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A high-capacitance flexible solid-state supercapacitor based on polyaniline and Metal-Organic Framework (UiO-66) composites

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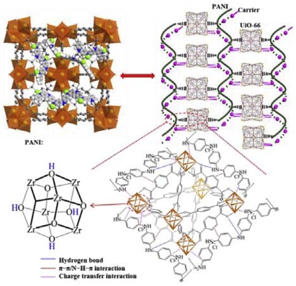
HIGHLIGHTS

- Polyaniline/UiO-66 composites have a fixed interpenetrating network structure.
- The synergies between PANI and UiO-66 improve the electrochemical performance.
- PANI/UiO-66 electrode can reach a specific capacitance of 1015 F g^{-1} at 1 A g^{-1}.
- The as-synthesized material shows high performance of flexible supercapacitor.

GRAPHICAL ABSTRACT



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ABSTRACT

Metal-Organic Frameworks (MOFs) attract increasing attention in the field of energy storage, however, poor conductivity in most MOFs largely hinders their electrical properties. In this work, an effective strategy is developed to make the polyaniline (PANI) molecular chains grow in the pores of UiO-66 as one of the MOFs (labeled as PANI/UiO-66) to form a fixed interpenetrating network structure by using the highly stable porous MOFs, through a variety of synergistic effects to enhance the conductivity and electrochemical properties. Moreover, the design and analysis about PANI/UiO-66 is reported for the first time to our knowledge. In addition, PANI/UiO-66 exhibits an extraordinary capacitance of 1015 F g^{-1} at 1 A g^{-1} by electrochemical test. At the same time, the symmetric flexible solid-state supercapacitors is also assembled and tested. The resultant supercapacitor shows a favorable specific capacitance of 647 F g^{-1} at 1 A g^{-1} and a high cycling stability (91% capacitance retention after 5000 cycles). The bending test indicates that the obtained supercapacitor is flexible and its performance is only decreased 10% after 800 bending cycles with a bending angle of 180. This flexible solid-state supercapacitor shows great potential in energy storage device.

1. Introduction

The development of miniaturization, lightweight, flexible, and high-performance energy storage system is essential to meet the growing demands for portable and wearable electronic equipments [1,2]. Traditional lithium-ion batteries, supercapacitors, and other products are rigid, when bending and folding, easy to cause the separation between electrode materials and current collector and liquid electrolyte leakage, influencing the electrochemical properties, and causing short-circuit, even serious safety problems. So in order to adapt to the development of the next generation of flexible electronics, flexible energy storage device has become the research focus in recent years. Supercapacitors

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(SCs) have attracted intense attention in the past years because they are recognized as one of new generation of clean energy-storage devices due to their advanced features, such as fast charge-discharge rate, high power density, and long cycling life [3–5]. However, among these SCs, most of the commercially available SCs are incorporated with liquid electrolytes, which are not suitable for portable, wearable, and flexible electronics, as well as possible the liquid electrolytes may permeate from SCs to destroy other electronic parts [6,7]. While solid-state electrolytes are preferred in flexible supercapacitors because of their advantages in terms of the compactness, reliability, and freedom from liquid leakage [8].

So flexible solid-state supercapacitors (SSCs) are considered to be promising candidates for electrochemical energy storage toward light-weight, safe, eco-friendly, and easy to-handle devices since they avoid using liquid electrolyte and can be easily folded or attached to any surfaces [9]. Current flexible supercapacitor electrodes are generally made of electroactive carbon-based materials, metal oxides, conductive polymers, and the composites of these materials [10–12]. The conductive polymers (CPs) are widely studied as electrode materials for supercapacitors because of their large energy storage, reasonable price, easy preparation, light weight, and flexibility. Among them, the polyaniline (PANI) has the advantage of high doping ability, good conductivity, high specific capacity and good environmental stability. It can be regarded as an ideal material for studying pseudocapacitors [13]. In order to improve the electrochemical performance of polyaniline and enhance its use in supercapacitors, many researchers have mixed polyaniline with other substances such as metal oxides [14,15], graphene [3,16–19]. Carbon black [20,21], carbon nanotubes [22–24], and other organic matters [25–28]. However, the capacitances are not much higher than the theoretical value, and some capacitances are even lower than the theoretical value (550 F g^{-1}) [29].

MOFs as a new class of porous crystal/powder materials has been employed in a variety of prospective applications [30], the conductivity of most MOFs are very poor, and the insulating nature of organic-ligands along with *d*-orbital participation of metal-ions in coordination bonds with the organic-ligands does not allow efficient delocalization of electrons across the framework [31]. For the application of MOFs in electrochemical energy storage, the carbonization of MOFs and their incorporation with carbon-based materials have been reported [32,33]. However, studies on energy storage that take advantage of the performance of carbon-based MOFs are still limited. On the other hand, over the past two decades, many researchers have made the polymer a porous coordination polymer (PCPs), which can also be called MOFs, but the applications of PCPs in the field of electrochemistry remain scarce, especially when excluding the field of ion-conductive networks. The main reason for this is the lack of electronic conductivity of most frameworks, with only a few PCPs reported as electron conductors [34]. So it is critical to apply MOFs in electrochemical devices to achieve a reasonable electrochemical performance.

In this study, a high-capacitance flexible solid-state SC using PANI-based MOFs composites was reported. A well-designed composite material containing MOFs as the porous frame and PANI as the interludes lines has an ideal reinforced-concrete architecture (Scheme S1). This method could avoid the insulation of MOFs, in addition, the porosity of MOFs can be used to store the charge, increase the charge path, as well as to improve the conductivity, specific capacity and other electrochemical properties of PANI. UiO-66 as one of the MOFs was used to prepare the composites with PANI (PANI/UiO-66) for the first time to our knowledge, moreover, the reason for the choice is that UiO-66 shows excellent aqueous, acid and thermal stability [35–37]. PANI/UiO-66 are prepared by in situ chemical polymerization of PANI on the surface and inside the pores of UiO-66. The structure and properties of flexible solid-state SCs based on PANI/UiO-66 are systematically investigated in this paper.

2. Experimental section

2.1. Materials

All chemicals and solvents were analytical grade, obtained commercially and were used as received without any further purification, except aniline, which was distilled under reduced pressure before use. Aniline (Ani), Ammonium persulfate (APS), N,N′- dimethylformamide (DMF), Ethanol and Methanol were purchased from Tianjin Tianli Chemical Reagent Co., Ltd. Sulfuric acid (H_2SO_4) and Hydrochloric acid (HCl) were purchased from Sinopharm Chemical Reagent Co., Ltd. 1,4-benzenedicarboxylic acid (H_2BDC), $ZrCl_4$ and paminodiphenylamine (AD) were purchased from Aladdin Reagent Co., Ltd. Carbon cloth (CC) was purchased from CeTech Co., Ltd. (Taiwan).

2.2. Preparation of UiO-66

The synthesis of Zr-MOF(UiO-66) was based on a previously reported procedure with some modification [35,36]. First, $ZrCl_4$ (0.63 g, 2.7 mmol) was dissolved through ultrasound in DMF (25 mL) for 3–5 min, until it became clear, then concentrated HCl (5 mL, 60 mmol) was added and the mixture was sonicated by ultrasound for 5 min. H_2BDC (0.63 g, 3.79 mmol) was dissolved through ultrasound in DMF (31 mL, 400 mmol) at room temperature for several minutes, until it became clear, and it was poured into the $ZrCl_4$ solution. The final mixture was introduced in a 100 mL and a 50 mL teflon-lined autoclave which were put in an electric blast oven at 120 °C for 24 h. After cooling in air to room temperature, the resulted white solid powders were collected via centrifugation, thoroughly washing with DMF (3 times) and methanol (3 times) and drying at 120 °C overnight.

2.3. Preparation of PANI nanofibers

PANI nanofibers were synthesized by a Typically method [38,39], with some slight modifications. Solution A was prepared by dissolving 0.93 g of aniline in 30 mL of HCl solution (1.0 M). The aniline solution was then mixed with 1 mL of absolute alcohol containing 0.5 wt% AD (use the mass ratio of additive to aniline to represent the dosage of additive). 2.28 g APS was dissolved in another 20 mL of HCl solution (1.0 M) to form solution B. Solution A and B were pre-cooled for 20 min at 0–4 °C and then solution B was added into the above solution A with mixed quickly and stirred at room temperature. The polymerization proceeded for 0.5 h, and then the resulting deep green product was washed with excess ethanol and water and dried at 60 °C overnight.

2.4. Preparation of PANI/UiO-66 composites

UiO-66 was degassed overnight at 120 °C under reduced pressure. Then aniline monomers were allowed to absorb in the activated UiO-66 channels at room temperature for 15 min upon applying reduced pressure and ultrasound. 0.0047 g AD was added to the above mixture, followed by continued ultrasonic shock and reduced pressure for 20 min. Then, 30 mL 1.0 M HCl solution was added with ultrasonic shock for 10 min (removing the decompression device) to form A solution. 2.28 g APS was dissolved 20 mL of HCl solution (1.0 M) to form solution B. Solution A and B were pre-cooled for 20 min at 0–4 °C and then solution B was taken into the above solution A with mixing quickly and stirring at room temperature. The polymerization had proceeded for 0.5 h, and then the resulting deep green product (PANI/UiO-66) was washed with excess ethanol and water and dried at 60 °C overnight. The PANI/UiO-66 composites with various PANI contents and UiO-66 contents were prepared by adjusting the aniline concentrations (0.05, 0.1, 0.2, 0.3, 0.4, 0.5 mol L^{-1}) and the mass fraction of UiO-66 (use the mass percentage of UiO-66 to aniline to represent the dosage of UiO-66, for example UiO-66 (10) represents UiO-66 relative to the aniline mass percentage of 10%) in the original mixed solution. The parameters of