Electrochimica Acta 281 (2018) 69–77

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

# Flower-shaped multiwalled carbon nanotubes@nickel-trimesic acid MOF composite as a high-performance cathode material for energy storage

Qinghua Wang [a], Qingxiang Wang [a, b, *], Biyan Xu [a], Feng Gao [a], Fei Gao [a], Chuan Zhao [b, **]

[a] College of Chemistry and Environment, Minnan Normal University, Zhangzhou, 363000, PR China
[b] School of Chemistry, The University of New South Wales, Sydney, NSW, 2052, Australia

## ARTICLE INFO

*Article history:*
Received 15 November 2017
Received in revised form
3 May 2018
Accepted 24 May 2018
Available online 25 May 2018

*Keywords:*
Nickel-trimesic acid
Multiwalled carbon nanotubes
Nickel-trimesic acid
Metal-organic frameworks
Energy storage

## ABSTRACT

Metal-organic frameworks (MOFs) have received considerable attention in electrochemical fields due to their tunable morphology, open topological structure, large surface, and intense redox-activity. Herein, a novel flower-shaped multiwalled carbon nanotubes/nickel-trimesic acid composite (MWCNTs@Ni(TA)) was synthesized via one-step solvothermal method. The morphology and composition of the composite were characterized and compared with the single-component counterpart of spherical Ni(TA) by SEM, TEM, XRD, BET and FT-IR. The characterization results showed that the presence of carboxyl functionalized MWCNTs played a critical role to induce transformation of Ni(TA) from solid spherical shape in the single-component situation to the nanosheet-assembled flower shape in the composite. Electrochemical experiments showed that the flower-shaped MWCNTs@Ni(TA) composite have higher specific capacity (115 mAh $g^{-1}$ at a current density of 2 A $g^{-1}$) and better rate capability than the spherical Ni(TA). The MWCNTs@Ni(TA) based electrode also presented outstanding cycling stability with 81.6% specific capacity remained after 5000 charge-discharge cycles at a current density of 10 A $g^{-1}$ in KOH electrolyte.

## 1. Introduction

As the quick progress of electric vehicle and portable electronic equipment in modern society, there are increasing needs for developing energy storage devices with both high energy and power densities. Nowadays, the energy storage devices mainly include superconducting magnetic energy storage coil [1], lithium batteries [2], fuel cell [3], supercapacitor [4], and *etc*. Among these various energy storage devices, supercapacitor has attracted much concern due to its quick charge-discharge process, excellent cycling stability, high coulombic efficiency, and outstanding environment-friendliness [5–7]. Electrode materials with high power density and energy density play a key role in the construction of high-performance supercapacitors [8].

At present, there are three broad categories of electrode materials for supercapacitor, including carbon [9,10], metal oxide/hydroxide [11,12] and conductive polymers [13,14]. Carbonaceous materials have been widely used in commercial electrochemical double-layer supercapacitors due to their excellent stability. However, the low specific capacitance of the carbonaceous materials seriously limits their electrochemical performance. On the other hand, metal oxide such as $RuO_2$ has higher specific capacitance than carbon, but the high price hampers its industrial application [15]. Alternatively, some non-precious transition metal oxide such as NiO [16] and $Co_3O_4$ [17] have been developed due to their good electrochemical behaviors, easy preparation and low cost. Nevertheless, the practical application of this kind of materials is also limited by their poor cycle stability. As the third kind of electrode material, conductive polymers have wide working voltage window, but their large volume contraction and expansion during the charge-discharge process can cause structural instability and fast capacitance recession during long-term application. Therefore, it is still a great challenge to seek novel high capacitance, low cost and robust electrode materials for the fabrication of the high-performance supercapacitors.

Metal-organic frameworks (MOFs) are a type of porous material formed by transition metal ions linked with oxygen or nitrogen

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* Corresponding author. College of Chemistry and Environment, Minnan Normal University, Zhangzhou, 363000, PR China.
** Corresponding author. School of Chemistry, The University of New South Wales, Sydney, NSW, 2052, Australia.
*E-mail addresses:* axiang236@126.com (Q. Wang), chuan.zhao@unsw.edu.au (C. Zhao).

https://doi.org/10.1016/j.electacta.2018.05.159

containing organic ligands [18,19]. MOFs have the features of large specific surface area, adjustable pore size, and versatile structures. Based on these merits, MOFs have been used in the area of catalysis [20,21], gas adsorption [22], sensing [23,24], *etc*. In addition, MOFs present good electrochemical activities through choosing appropriate metal centers or bridging ligands, which enable them owning great potential in the applications of electrochemistry. In addition, MOFs can provide more electrochemical active sites and promote the ions diffusion through controlling the structure and pore size. Thus, MOFs are recently used as a new type of outstanding electrode materials of supercapacitors [25–29]. However, the poor conductivity and inferior stability of MOFs result in the fact that the supercapacitors constructed by pure MOFs generally exhibit poor rate capability and cycle stability, which limit their wide applications as electrode materials in supercapacitors.

To overcome these shortcomings of MOFs, the materials with high conductivity and mechanical stability have been utilized to form composites with MOFs. As a type of tube-structured carbon material, carbon nanotubes (CNTs) possess excellent conductivity, outstanding chemical stability, high mechanical strength, and good flexibility [30]. So far, CNTs were frequently used as substrates for the growth and fixation of active materials in energy storage devices, which enhances both the conductivity and stability of the electrode materials [31,32]. Thus, the decoration of porous MOFs with highly conductive CNTs should also be an effective strategy to enhance the electrochemical performance of the MOFs materials. For example, Zhang et al. synthesized a composite material of CNTs and Mn-MOF and used it as the electrode material to construct a symmetric supercapacitor [31]. The result displays that the hybridization of CNTs with the Mn-MOF result in an inherent improvement of electrochemical conductivity and specific capacitance (from 43 F $g^{-1}$ for pure Mn-MOF to 203 F $g^{-1}$ for the composite). Wen et al. have also prepared nickel-dicarboxybenzene MOF/CNTs (Ni-MOF/CNTs) composite-based electrode material [32]. Electrochemical results demonstrated that outstanding electronic conductivity of CNTs can provide small charge diffusion resistance and decreased path of electron collection/transport. All these studies indicate the hybridization of MOFs and CNTs can effectively improve the electrochemical performance of the materials with respect to single component.

In this paper, the novel nickel-based MOF, $Ni^{2+}$-trimesic acid (Ni(TA)) and its composite with multiwalled carbon nanotubes were prepared by a facile solvothermal method. The results displayed that the CNTs can act as the backbone for the *in-situ* formation of the Ni-MOF nanosheets, and effectively trigger the transformation of solid spherical Ni(TA) to the core-shell structured flower-like composite, MWCNTs@Ni(TA) (Scheme 1), through which the surface area and the electroactivity of the material was greatly improved. In addition, the capacitive behaviors of the synthesized materials were investigated and compared by cyclic voltammetry (CV), galvanostatic charge-discharge test (GCD), and electrochemical impedance spectroscopy (EIS). The results showed that the flower-shaped MWCNTs@Ni(TA) composite has higher specific capacity, better rate capability and superior cycling stability than the spherical Ni(TA), due to the synergetic effect of the nanosheet-structured Ni(TA) and the highly conductive MWCNTs.

## 2. Experimental

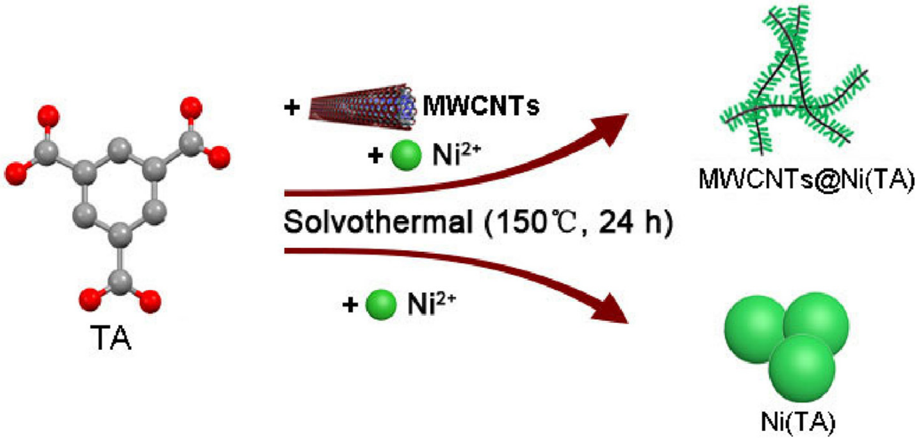
### 2.1. Apparatus and reagent

The powder X-ray diffraction data (XRD) of the samples were recorded on a Bruker D8 Advance powder diffractometer (Germany) using Cu $K_{\alpha}$ radiation ($\lambda = 1.54056$ Å). The morphology was analyzed on an FEI Tecnai G2 F20 transmission electron microscope (TEM, USA) and a Hitachi SU8020 scanning electron microscope (SEM, Japan) with an X-ray energy dispersive spectrometer (EDS). The infrared spectrum was tested on a Nicolet 750 FT-IR spectrometer (USA). The $N_2$ adsorption–desorption isotherms were measured using a Quantachrome Autosorb-IQ automated gas sorption analyzer (USA) at 77 K. The electrochemical measurements were carried out on a Chenhua CHI660 electrochemical workstation (China). The cycling stability tests were performed on a Land CT2001A battery test system (China).

Multiwalled carbon nanotubes (MWCNTs) were provided by Shenzhen Nanotech Port Corporation (China), and acidified to form functional carboxyl group according to literature [31] before use. $Ni(NO_3)_2 \cdot 6H_2O$, polyvinylpyrrolidone (PVP) and KOH were bought from Xilong reagent Inc. Corp. (China), trimesic acid (TA) and polytetrafluoroethylene (PTFE) were provided by Aladdin Reagent Inc. Corporation (China). The water used throughout the experiments was ultra-pure water purified by a Millipore-Q system.

### 2.2. Hydrothermal synthesis of MWCNTs@Ni(TA) composite

Typically, 70 mg of carboxyl functionalized MWCNTs was added into 70 mL of methanol and dispersed with ultrasonication until homogeneous black solution was formed. Then 250 mg of PVP, 0.637 g (2.2 mmol) of $Ni(NO_3)_2 \cdot 6H_2O$ and 0.256 g (1.2 mmol) of TA were added to the above MWCNTs dispersion. After further stirring



**Scheme 1.** Schematic illustration of the synthesis process of Ni(TA) and MWCNTs@Ni(TA)