^{-1}

at 0.5 A g^{-1}. The symmetric supercapacitor delivered an energy density of 101 Wh kg^{-1} at the power density of 900 W kg^{-1} in $EMIMBF_4$ ionic liquid electrolyte. This work revealed a combined strategy for preparing the porous carbon for capacitive energy storage.



Graphical abstract 4). Synthesis of glucose-derived two-dimensional nitrogen-doped hierarchical porous carbon and its electrochemical performance.

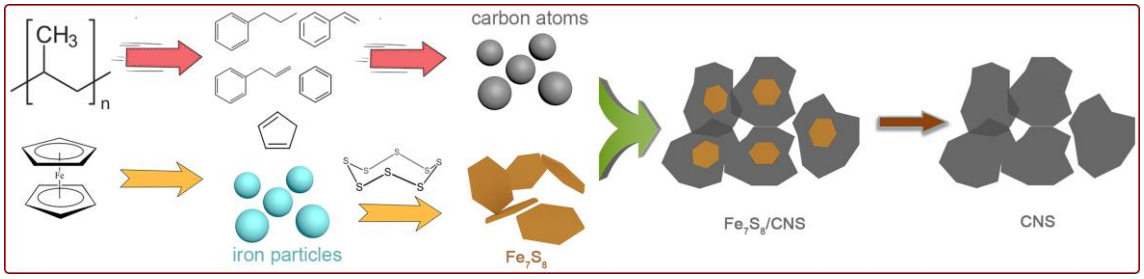
4) The glucose-derived two-dimensional nitrogen-doped hierarchical porous carbon nanosheets (2D-NPC) were synthesized through a one-step pyrolysis-activation process. The melamine/potassium oxalate was used to provide the synergistic blowing/activation effect, endowing the obtained 2D-NPC with two-dimensional (2D) morphology, high SSA, well-defined hierarchical pores, and rich N-content (6.1 %). The 2D-NPC based electrode showed a maximum specific capacitance of 523 F g^{-1} in 6 M KOH electrolyte in a three-electrode system. The symmetric supercapacitor exhibited a high energy density of 108 Wh kg^{-1} at 900 W kg^{-1} in $EMIMBF_4$ ionic liquid electrolyte. The fabricated flexible supercapacitor manifested an areal energy density of 83 μWh cm^{-2} in PVA/LiCl gel electrolyte. These results provided a reference to tailor the physicochemical properties of carbon materials for high-performance supercapacitors.



Graphical abstract 5). Preparation of microporous carbon/hierarchical porous carbon from waste polyethylene terephthalate (PET). The black arrows illustrate the various transfer channels of electrolyte ions (red/blue balls) in carbons.

5) The hierarchical porous carbon (HPC) and microporous carbon were synthesized from waste PET by changing the carbonization temperatures. The HPC exhibited a high SSA

of 2238 $m^2 g^{-1}$ and many meso-/macropores. The microporous carbon possessed mainly micropores. The formation mechanism of HPC was studied, which showed that the co-etching effect of sp^2 hybridized carbon and sp^3 hybridized carbon produced micropores and meso-/macropores, respectively. In a three-electrode system, HPC based electrode exhibited a high capacitance of 413 F g^{-1} at 0.5 A g^{-1}, while the microporous carbon showed a low capacitance (142 F g^{-1}). In a two-electrode system, it manifested a maximum capacitance of 301 F g^{-1}. The symmetric supercapacitor delivered an energy density as high as 25 Wh kg^{-1} at a power density of 450 W kg^{-1} in 1M Li_2SO_4 electrolyte. This work gave an example of the production of hierarchical porous carbon from waste plastics.



Graphical abstract 6). Illustration of the formation process of carbon nanosheets (CNS) from waste PP.

6) A combined catalyst of ferrocene and sulfur was applied to convert the waste polypropylene (PP) into 2D carbon nanosheets. The highly efficient carbonization process in sealed space provided an ultrahigh yield (62.8 %) and thin thickness (4-4.5 nm) of carbon nanosheets (CNS), even though little catalyst was used. After activation, the activated carbon nanosheets (ACNS) possessed a well-defined hierarchical porous structure with a large specific surface area (3200 $m^2 g^{-1}$) and a big pore volume (3.71 $cm^3 g^{-1}$). The ACNS based electrode exhibited a high specific capacitance of 349 F g^{-1} at 0.5 A g^{-1} with a superior cycling performance (99% capacitance retention over 10000 cycles at 5 A g^{-1}). The fabricated symmetric supercapacitor manifested a high energy density of 23 Wh kg^{-1} at 225 W kg^{-1} in 1M Li_2SO_4 electrolyte. These findings provided a reference for the efficient conversion of waste plastic into high-performance electrode material.

Keywords: porous carbons; biomass; small organic molecule; waste polymer; carbonization; activation; catalyst; catalytic-carbonization; capacitive energy storage

07.10.2020 Xiaoguang Liu