

CARBON MATERIALS AS ULTRACAPACITOR ELECTRODES

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Introduction

Energy storage devices with high power and energy densities are increasingly desired in many applications, such as electronic and hybrid vehicles. Ultracapacitors (also known as supercapacitors or electrical double-layer capacitors) can in principle meet both high-density and high-power requirements. Presently, the key issue on developing supercapacitors is to increase the energy density, which is largely determined by the electrode materials. Activated carbon (AC) is the most popular electrode materials. But the AC has a number of electrokinetic problems related to ion transport in the small micropores [1,2]. Here, we discuss some carbon structures with controllable properties for ultracapacitor applications.

Results and Discussion

Ordered mesoporous carbon with a lower ion transport resistance in comparison with AC is favorable for high-rate energy storage system [3]. Nitrogen-doped mesoporous CMK-5 (NCMK-5) was synthesized using the chemical vapor deposition method with pyridine as a carbon and SBA-15 as template precursor in the presence of a transition metal. **Fig. 1** (a and b) shows the FESEM and TEM images of NCMK-5. The mesoporous channels are clearly seen. Both the structure and surface area of the templated mesoporous carbon was found to be strongly dependent on the amount of the transition metal presented. The gravimetric capacitance of NCMK-5 was measured to be about 150 F/g at a current loading of 2 A/g.

Further reduction of ion transport resistance can be achieved by reducing the diffusion length with smaller mesoporous carbon particles. Hollow carbon spheres with a mesoporous shell (mesoshell carbon) was prepared by using silica spheres as template. Typical FESEM and TEM images of the mesoshell carbon are shown in **Fig. 1**(c and d). The electrochemical performance of the mesoshell carbon was found to be indeed better than CMK-5. This is attributed to the high accessible surface area (2200 m²/g) and short ion diffusion length.

Three-dimensionally ordered macroporous (3DOM) carbon with a hierarchical porous structure can facilitate ion transport due to the well interconnected porous structure and large pores. But the energy storage capacity of the 3DOM carbon is lower as compared to the AC. To improve the electrochemical performance, a thin layer of conducting polymer polyaniline (PANI) was coated on the surface of 3DOM carbon to fabricate PANI-3DOM composite electrode [4]. **Fig. 2** shows the FESEM images of pure 3DOM carbon and the composites

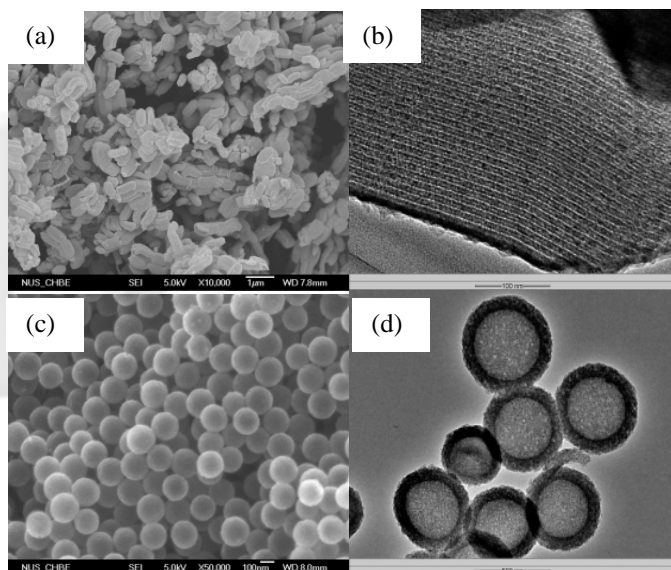


Fig. 1 (a) FESEM and (b) TEM images of NCMK-5; (c) FESEM and (d) TEM images of hollow carbon spheres with mesoporous shell structure.

PANI-3DOM with various loading of PANI. A specific capacitance of 1490 F/g was observed over the deposited PANI in the composite electrode with 8wt% loading of PANI. Over 2.5 times improvement in the total capacitance was achieved by the composite electrode (18wt% PANI) with little rate deterioration. Such composite materials embrace desirable electrode properties, such as chemical stability because of the carbon matrix, small mass transport resistance owing to the hierarchical porous structure, and pseudocapacitive properties due to the presence of active species PANI.

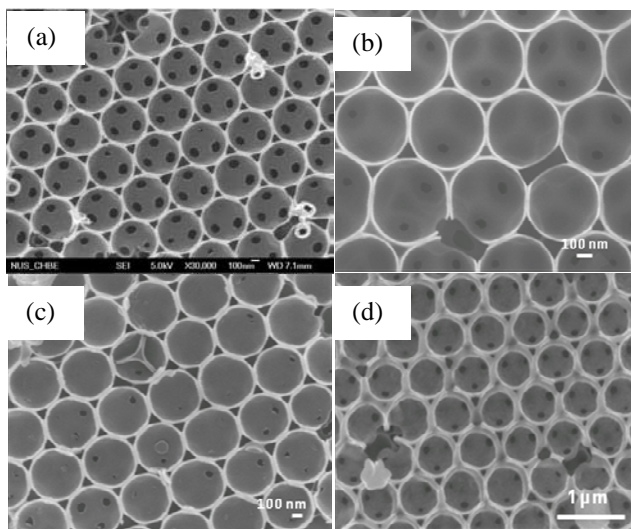


Fig. 2 FESEM images of (a) 3DOM carbon, PANI- 3DOM composites with PANI loadings of (b) 8 wt%, (c) 11 wt% and (d) 18 wt%.

The electrical conductivity (EC) of an electrode plays another important part in deciding the overall electrocapacitive performance of the electrode. We have demonstrated an approach to increasing the EC of mesoporous carbon by bridging carbon particles with carbon nanotubes (CNTs) [5]. The EC of the resultant carbon material was measured to be 645 S/m, about five times higher than that before modification (138 S/m). **Fig. 3** shows the SEM images before (Fig. 3a) and after bridging (Fig. 3b). Because of the significant enhancement of EC and the availability of mesopores, the cyclability of the hybrid carbon materials as a negative electrode used in rechargeable lithium-ion batteries was significantly improved.

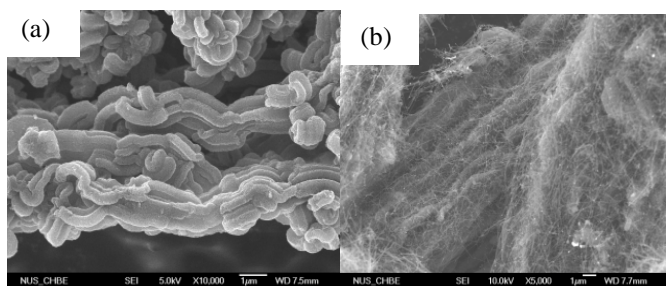


Fig. 3 FESEM images of mesoporous carbon (a) before CNT bridging and (b) after CNT bridging.

Graphene is receiving rapidly growing interest in the recent years due to its unusual properties. The superior electrical conductivity and stability makes it a suitable electrode material for energy storage. However, the specific capacitance of graphene electrode is comparable to that of AC electrode [6]. To explore the potential of graphene-based materials for supercapacitor applications, chemically modified graphene and PANI nanofiber composites were prepared by using an in-situ polymerization method to achieve a homogeneous dispersion of individual graphene sheets within the polymer matrix [7]. Results have shown that high specific capacitance and good cycling stability can be obtained either by doping graphene with a small amount of PANI or by doping bulky PANI with a small amount of graphene.

Recently, we succeeded in preparing graphene oxide (GO)-polypyrrole (PPy) composite materials by sandwiching PPy between GO layers using a method as illustrated in **Fig. 4**. Here we use a cationic surfactant solution with rodlike micelles to interact with a GO dispersion. Due to the strong electrostatic interactions between the negatively charged GO sheets and the surfactant micelles, the rodlike micelles will assemble on the GO surface. The pyrrole monomer will predominantly reside in the micelle core and polymerization begins upon adding ammonium persulfate (APS). After repeated washing to remove excess ingredients, PPy fibers sandwiched between GO sheets forming a layered composite structure can be obtained as shown in **Fig. 4**. The GO-Ppy composite with an opened-pore system was found to effectively reduce the dynamic resistance of electrolyte ions to allow easy access of the electrode surface, thus not only

providing an effective area for the attachment of polymer on both sides, but also serves as excellent support to enhance the mechanical strength of the polymer structure. The highest energy density of the electrode reached 70 Wh/kg, showing a very promising electrode material for high-performance supercapacitors.

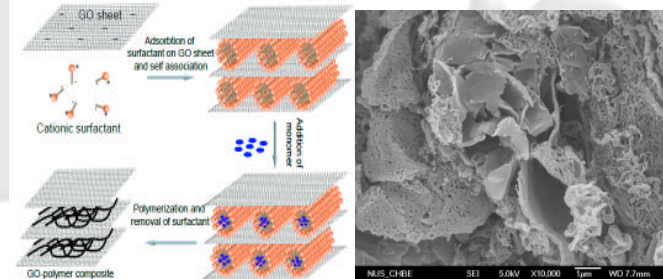


Fig. 4 Schematic illustration of the preparation of graphene oxide polypyrrole composite.

Conclusions

We have shown a few methods of preparing carbon electrodes with designed physicochemical and morphological properties for high-energy supercapacitor applications. Important properties of supercapacitor electrodes, such as surface area, porous structure, pore size, electrical conductivity, and pseudo-properties, are the crucial parameters that must be considered for the design and development of high-performance supercapacitor devices. With continuous advancements in nanotechnology, design and preparation of innovative carbon materials with a robust architecture and favorable properties as advanced electrodes will be one of the foremost areas in carbon research.

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