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Rapid communication

A porous 2D Ni-MOF material with a high supercapacitive performance

Chao Feng[a,*], Chang-Peng Lv[a], Zong-Qun Li[a], Hong Zhao[b,*], Huan-Huan Huang[b]

[a] School of Materials and Chemical Engineering, Bengbu University, Bengbu 233030, PR China
[b] School of Chemistry and Chemical Engineering, Southeast University, Nanjing 211189, PR China

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ABSTRACT

A layered structural MOF $[Ni(Hppza)_2]_n$ (**1**) was synthesized and characterized by single-crystal X-ray diffraction, elemental analyses and IR spectroscopy. For complex **1**, the crystal structure is extended into 3D structure through N–H···O hydrogen bond. And for the first time, this complex used as an electrode material for a supercapacitor. It exhibited large specific capacitance of 184 F g^{-1} can be achieved at rates of 5 mV s^{-1}. The value demonstrated the best performance of all the MOF materials in supercapacitor at present. Such an excellent electrochemical property may be attributed to the intrinsic characteristics of Ni-MOF material including its crystal structure and morphology.

With the increasing consumption of non-renewable resources, the environmental pollution becomes more and more serious, thus the research and development of a new highly efficient and environmentally friendly electrochemical energy storage device that replaces the internal combustion engine has become an important strategic choice for the sustainable development of the society. Currently, remarkable achievements have been made in the fields of energy storage devices such as hybrid power, supercapacitors, fuel cells, and chemical batteries. Among which, the supercapacitor as a new type of energy storage device between the traditional capacitor and the rechargeable battery has significant power density. Thus, they can be widely used in areas such as mobile electronic devices, camera flash equipment, and back-up power supplies [1–4].

Metal-Organic Frameworks (MOFs), which is a new class of crystalline porous materials that metal ions and clusters are linked by organic units [5,6]. Compared with traditional porous materials, MOFs have the advantages of multiple structures, high porosity, large specific surface area, adjustable pore volume, and easy functionalization of pore surfaces [7] and lead to their potential applications in ion exchange, sorption, catalysis, *etc* [8,9]. In recent years, porous MOFs and derivatives have been gradually applied to the field of electrochemical energy storage, such as lithium ion batteries, fuel cells, and supercapacitors [10]. Theoretically, MOFs can be directly applied to supercapacitors as electrode materials [11]. On the one hand, MOFs have abundant interpenetrating pore structures that facilitate the transport of electrons and ions. On the other hand, MOFs are crystalline materials. The structure is highly ordered, the active sites are uniformly dispersed, and the exposed active sites are conducive to energy conversion. The process can ultimately effectively improve the electrochemical energy storage performance of the SC [12]. Díaz and his coworkers first reported the use of simple MOFs as supercapacitor electrode materials and found out that the MOFs electrode shows obvious double-layer capacitance behavior, but the capacitance is low. [13]. Lee et al. assembled a supercapacitor using Co-MOF-71 as an active electrode, and studied the electrochemical performance when using different aqueous solutions as electrolytes, resulting pseudocapacitor performance [14]. At the same time, Francaer et al. synthesized three Fe-MOFs [15], namely MIL-53(Fe), MIL-88B and MIL-l00(Fe), and studied them with different neutral aqueous solutions as electrolytes. The effect of different pore size, spherical wall thickness, and electrolyte cations on electrochemical performance was obtained, with the highest specific capacitance being only 57.5 F g^{-1}. These studies are the starting point for MOFs materials directly used in supercapacitor electrodes. It can be said that they are not successful because the supercapacitor performance is generally not good. Thus, it is quite necessary to find a new type of MOF material with a unique structure, which have good electrolyte compatibility and exhibit high performance [16].

In this work, a two-dimensional (2D) layered Ni-based MOF $[Ni(Hppza)_2]_n$ **(1)** was successfully synthesized by 5-(pyridin-4-yl)-1*H*-pyrazole-3-carboxylic acid (H_2ppza) with $NiCl_2·6H_2O$ and used as a supercapacitor electrode with KOH electrolyte. This material exhibited large capacitance, high-rate capability and cycling stability. The relationships between the intrinsic characteristics of the Ni-MOF material and its electrochemical properties were investigated in detail. Additionally, we expect that this work would attract more and more

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* Corresponding authors.
E-mail addresses: fchg042@163.com (C. Feng), zhaohong@seu.edu.cn (H. Zhao).

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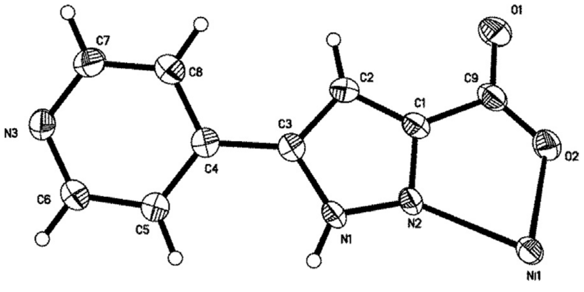

Fig. 1. The asymmetric unit of complex **1**.

crystallographers focus on the application of MOFs in the electrochemical material filed.

Perspective view of the asymmetric unit of complex **1** is shown in Fig. 1. It crystallizes in the monoclinic space group *C2/c*, where half a Ni(II) ion and one ligand (Hppza)$^-$ constitute the asymmetric unit. The central Ni(II) ion is six-coordinated by four nitrogen atoms (two pyridine N atoms and two pyrazole N atoms from different H_2ppza ligands) and two carboxyl oxygen atoms, with the Ni–O bond lengths of 2.0603 (14) Å as well as four nitrogen atoms (two pyridyl and two pyrazole from different ligands) with the Ni–N distances of 2.0866 (17) and 2.1340 (16) Å, respectively, as shown in Fig. 2. The coordination geometry of central Ni(II) ion can be described as the distorted octahedron due to Jahn-Teller effect [17]. It is obviously to see that the H atom of –NH is located on the pyrazole ring without deprotonation. The ligand H_2ppza adopts $\mu_3 = \eta^2 \colon \eta^1$ coordination mode and acts as a tridentate bridging ligand in **1**, extending the structure into an infinite 2D framework. It is noted that a novel grid-like unit is formed with porous size 13.786 Å and neighboring Ni···Ni distance of 10.5645 (7) Å (Fig. 3). In addition, the 2D framework is linking by N1–H1···O1^{v} hydrogen bonding interactions into 3D supermolecular architecture (Fig. 4), and the structure is further stabilized by intramolecular hydrogen bond C7–H7···O2^{vi} and $\pi \cdots \pi$ stacking interactions between adjacent pyrazole rings with the centroid to centroid separation of 4.126 (6) Å.

The solvent-accessible volume of the unit cell of complex **1** is 1173.5 Å^3, which is approximately 44% of the unit cell volume (2660.0 Å^3) [18,19]. As the porous MOF possessing high surface area and clear porous size, it predicts the potential applications in supercapacitors.

To confirm whether the crystal structures are truly representative of the bulk materials, X-ray powder diffraction (PXRD) experiment has been carried out for complex **1**, and the thermogravimetry studies are also carried on **1**, seen in Figs. S1 and S2.

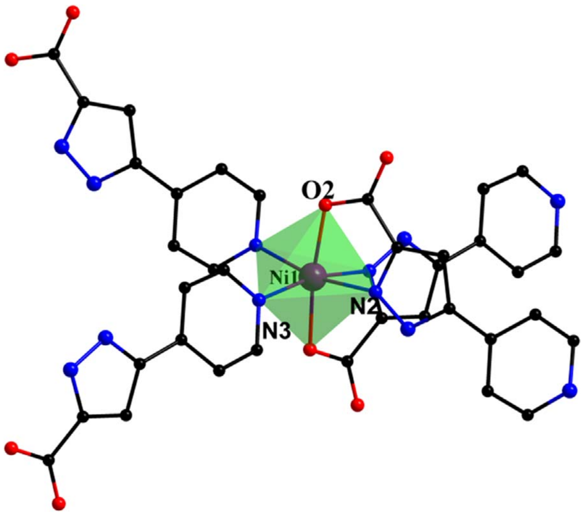

Fig. 2. The coordination environment of Ni (II) with octahedral.

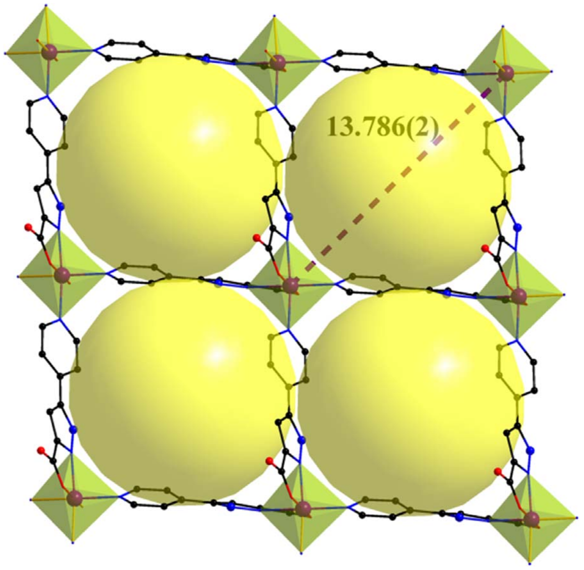

Fig. 3. 2D network of complex **1**.

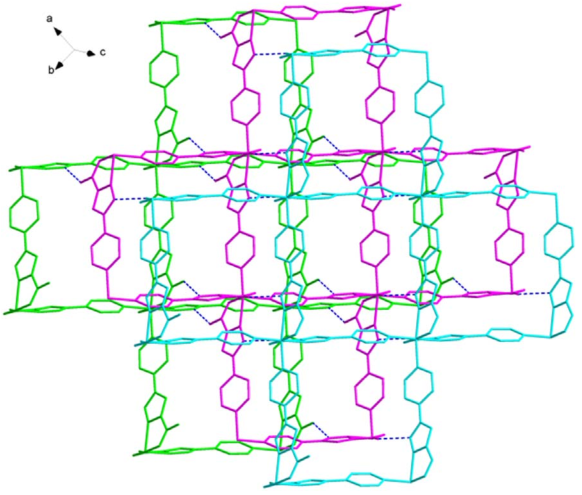

Fig. 4. 3D supermolecular architecture formed by 2D layers linking by hydrogen bonds.

The title complex $[Ni(Hppza)_2]_n$ **(1)** was usde as supercapacitor electrode by CV and GCD tests. Fig. 5a gives CV curves at scan rates of 5–100 mV s^{-1} under the potential of 0–0.4 V *vs* saturated calomel electrode (SCE). The pseudo capacitive behavior of **1** was clearly observed when redox peaks around 0.35 V. The CV curves are irregular at 100 mV s^{-1}, which may be according to the kinetics of electron transportation in the electrode material and the limited ion adsorption–desorption at electrode and electrolyte interface [20,21]. The CV behavior of complex **1** is similar to that of the reported Ni- MOFs [22,23]. The probable charge transfer mechanism as follows:

$$Ni(Hppza)_2 + OH^- \leftrightarrow Ni(Hppza)_2(OH) + e \quad (1)$$

GCD measurements were further studied, where the charge and discharge curves were at different current rates, including 0.5, 1, 1.5, 2.5, 5 and 10 A g^{-1} (Fig. 5b). These curves show symmetrical characteristics, indicating that the fast charge/discharge process has good pseudo capacitance properties. The gravimetric specific capacitance (C_{sp}) from CV test is calculated based on the equation: [24]

$$C_{sp} = \frac{\int IdV}{S \times \Delta V \times m} \quad (2)$$

The C_{sp} from GCD test is calculated based on the equation: [24]