



## Regular Article

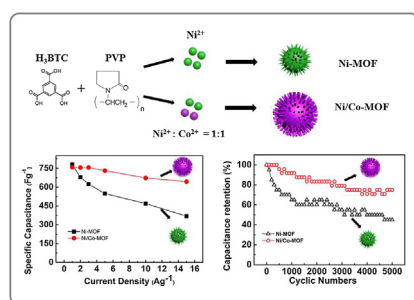
## Dandelion-like nickel/cobalt metal-organic framework based electrode materials for high performance supercapacitors



Shuwen Gao, Yanwei Sui, Fuxiang Wei, Jiqui Qi, Qingkun Meng, Yaojian Ren, Yezeng He\*

School of Materials Science and Engineering, China University of Mining and Technology, Xuzhou 221116, People's Republic of China

## GRAPHICAL ABSTRACT



## ARTICLE INFO

## Article history:

Received 19 May 2018

Revised 10 July 2018

Accepted 12 July 2018

## Keywords:

Ni-MOF

Ni/Co-MOF

Supercapacitors

## ABSTRACT

Metal-organic frameworks (MOFs), serving as a promising electrode material in the supercapacitors, have attracted tremendous interests in recent years. Here, through modifying the molar ratio of the  $Ni^{2+}$  and  $Co^{2+}$ , we have successfully fabricated Ni-MOF and Ni/Co-MOF by a facile hydrothermal method. The Ni/Co-MOF with a dandelion-like hollow structure shows an excellent specific capacitance of  $758 F g^{-1}$  at  $1 A g^{-1}$  in the three-electrode system. Comparing with Ni-MOF, the obtained Ni/Co-MOF has a better rate capacitance ( $89\%$  retention at  $10 A g^{-1}$ ) and cycling life ( $75\%$  retention after 5000 circulations). Besides, the assembled asymmetric supercapacitor based on Ni/Co-MOF and active carbon exhibits a high specific energy density of  $20.9 W h kg^{-1}$  at the power density of  $800 W kg^{-1}$ . All these results demonstrate that the mixed-metal strategy is an effective way to optimize the morphology and improve the electrochemical property of the MOFs.

© 2018 Elsevier Inc. All rights reserved.

## 1. Introduction

Over the years, supercapacitors (SCs) have drawn a lot of attention in the field of energy storage, due to their fascinating electrochemical properties such as high power density, long cycle life and low maintenance cost [1–3]. Scientists have classified the supercapacitors into two categories according to the energy storage mechanisms: the electric double-layer capacitors (EDLCs)

and pseudocapacitors. The former stores the energy by forming Helmholtz double layers of ions on the electrode surface, and the latter by fast surface and near-surface redox reactions between the electrode and the electrolyte, respectively [4–6]. For the materials used in the electrode, the carbonaceous materials primarily constitute the electrodes of the EDLCs, including the graphene, active carbon (AC) and carbon nanotube; while the transition metal oxides and conduction polymers make up electrode materials of the pseudocapacitors [7–9]. Compared with EDLCs, the pseudocapacitors attract more attention due to their outstanding specific capacitance [10,11].

\* Corresponding author.

E-mail address: [hyz0217@hotmail.com](mailto:hyz0217@hotmail.com) (Y. He).

Metal organic frameworks (MOFs), a kind of porous material comprised of metal ions and organic ligands primarily, have been investigated lately in a broad research field, such as gas storage and separation, catalysis, sensors, drug delivery, due to their fascinating merits of tunable metrics, porosity and organic functionality [12–16]. Recently, many researchers have fixed their attention on their application in the energy storage, especially in supercapacitors [17,18]. According to previous reports, MOFs could be applied as electrode materials of supercapacitors in various ways, for example, as templates via carbonization for EDLCs electrode [19,20], or as precursors to prepare metal oxides for pseudocapacitors [21,22]. MOFs can also be used for SCs directly, due to their unique structures able to provide plentiful pseudocapacitive redox centers [23]. However, the existence of some intrinsic defects, such as the pore sizes unfitting for the ion transportation, the poor electrical conductivity for the electric transfer [24], and the relative weak stability during charge-discharge process [25], will lead to a comparatively lower specific capacitance and poorer cycling stability of MOFs than those of the transition metal oxides. Fortunately, the inherent features, including tunable metrics, designable structure, and adjustable porosity as well as organic functionality for MOFs, endow them the specificity to change into a preferable structure for the utility in supercapacitors. Therefore, many approaches have been taken in to consideration to solve the problems [26,27]. For instance, Yang et al. [28] have prepared a layered structural Co-based MOF for supercapacitors with high specific capacitance, of which the layered structure provides enough space for OH<sup>-</sup> intercalation/de-intercalation process and acts as an electron transport channel to promote the electrochemical performance. Du et al. [29] have facilely fabricated a series of different structural Ni-MOFs by adjusting the molar ratio of metal ion and organic ligands and found that the optimal hierarchical porous structural Ni-MOF possesses a high specific capacitance of 1057 F g<sup>-1</sup> at 1 A g<sup>-1</sup> and keeps 70% of the original specific capacitance after 2500 cycles, due to its largest specific surface supplying more active sites for electrochemical reactions. Moreover, some dopants methods have been reported to improve MOFs' performance for supercapacitors, such as the graphene [30,31], polymers [32] and other metals [33].

In this work, we have synthesized a dandelion-like hollow Ni/Co-MOF through doping Co<sup>2+</sup> to the original Ni-MOF by a facile hydrothermal synthesis. The doping cobalt ions would occupy the position of the nickel ions, which not only results in the decrease of crystallinity, but also alters the waxberry-like structure of Ni-MOF to a dandelion-like structure of Ni/Co-MOF. The less crystal structure and novel dandelion-like morphology are advantageous for the rate capacitance and cycling life improvement when it is used as the supercapacitor electrode material. The obtained Ni/Co-MOF possesses a high specific capacitance of 758 F g<sup>-1</sup> at 1 A g<sup>-1</sup>, with a superior rate performance of 89% retention at 10 A g<sup>-1</sup>, as well as a good cycling stability of 75% retention after 5000 cycles. To further study its practical application, the asymmetric supercapacitor Ni/Co-MOF//AC is assembled, which exhibits a high specific energy density of 20.9 W h kg<sup>-1</sup> at the power density of 800 W kg<sup>-1</sup>. This synthetic method provides a facile mixed-metal strategy to facilitate MOFs directly used in supercapacitors.

## 2. Experimental

### 2.1. Preparation of Ni-MOF and Ni/Co-MOF

The reagents used for the synthesis of the Ni-MOF, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 1,3,5-benzenetricarboxylic acid, polyvinylpyrrolidone K-30 (PVP) were purchased from Aladdin.

Some other frequently used reagents and solvents were used as supplied without further purification.

The Ni/Co-MOF was synthesized by a hydrothermal method. 0.216 g Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 0.216 g Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 0.15 g 1,3,5-benzenetricarboxylic acid, and 1.5 g PVP were dissolved in 30 mL mixture solution with the volume ratio of water: ethanol: DMF = 1:1:1 at room temperature under supersonic vibration for 30 min. The mixture solution was then transferred into a 50 mL Teflon-line autoclave and kept at 150 °C for 10 h. At last the purple product were washed with ethanol for three times and dried in vacuum at 70 °C overnight. This purple sample is denoted as Ni/Co-MOF. In contrast, the other sample was prepared by the similar method, in which the two metal salts were changed to 0.432 g Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O as reported by Wang et al. [34]. This obtained green sample is denoted as Ni-MOF. The brief synthesis process is shown in Fig. 1.

### 2.2. Characterization of the Ni-MOFs

The structure of Ni-MOF was determined by X-ray powder diffraction (XRD) using Cu-K α radiation. The microstructures of the samples were observed by scanning electron microscopy (SEM) (Hitachi SU-8000), transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) (HRTEM, Tecnai G2F20). The electronic state of ions was analysis by X-ray photoelectron spectroscopy (XPS) by Al-Kα as X-ray source (ESCALAB 250Xi). FT-IR was used to determine different functional groups in the materials by VERTEX 80 V.

### 2.3. Electrochemical measurement

Electrochemical properties were tested at CHI660D (Chenhua, Shanghai, China) electrochemical station and analyzed by cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance studies (EIS). The tests were executed in 2 M KOH within the three-electrode system, in which a Pt foil served as the counter electrode, a saturated calomel electrode (SCE) as the reference electrode and the active material as the work electrode. The work electrode was fabricated by decentralizing the compound of the active material (Ni-MOF and Ni/Co-MOF), acetylene black and PVDF (Polyvinylidene Fluoride) at a mass ratio 8:1:1 in *N*-methyl 2-pyrrolidinone (NMP), then the mixture was coated on 1 \* 2 cm Ni foam and dried in vacuum overnight. The EIS was detected at the parameter of frequency of 0.01–100 kHz and an AC perturbation of 0.5 mV at an open circuit potential.

According to the following Eq. (1), the specific capacitance will be obtained,

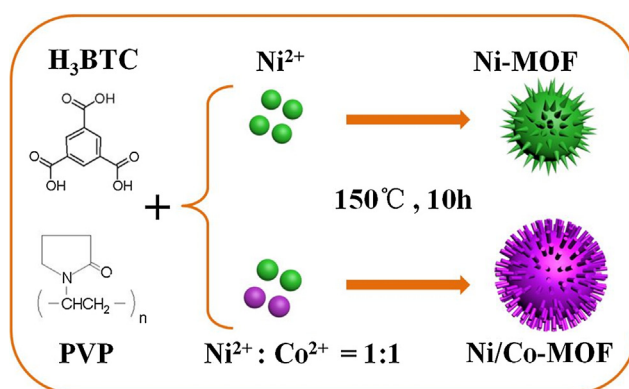


Fig. 1. Schematic illustration of the synthesis process for the Ni-MOF and Ni/Co-MOF.

Download English Version:

<https://daneshyari.com/en/article/6989479>

Download Persian Version:

<https://daneshyari.com/article/6989479>

[Daneshyari.com](https://daneshyari.com)