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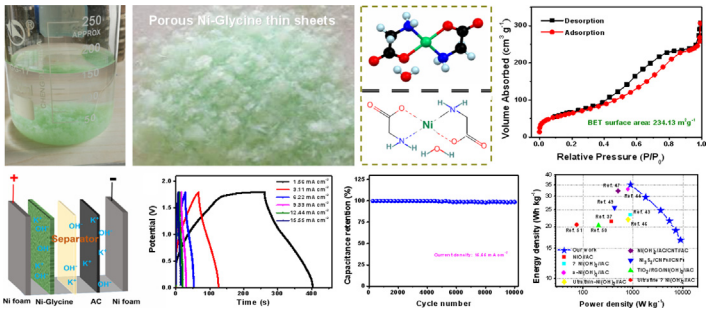
Regular Article

Scalable synthesis of two-dimensional porous sheets of Ni-glycine coordination complexes: A novel high-performance energy storage material

Jie Li [a], Tao Pu [a], Biao Huang [a], Xiaohuan Hou [a], Chenglan Zhao [a], Li Xie [a], Lingyun Chen [a,b,*]

[a] School of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400044, China
[b] National-Municipal Joint Engineering Laboratory for Chemical Process Intensification and Reaction, Chongqing University, Chongqing 400044, China

GRAPHICAL ABSTRACT



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ABSTRACT

A novel metal-amino acid assembly is successfully prepared using the simplest amino acid structure – glycine – and nickel nitrate hexahydrate. Two-dimensional porous Ni-Glycine coordination complex $[Ni(NH_2CH_2COO)_2](H_2O)$ (CQU-Chen-Gly-Ni-2-1) sheets with 3D nanoflake array structures have been prepared by a facile and cost-effective method. As electrode materials for supercapacitors, the Ni-Glycine coordination complexes display a high specific capacitance of 2.34 $F{\cdot}cm^{-2}$ at 1.08 $mA{\cdot}cm^{-2}$ (2171.71$F{\cdot}g^{-1}$ at a current density of 1 $A{\cdot}g^{-1}$), outstanding rate performance (80.77% capacity retention from 1.08 to 10.8 $mA{\cdot}cm^{-2}$) and superior cycling performance (2.4% loss after 5000 cycles at 10.8 $mA{\cdot}cm^{-2}$). In addition, the optimized asymmetric supercapacitor could be cycled reversibly in the high-voltage region of 0–1.8 V. Furthermore, excellent asymmetric supercapacitors of Ni-Glycine// activated carbon were also fabricated, and exhibited high energy densities of 35.05 and 16.75 $Wh{\cdot}kg^{-1}$ at power densities of 900 and 9000 $W{\cdot}kg^{-1}$, respectively. These fascinating performances can be attributed to the high capacitances and positive synergistic effects of the two electrodes. The impressive results presented here may pave the way for promising applications in high energy density storage systems.

1. Introduction

The ever-worsening issues of energy depletion and global warming call for the urgent development of clean alternative energies and energy storage or conversion devices. Supercapacitors (SCs), offer transient but extremely high power and, are probably

* Corresponding author at: School of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400044, China.
E-mail address: lychen@cqu.edu.cn (L. Chen).

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the most important next-generation energy storage devices [1–3]. To boost the specific capacitances of SCs, the specific surface area of the electrode materials needs to be as high as possible to accommodate a large amount of superficial electro-active sites that can participate in faradic redox reactions. In addition, suitable pore sizes of the porous electrode materials are critical to facilitate the mass transfer of electrolytes within the pores for fast redox reactions [4–6]. The electrode materials are the key component of SCs, and mainly determine their performance. Therefore, it is essential to develop suitable high-performance electrode materials for SCs.

So far, mesoporous 2D materials have been extensively explored for devices due to their large specific surface areas, high in-plane conductivities, abundant electro-active sites, and outstanding mechanical and chemical stability [7–11]. Recently, nickel-based 2D coordination complexes have been successfully used as electrode materials for SCs. For example, Wei et al reported the solvothermal synthesis of a layered Ni-MOF of $[Ni_3(OH)_2(C_8H_4O_4)_2\cdot(H_2O)_4]\cdot 2H_2O$ with a specific capacitance of 1127 $F\cdot g^{-1}$ at a current density of 0.5 $A\cdot g^{-1}$ [12]. Hui et al. demonstrated that Ni/Co-MOF 2D nanoflakes exhibited a significantly superior performance with a specific capacitance of 530.4 $F\cdot g^{-1}$ at a current density of 0.5 $A\cdot g^{-1}$ [13]. Pei and Chen et al reported a layered Ni-MOF of $[Ni_3(OH)_2(C_8H_4O_4)_2\cdot(H_2O)_4]\cdot 2H_2O$ for alkaline battery-SC hybrid devices with high performance [14]. To date, the controlled and orientated growth of 2D coordination complexes is of outmost importance for their applications in SCs.

As for the electrode material, electroactive materials with multiple oxidation states/structures that enable rich redox reactions for the generation of pseudocapacitance are desirable for SCs. Nickel-based materials (such as NiO, $Ni(OH)_2$ and Ni-MOF) are a class of materials that have drawn extensive attention by and researchers in recent years [15–18]. Their thermal stability, large surface area, hierarchical porous structures and high electronic conductivities make them ideal candidates for SC applications, as they can provide both high specific capacitances and also superior cycling performance. For instance, Park and co-workers reported hierarchical nanoflakes structure of NiO thin films for SCs, which achieved a high specific capacitance of 674 $F\cdot g^{-1}$ and a cycling stability of 72.5% over 2000 cycles [19]. Lokhande and Chavan reported nanoflower-like $Ni(OH)_2$, which exhibited a specific capacitance of 1065 $F\cdot g^{-1}$ at a current density of 15 $mA\cdot s^{-1}$ with excellent rate capability [20]. Liu and coworkers reported nickel-based pillared metal–organic frameworks (MOFs) of $[Ni(L)(DABCO)_{0.5}]$ (DABCO = 1,4-diazabicyclo[2.2.2]-octane and L = 9,10-anthracenedicarboxylic acid and 2,3,5,6-tetramethyl-1,4-benzenedicarboxylicacid), which maintained a specific capacitance of 552 $F\cdot g^{-1}$ at a current density of 1 $A\cdot g^{-1}$ [21]. Meanwhile, coordination complexes from the self-assembly of metal ions and organic ligands have been demonstrated as a promising class of inorganic-organic hybrid materials with desirable properties and potential applications in the development of novel functional materials, in the fields of optics, gas storage, separations, catalysis, chemical sensing and magnetism [22,23]. Their application in SCs, however, has received much less attention.

Based on the above considerations, one would expect Ni-Glycine coordination complexes, which should have good electronic conductivity, low diffusion resistance to protons/cations, easy electrolyte penetration, and high electroactive areas, to be promising candidates for the construction of next-generation, ultrahigh-performance SCs. We are interested in the controlled synthesis of 2D porous functional materials containing transition metal oxides, coordination complexes with defined 3D nanostructures and their application for electrochemical energy storage [24–29]. In this work, we report the successful preparation of complexes via a one-step hydrothermal route. With an initial Ni/glycine ratio of 0.5 and at a hydrothermal temperature of 220 °C for 12 h, an optimal combination of composition, specific surface area, pore volume, and pore size was achieved to afford complexes that showed an extremely high-specific capacitance of 2.34 $F\cdot cm^{-2}$ at 1.08 $mA\cdot cm^{-2}$ (2171.71 $F\cdot g^{-1}$ at a current density of 1 $A\cdot g^{-1}$) and excellent cycling stability (2.4% loss in initial capacitance at 10.80 $mA\cdot cm^{-2}$ over 5000 cycles).

2. Experimental

2.1. Preparation of CQU-Chen-Gly-Ni-2-1

All of the reagents were of analytical grade, except glycine (NH_2CH_2COOH) which is a biological reagent and was used as received without any further purification. Nickel (II) nitrate hexahydrate ($Ni(NO_3)_2\cdot 6H_2O$, ≥98.0%) was purchased from Kelong Chemical Co., Ltd. (Chengdu, China). Absolute ethanol (C_2H_5OH, ≥99.7%) was purchased from Chuandong Chemical (Group) Co., Ltd. (Chongqing, China). Glycine (NH_2CH_2COOH, ≥99.0%) was obtained from Adamasbeta. Double-distilled water (DDW) was used throughout all the syntheses. The 2D Ni-Glycine coordination complex thin sheets were prepared by a facile hydrothermal self-assembly method with the process shown in Fig. 1. In a typical process, 0.0009 mol of $Ni(NO_3)_2\cdot 6H_2O$ were dissolved in 40 mL of double-distilled water (DDW), while 0.0018 mol of glycine were

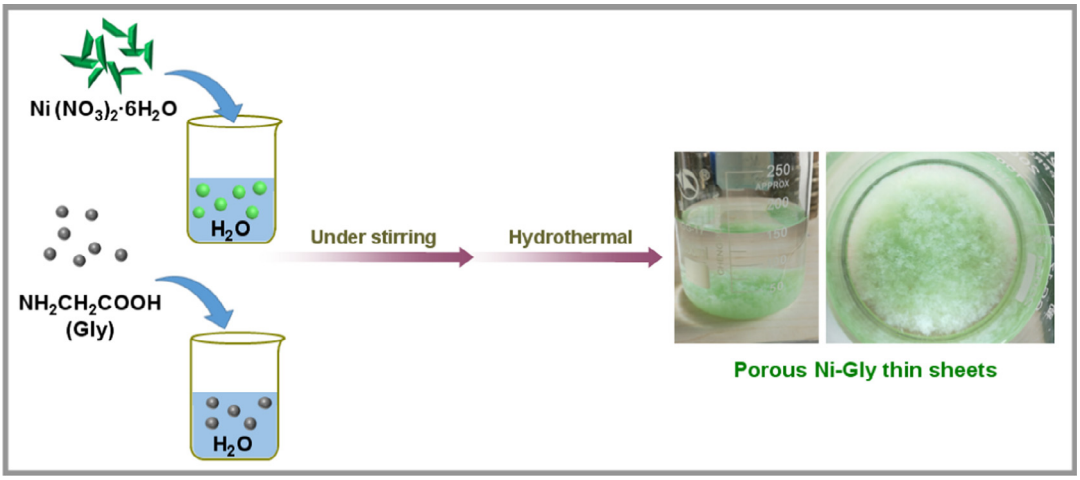

Fig. 1. Schematic illustration of the synthesis of 2D Ni-Glycine complex thin sheets.