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Review

PVP-assisted synthesis of nitrogen-doped hollow carbon spheres for supercapacitors

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ABSTRACT

Nitrogen-doped hollow carbon spheres (N-HCS) show advantages of regular hollow structure, large surface area, and nitrogen functionality, which make them widely applied in many fields, especially as electrode materials for supercapacitors. Herein, we demonstrated a facile way to prepare N-HCS by using SiO_2 spheres as hard template, resorcinol-formaldehyde resin as carbon precursor. Polyvinyl pyrrolidone (PVP) was specially applied to introduce nitrogen and concurrently help resin coat on the surface of SiO_2. With assistance of PVP, the resin uniformly coated on the surface of SiO_2 by electrostatic adsorption and hydrogen bonding force and agglomeration of SiO_2 spheres was prevented, resulting in improved dispersity of carbon spheres. The obtained N-HCS duplicated the morphology of the silica spheres faithfully with regular hollow structure and smooth surface, showing high surface areas and large pore volumes. As electrode material for supercapacitors, N-HCS exhibited good electrochemical performances with capacitance of $173\ F\ g^{-1}$ at the current of $0.5\ A\ g^{-1}$ and favorable cycling stability of 96.4% after 5000 cycles at current density of $5\ A\ g^{-1}$, which make N-HCS become promising electrode material for high-performance supercapacitors.

Contents

1. Introduction . . . 42
2. Experimental . . . 43
  2.1. Chemicals . . . 43
  2.2. Synthesis of monodisperse SiO_2 solid spheres . . . 43
  2.3. PVP pretreatment of SiO_2 . . . 43
  2.4. Preparation of the N-HCS . . . 43
  2.5. Characterizations . . . 43
  2.6. Electrochemical evaluation . . . 44
3. Results and discussion . . . 44
4. Conclusion . . . 47
Acknowledgements . . . 47
References . . . 48

1. Introduction

Supercapacitors are potential energy storage device with high power, long cycle stability, high charging and discharging capacity, which has broad prospects in electric vehicle, electronic communication and other fields [1,2]. Electrode material is one of the important factors for performances of supercapacitors. Carbon materials (including activated carbon, fiber carbon, carbon nanotubes, carbon aerogels and carbon spheres) with regular structure, high surface area, uniform and tunable pore size, good conductivity

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and stability, are considered to be one of the most attractive electrode materials [3–7]. Among various carbon materials, hollow carbon spheres (HCSs) have received interest especially because of their integrated structural parameters including spherical structure, hollow cavity, and large specific surface area and potential applications in gas/energy storage, supports of catalytic systems, adsorbents, lubricants and so on [8–11].

The methods of preparing HCSs can be classified into solvothermal [12], chemical vapor deposition (CVD) [13], template method [14], etc. Template method is a powerful approach to fabricate HCSs in terms of its ability to fabricate desired hollow carbon structure based on selective hard and soft template. Especially, hard template method can control the size and structure of HCSs precisely, for which appropriate hard template is necessary [14,15]. SiO_2 sphere is a popular hard template because it is easy to synthesize and has uniform particle size. Biomass, macromolecular organic compounds and resorcinol-formaldehyde (RF), etc. have been used as carbon sources in different processes. Among them, RF resin seems to be a favored carbon source due to facile synthesis and high carbon residue [16,17]. However, RF resin is obtained through polymerization process in alkaline condition, with negative charge on its surface. It's difficult for RF resin to coat on SiO_2 sphere, which is also negatively charged. A common method to promote the coating of RF resin on SiO_2 sphere effectively and uniformly is using surfactant, such as cetyltrimethylammonium bromide (CTAB), to modify surface properties of SiO_2 spheres. CTAB-modified SiO_2 spheres are positively charged, which make negatively charged RF coating easily, as Fang and Guan's reported [18,19]. Although the core diameter and shell thickness can be controlled accurately, the HCSs composed of C and a little O element, which causing its inert surface property and limiting its application extremely.

Introducing functional groups and heteroatom (especially N) into carbon has been well demonstrated as a robust and versatile route to improve electronic conductivity and capacitance of the carbon electrode [20–24]. Nitrogen-doping is an effective route to enhance hydrophilicity and electron transfer rate of the electrode [25–32]. Various nitrogen containing compounds have been used as nitrogen precursor to modulate the structure and surface property of HCSs, including melamine [33], ethylene diamine [34], hexamethylenetetramine (HMT) [35], etc. In our previous work [36], ionic liquids (ILs) have been successfully applied as soft template, partial carbon precursor and nitrogen source to prepare N-doped HCSs (N-HCSs). But the high cost of ILs and low doping level make this method unsatisfying towards industrial production. There is still room to improve synthesis method for low-cost, high-performance N-HCSs.

Herein, we use polyvinyl pyrrolidone (PVP) as modifier and N precursor, SiO_2 spheres as hard templates, RF resin as carbon precursor to synthesize N-HCS. PVP facilitates coating of RF on SiO_2 sphere uniformly via hydrogen bonding force and electrostatic adsorption among PVP, SiO_2 spheres and RF resin [37,38]. Meanwhile the thermal decomposition of PVP leads to nitrogen doping in situ in the carbon skeleton, which enhances the electrochemical properties of N-HCS. The N-HCS completely duplicate the size and morphology of the SiO_2 spheres after carbonization and removal of the template exhibiting thin wall, large void and smooth surface. The obtained N-HCS showed favorable capacitance and cycling stability for supercapacitors.

2. Experimental

2.1. Chemicals

Tetraethyl orthosilicate (TEOS), resorcinol, formaldehyde solution (37 wt%), ethanol and concentrated ammonia solution (28 wt%), hydrofluoric acid (10%) were of analytical grade and purchased from Tianjin Yongda Chemical Corp. Polyvinyl pyrrolidone (PVP) was purchased from Tianjin Damao Chemical Corp. All chemicals were used as received without any further purification. Deionized water was used in all experiments.

2.2. Synthesis of monodisperse SiO_2 solid spheres

Monodisperse SiO_2 solid spheres in diameter were prepared by using a slightly modified Stöber process. In a typical synthesis of 250 nm SiO_2 solid spheres [39], 4.5 mL of TEOS was rapidly added into a mixture of 61.75 mL of ethanol, 24.75 mL of H_2O, and 9.0 mL of ammonium. The SiO_2 spheres were isolated by centrifugation and washed with ethanol and water repeatedly and air-dried at 60 °C overnight.

2.3. PVP pretreatment of SiO_2

The SiO_2 spheres (0.4 g) were mixed with PVP (0.6 g) and 30 mL DI water at 100 °C in under magnetic stirring. After refluxing for 3 h, the solution was then cooled down to room temperature. Finally, the PVP treated SiO_2 spheres were collected by centrifugation and re-dispersed in 35.2 mL DI water.

2.4. Preparation of the N-HCS

Followed by the addition of 0.175 g of resorcinol, 14.1 mL of ethanol and 0.05 mL of ammonia was added in, then stirring at 35 °C for 30 min to form a uniform dispersion. Then, 0.25 mL of a formalin solution was added to the dispersion under stirring. The mixture was cooled to room temperature after 6 h. The product SiO_2@RF-N was collected by centrifugation and then washed with water and ethanol several times. The obtained SiO_2@RF-N was heated at 3 °C min^{-1} from room temperature to 350 °C and kept at this temperature for 2 h under a nitrogen atmosphere. The temperature was then raised at 5 °C min^{-1} to 600 °C and kept at this temperature for 4 h. The pyrolyzed product SiO_2@C-N was treated with a 10% HF solution to remove the silica and generate nitrogen-doped hollow carbon spheres (N-HCS). CTAB was selected to modify SiO_2 instead of PVP for preparing HCS in the same conditions. Under the same reaction conditions for synthesis of N-HCSs, the weight ratios of SiO2/resorcinol used in the synthesis of N-HCS-0.22, N-HCS-0.44 and N-HCS-0.66, are 1/0.22, 1/0.44, 1/0.66, and we changed the reflux time of PVP (1, 2, 3 h) for preparing N-HCS-1h, N-HCS-2h and N-HCS-3h.

2.5. Characterizations

Scanning electron microscopy (SEM) analysis was conducted using a HITACHI S-4800-I scanning electron microscope. High-resolution Transmission electron micrographs (HR-TEM) were obtained on a JEOL JEM-2010 electron microscope. Nitrogen adsorption-desorption isotherm measurements were performed on a Micromeritics TriStar 3020 volumetric adsorption analyzer at 77 K. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface area of each sample and the average pore size distribution was derived from the desorption branch of the corresponding isotherm using the Barrett-Joyner-Halenda (BJH) method. The total pore volume was estimated from the amount of N_2 adsorbed at the relative pressure ($P/P_0 = 0.97$). X-ray photoelectron spectrometer (XPS) data were collected by using AXIS ULTRA DLD spectrometer with Al K radiation as the excitation source and the peak positions were referenced internally to the C1s