Scalable in-situ growth of self-assembled coordination supramolecular network arrays: A novel high-performance energy storage material

Feng Zhang[1], Gaowei Zhang[1], Hua Yao, Zitao Gao, Xiaojuan Chen, Yangyi Yang[*]

School of Materials Science and Engineering, School of Chemistry, Sun Yat-sen University, Guangzhou 510275, China

HIGHLIGHTS

- A novel coordination supramolecular network material is fabricated on Ni foam.
- The nickel foam functionalized as both nickel ions source and current collector.
- The unique material structure leads to excellent electrochemical performance.
- The assembled asymmetric supercapacitor exhibits high energy and power densities.

GRAPHICAL ABSTRACT
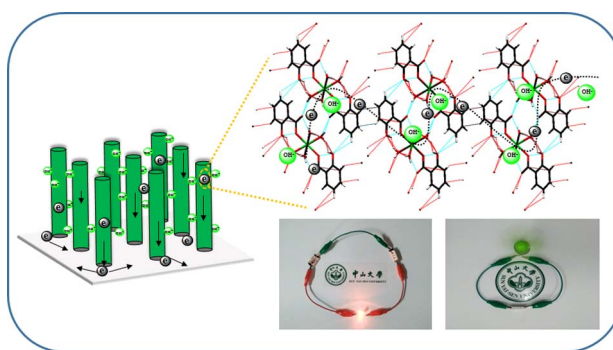
ABSTRACT

The exploration and rational design of new micro/nanostructured electrode materials with high capacitance performance is highly desired for supercapacitors. In this study, a novel coordination supramolecular network (CSN) of $[Ni(Hsal)_2(H_2O)_4]$ (Ni-Hsal, where Hsal is salicylate) sub-micrometer rod arrays has been synthesized directly on nickel foam by a facile solvothermal method. The nickel foam functionalized as both nickel ions source and current collector. The electrochemical tests demonstrate that this Ni-Hsal electrode has high areal capacitance of $6.04 \, F \, cm^{-2}$ at a current density of $10 \, mA \, cm^{-2}$, good rate capability with 76.2% capacitance retention when the current density increased from $10 \, mA \, cm^{-2}$ to $50 \, mA \, cm^{-2}$, and excellent cycling stability (showing no performance degradation after cycling 6000 times at $80 \, mV \, s^{-1}$). Furthermore, an asymmetrical supercapacitor (ASC) using the Ni-Hsal cathode and activated carbon (AC) anode is fabricated, which achieves an energy density of $2.39 \, mW \, h \, cm^{-3}$ and a maximum power density of $1.82 \, W \, cm^{-3}$ as well as excellent stability with a capacitance retention of 94% after 15,000 cycles. These results demonstrate that the CSNs can be a competitive electrode materials for supercapacitors in energy storages.

1. Introdcution

Supercapacitors (SCs) as an important class of the energy storage devices have attracted tremendous attention in recent years due to their high power density, fast charge/discharge ability, and long cycle life [1–5]. Currently, electrodes of the most of the commercially available supercapacitors are carbonaceous materials, such as activated, templated and carbide-derived carbons, graphene and carbon nanotubes [6,7]. The charge storage mechanism of these carbon-based supercapacitors are always electric double-layer capacitors (EDLCs), which

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originates from pure electrostatic charge accumulated at the electrode/electrolyte interface and no electrons are passed between the solution and the electrode. Although they behaved huge advantages such as large surface area, good electrical conductivity and excellent cycle lifetime, the intrinsic low specific capacitance seriously constrains their use in large backup power supplies and electric vehicles [8,9]. In contrast to EDLCs, pseudocapacitors have high specific capacitance and energy density, which produced by redox reactions involving the surface regions of electrode materials and involves interfacial electron transfer between the electrolyte and the electrode [10]. The pseudocapacitive materials such as transition metal oxides, hydroxides, sulfides and conducting polymers, et al., have been widely investigated. They exhibit several times higher specific capacitance than carbon materials [11–13]. Nevertheless, most of these pseudocapacitive materials suffer high resistance and plagued with poor cycle stabilities [14,15]. Therefore, it is highly desirable to explore and design newly advanced materials to meet the requirements of higher performance.

As one kinds of coordination supramolecular materials, porous coordination polymers or metal-organic frameworks (MOFs) are new type of porous materials constructed by the self-assembly of metal ions/clusters and organic ligands [16]. They have shown a wide range of potential applications in many fields, such as gas storage, drug delivery, nanoscale reactors, proton conduction, and chemical sensors [17–19]. In view of their large surface areas, adjustable pore size, diverse skeletal structures and plenty of metal active sites, the applications of MOFs in supercapacitors and Li-ion batteries have also obtained extensive attentions in recent years [20,21]. For instance, Liu et al. reported a Ni-DMOF-ADC electrode showed specific capacitances of 552 and 438 $F\,g^{-1}$ at current densities of 1 and 20 $A\,g^{-1}$, respectively [22]. Pang and Xue et al. synthesized a novel accordion-like Ni-MOF superstructure, which shows specific capacitances of 988 $F\,g^{-1}$ at current densities of 1.4 $A\,g^{-1}$ and capacitance retention of 96.5% after 5000 cycles [23]. Very recently, Xu and co-workers reported a conductive Cu–CAT MOF nanowire arrays on carbon fiber paper as additives and binders free electrode, which achieves a very high surface area-normalized capacitance of about 22 $\mu F\,cm^{-2}$ [24]. Although these successful examples demonstrated that MOFs can be used as electrode materials, the direct application of MOFs as supercapacitor electrode materials is still limited due to the poor intrinsic electrical conductivity, mechanical/chemical stability, steric hindrance to ion insertion and incompatibility between these MOFs and the electrolyte [25]. To overcome these disadvantages, it is urgently needed to assemble coordination supramolecular materials with better electrons transfer capability and larger space to permit quick electrolyte ion diffusion.

Coordination supramolecular networks (CSNs), the other kind of coordination supramolecular materials in which the supramolecular synthons include: simple metal-organic complexes (mononuclear, dinuclear, et al.) or oligomeric coordination entities are firstly formed by metal ions/clusters and organic ligands, then the networks constructed via intermolecular interactions such as hydrogen bond, π-π selfstacking, Van der Waals interaction, hydrophobic effect and so on. Contrary to the rigid crystalline MOFs, the weak-interactions among the supramolecular synthons make the structure of CSNs more flexible. As a result, the pore size or space of CSNs can be self-adjustable to match the electrolytes, and the steric hindrance to ion insertion greatly reduced. Therefore, the active metal ions inside of CSNs have ample opportunity to interact with electrolytes. Based on our previous work about coordination supramolecular materials [26–29] and supercapacitor [30–32], we found that the CSNs exhibit intriguing potential as electrode materials for supercapacitor. Unfortunately, due to the powder nature of the CSNs, insulated polymer binders and conductive additives were used to fabricate the bulk electrodes, which would decrease the effective surface area of CSNs, lead to extra weight and increase inner resistance of the electrodes [33]. Moreover, the bulk crystals of CSNs inevitably increase the diffusion distance of the electrolyte ions, thus bringing a poor rate performance. In contrast, direct growth of nano-

architectures active material on conducting substrates has proved to be an effect way to improve the electrochemical performance [34–39]. However, it is challenging to prepare CSNs materials into micro/nanostructure arrays on current collector as binder-free electrodes, and research on this has never been reported.

In this work, we first in situ self-assemble Ni-Hsal sub-micrometer rod arrays on Ni foam via facile one step solvothermal method. In our synthesis strategy, the Ni foam is adopted as both nickel ions source and current collector, which can significantly improve the stability of the electrode materials and reduce the internal resistance. Especially to deserve to be mentioned, the commercially available carbonaceous materials, such as graphene and carbon nanotubes, are always prepared by electric arc discharge, laser ablation, chemical vapor deposition, solid phase pyrolysis, glow discharge, gas combustion and polymerization reaction synthesis method. These methods are complex, time-consuming and need expensive instruments. In contrast, our processing method can be easily engineering scale-up by simply adding rolled Ni foams into large volume stainless steel autoclaves. Additionally, the uncoordinated hydroxyl groups in the network of Ni-Hsal can strengthen the hydrophilic of the active material and facilitate the electrolyte ions to intercalate/deintercalate. The electrochemical measurements show that the Ni-Hsal CSN sub-micrometer rod arrays electrodes have excellent electrochemical properties with areal capacitance of 6.04 $F\,cm^{-2}$ at a current density of 10 $mA\,cm^{-2}$, good rate capability with 76.2% capacitance retention at 50 $mA\,cm^{-2}$, and excellent cycling stability. Furthermore, the fabricated Ni-Hsal CSN-25//AC ASC device can achieve an energy density of 2.39 $mW\,h\,cm^{-3}$ and a maximum power density of 1.82 $W\,cm^{-3}$, which are substantially higher than the values obtained for most reported SCs. Interestingly, the tandem devices can power a red LED well for about 8 min and the single device can power a fan motor for about 2.5 min. The capability of effectively stabilizing Ni-Hsal CSN materials could open up new opportunities in developing high-performance ASCs.

2. Experimental section

2.1. Materials

All reagents were of analytical grade, purchased from commercial sources and used directly without further purification. Nickel foam (thickness: 1 mm, surface density: 320 g/m^2 ± 20, average pore density: 110 ppi) was purchased from JSD Foam Metal Company (Suzhou, China). Salicylic acid and alcohol were purchased from Xilong Chemical Co. (Guangzhou, China). All aqueous solutions were freshly prepared with deionized water.

2.2. Characterization

The powder X-ray powder diffraction patterns (PXRD) were collected using a D/MAX 2200VPC diffractometer with Cu Kα radiation (λ = 1.5406 Å) at a voltage of 40 kV and a current of 26 $mA\,cm^{-2}$. The morphologies of the materials were characterized by an ultra-high resolution field-emission scanning electron microscope (FE-SEM, SU8010, Hitachi) equipped with energy dispersive X-ray spectroscopy (EDX, Germany, Bruker Quantax) and Leica M205FA fluorescence stereo microscope. FT-IR spectra were recorded from KBr pellets in the range of 4000–400 cm^{-1} on an FT-IR spectrometer (330FT-IR, Nicolet, USA). The chemical states were determined by using an Axis Ultra X-ray photoelectron spectrometer (XPS, Kratos Analytical Ltd., UK) with Al Kα radiation (hν = 1486.6 eV).

2.3. Synthesis of [Ni(Hsal)₂(H₂O)₄] sub-micrometer rod arrays

The Ni-Hsal CSN sub-micrometer rod arrays were fabricated by a facile one-pot solvothermal route. Different from the typical synthesis for MOFs or CSNs, herein, Ni foam was used as nickel ions source and