

# Construction and characterizations of hollow carbon microsphere@ polypyrrole composite for the high performance supercapacitor

Qun Lu, Jia Liu, Xianyou Wang\*, Bing Lu, Manfang Chen, Meihong Liu

National Base for International Science & Technology Cooperation, Key Laboratory of Environmentally Friendly Chemistry and Applications of Ministry of Education, Hunan Province Key Laboratory of Electrochemical Energy Storage and Conversion, School of Chemistry, Xiangtan University, Xiangtan 411105, Hunan, China



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## ABSTRACT

The hollow carbon microsphere@polypyrrole (HCS@PPy) composite has been designed, synthesized through in situ chemical oxidation polymerization, and used as the active electrode material of supercapacitor. The porous structure, morphology and supercapacitive behaviors of the HCS@PPy composite are investigated by various physical characterization techniques and electrochemical measurement. The results show that HCS has the lychee-like hollow spherical morphology, and a fluffy PPy thin layer with thickness of 13 nm is uniformly coated on the surface of the HCS. The HCS@PPy composite reveals a high specific capacitance of 508 F/g at 1 A/g since it is the combination of both double-layer capacitances of HCS and faradic capacitance of PPy. The supercapacitor using HCS@PPy composite as the active material delivers excellent rate performance and outstanding cycle stability. Furthermore, the asymmetrical supercapacitor based on the HCS@PPy composite shows a high energy density of 46 Wh/kg at the power density of 350 W/kg. The improved supercapacitive performance is closely related with the integrated advantage of unique hollow porous structure of HCS and faradaic redox behavior of PPy, indicating that the design and preparation of HCS@PPy composite is a promising strategy for active material of high performance supercapacitor.

## 1. Introduction

Nowadays, the depletion of fossil fuels and the serious deterioration of the global environment are getting more and more serious, and thus forcing scientists to develop renewable, clean, and inexpensive of energy and advanced, environmentally friendly energy conversion and storage equipment to satisfy the needs of development in social economy and improve environmental problems [1–3]. This inspires the development of many new energy technologies, such as supercapacitors, fuel cells, solar cells, lithium-ion batteries [4]. Among energy storage devices, supercapacitors as one of the energy conversion and storage devices have attracted significant attention, mainly due to their high power density, good rate capability, long cycle life ( $> 10^5$  cycles) and popular prices [5,6]. There are two types of supercapacitors according to energy storage mechanism. One is the electrical double layer capacitor (EDLC) arising from the accumulation of pure electrostatic charge at the electrode/electrolyte interface. The other is the pseudocapacitors, in which charge-transfer faradic capacitance or pseudocapacitance arises from reversible redox reactions occurring at the electrode materials [7–9].

Usually, the carbon materials with various morphologies (such as

carbon nanotubes [10,11], hollow carbon sphere [12,13], carbon aerogels [14,15] have been extensively used as the active electrode materials owing to their various special morphology, high surface area, excellent electronic conductivity and outstanding cycle stability [16,17]. Particularly, the hollow porous carbon sphere materials are recognized as one of the most potential materials for supercapacitor applications. Its unique hollow porous structure increases the surface-to-volume ratio and shortens the transmission distance for mass and charge transport [18]. Meanwhile, the cavity of hollow carbon sphere serves as “ion-buffering storage pool” to reduce the diffusion distances of electrolyte ions [19,20]. Based on these advantages, it can greatly improve the electrochemical performance. Hence, considerable efforts have been devoted to the preparation of various porous hollow carbon spheres as active electrode materials of supercapacitors.

However, the carbon materials can only provide the limited electrical double layer capacitance, which is significantly lower than faradic capacitance or pseudocapacitance provided by metal oxides or conducting polymers (CPs) [21]. Among the several conductive polymers, such as polypyrrole (PPy), polyaniline (PANI), polyacetylene (PA) and Polythiophene, PPy is considered to be one of the most potential electrode materials since its high conductivity, good thermal stability,

\* Corresponding author.

E-mail address: [xywangxtu@163.com](mailto:xywangxtu@163.com) (X. Wang).

low production cost, high storage ability, high redox capacitance [22,23]. Nevertheless, the PPy can't maintain the stability for long time in comparison with carbon-based electrodes owing to the expansion and contraction of the polymer skeleton in the long time charge/discharge process, which lead to the poor cycling performance and the decrease of the capacitance, and then handicap its application.

In order to solve the above mentioned problems for low specific capacitance of carbon materials and structural instability of PPy, a number of literatures on PPy/carbon composites are reported, in which various carbon materials are used as substrate materials to combine with PPy to prepare composites. In our previous work, the polypyrrole/carbon aerogel composites were prepared via chemical oxidation polymerization, in which the specific capacitance is up to 373 F/g at 5 mV/s [24]. Qian et al. [25] prepared PPy/CNT composite through chemical oxidation polymerization with the specific capacitance of 276.3 F/g at 1 A/g. However, until recently, there is rarely reported about the HCS@PPy composites as active electrode material of supercapacitor. In this work, in order to make the best of the admirable EDLC of HCS and faradic capacitance of PPy, the HCS@PPy composite with a uniformly fluffy PPy layer covered on the surface of the HCS via in situ chemical oxidation polymerization is deliberately designed and prepared. The physicochemical and electrochemical performances of the HCS@PPy composite are studied in detail.

## 2. Experimental section

### 2.1. Preparation of hollow carbon sphere

In a typical synthesis of hollow carbon sphere (HCS) according to the reported method [26], 5.38 mL TEOS was added to the solution containing 140 mL ethanol, 20 mL H<sub>2</sub>O and 4 mL NH<sub>3</sub>·H<sub>2</sub>O (25 wt%) under stirring constantly at room temperature. After 0.25 h, 0.8 g resorcinol was added to the solution until dissolution. Afterwards 1.12 mL formaldehyde (37 wt%) was added gradually to the above mentioned solution. The system was kept stirring for 24 h or more. The precipitates were centrifuged at 10000 rpm, washed alternately with water and ethanol three times, and then dried at 60 °C overnight. The HCS were obtained after carbonization at 700 °C in N<sub>2</sub> atmosphere for 6 h with a heating rate of 3 °C/min and removal of silica template by hydrofluoric acid (HF, 5 wt%).

### 2.2. Synthesis of HCS@PPy composite

The preparation process of the HCS@PPy composite is briefly presented in Fig. 1. The HCS@PPy composite was synthesized through chemical oxidation polymerization employing sodium dodecyl benzene sulfonate (SDBS) as the surfactant and dispersant [27,28]. The synthesis

process of the HCS@PPy composite can be simply divided two steps. Firstly, 0.1 g HCS was dispersed in 250 mL distilled water solution with 0.02 g SDBS, and then sonicated for 0.25 h. After that, 0.4 mL pyrrole monomer was added to the above mixed solution under intensive stirring for 1 h at 0 °C. Secondly, ammonium persulfate ((NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) dissolved in 20 mL distilled water as an oxidizing agent (the ratio of (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>: pyrrole = 2:1) was added dropwise to the above solution to initiate polymerization, then the mixture was continuously stirred at 0 ~ 5 °C for 12 h. Finally, the resulting HCS@PPy composite precipitate is obtained by filtration, washing and drying. In addition, the pure PPy was synthesized in the same manner with no addition of any HCS. The content of HCS and PPy in the HCS@PPy composite is 34% and 66%, respectively.

### 2.3. Characterization of physicochemical properties

The morphologies and structures of the HCS and HCS@PPy composite were characterized with scanning electron microscopy (SEM, Quanta FEG 250, FEI) and transmission electron microscopy (TEM, JEM-2100F, JEOL). Raman spectra were recorded on a LabRAM HR800 Raman spectrometer. Fourier transform infrared (FTIR) spectrometer (Perkin-Elmer Spectrum One) was utilized to confirm the functional groups of polypyrrole uniformly coated on the surface of HCS. The DC conductivity was tested based on the Four-probe Resistivity Tester. The textural properties of HCS@PPy composite were characterized via N<sub>2</sub> sorption measurements at 77.3 K (JW-BK112). The SSA was obtained by Brunauer-Emmett-Teller (BET) method. The pore size distribution (PSD) was calculated based on the Barrett-Joyner-Halenda (BJH) model.

### 2.4. Electrode preparation and electrochemical testing

The mixture containing the 80 wt% active material, 10 wt% carbon black and 10 wt% polyvinylidene fluoride (PVDF) was used to fabricate the working electrodes, which employed the N-methyl-2-pyrrolidone (NMP) as solvent and then painted onto nickel foam with the area of 1 cm<sup>2</sup>. The prepared electrodes subsequently dried under vacuum at 80 °C for 12 h and then pressed under a pressure of 16 MPa for 60 s. Afterwards, the electrodes were well tested. All electrochemical tests were conducted on the electrochemical workstation (VersaSTAT3, Princeton Applied Research, USA). The electrochemical performance was measured through cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) and electrochemical impedance spectroscopy (EIS). The conventional three-electrode system applying nickel sheet as the counter and using a Hg/HgO electrode the reference electrode, was employed in 6 mol/L KOH electrolyte at ambient temperature, in which the potential window is -1.0–0 V. The cycle performance of the coin

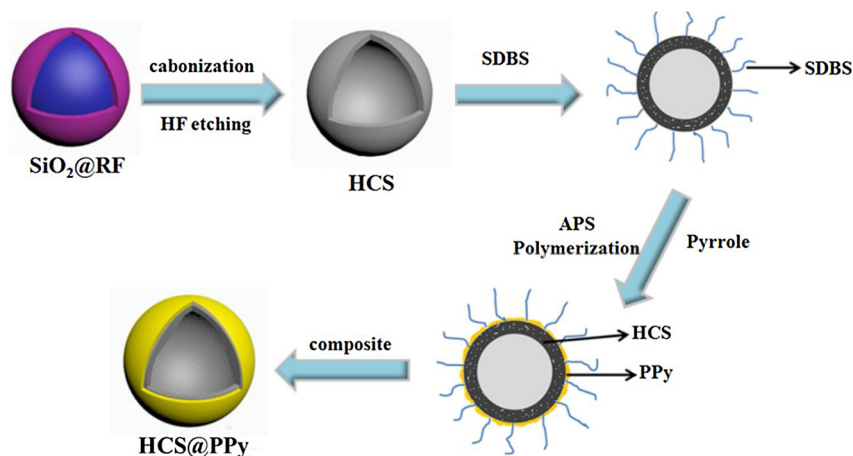


Fig. 1. Schematic illustration of synthesis procedure of HCS@PPy composite.

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