

Article



Electrochemical Detection of Sarcosine and Supercapacitor Based on a New Ni–Metal Organic Framework Electrode Material

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Abstract: A new Ni metal organic framework based on 2,2'-Biphenyldicarboxylic, 4,4'- bipyridine as linker is prepared by hydrothermal reaction and directly used as an electrode material for supercapacitor and the detection of sarcosine. $[Ni_3(BIPY)_3(BPDA)_2(HCOO)_2(H_2O)_2]_n$ (Ni-1; BIPY = 4,4'-bipyridine; BPDA = 2,2'-Biphenyldicarboxylate) displays the specific capacitance of the Ni-1 are 667 F/gat 1 A/g and retention is 82% of initial capacitance at 1 A/g. The excellent electrochemical property is ascribed to the intrinsic nature of Ni-1. Furthermore, the sarcosine sensing performance of the Ni-1 electrode is evaluated in 0.1 M of NaOH solution and the electrode showed a wider range of linear response 1×10^{-4} M to 1×10^{-3} M. Thus, the results show that the Ni-1 is a potential candidate for not only sensing of sarcosine but also supercapacitor application.

Keywords: electrochemical sensing; sarcosine; supercapacitor; Ni metal organic framework

1. Introduction

Potential threatening energy crisis and environmental pollution force scientists and engineers to develop clean and very efficient energy storage technologies to overcome these issues. Supercapacitors are among such novel energy solutions because they demonstrate high-power density, long-termstability, and fast charging and discharging when needed [1–6]. Pseudocapacitance is stored by the rapid Faraday redox reactions occurring on the active material surfaces. Pseudocapacitive materials have higher specific capacitances than carbon materials (EDLCs). For the purposes, MOFs have been demonstrated to be useful for electrochemical energy storage and are considered as the most promising electrode material candidatefor SCs due to their high surface area, tunable pore size, controllable pore structure, and special structures with potentialpseudo-capacitive redox centers [7–10].

Panprostate cancer (PCa), the most common malignant tumor diagnosed in males, if diagnosed early, could be successfully treated. Early diagnosis of PCA also significantly reduced the mortality rate [8]. Sarcosine, is considered as a differential metabolite, since sarcosine is increased during PCa progression to metastasis sarcosine and can be detected non-invasively in urine. Recently, many papers have reported sarcosine sensing [11–15]. Sarcosine detection techniques include high-performance liquid chromatography-mass spectrometry (HPLC-MS) [16,17] and gas chromatography. However, these methods are very specialized, expensive, and time-consuming. Therefore, new, very sensitive, specific, fast, and inexpensive alternative methods are still desired.



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). MOFs, highly ordered porous crystalline containing metal ions and organic ligands, attracted attention for applications related to gas storage and separation [18–20], luminescent sensing [21–27], and catalysis [28–31] due to high surface area and suitable pore size. MOF structures are very diverse because of limitless combinations of their building blocks, cations (from main and transition groups), and ligands [32–34]. Thus, by varying cation/ligand, combination MOFs with various functionalities can be obtained. MOFs are considered excellent materials for supercapacitor and sensing applications.

Herein, a new Ni metal organic framework was synthesized and directly used as an electrode material for super capacitor and electrochemical sensing for sarcosine. The $[Ni_3(BIPY)_3(BPDA)_2(HCOO)_2(H_2O)_2]_n$ (Ni-1; BIPY = 4,4'-bipyridine; BPDA = 2,2'-Biphenyldicarboxylate, CCDC number 1935262) exhibited a high specific capacitance, and long-term cycling stability. The Ni-1 exhibited good sensitivity and a wider range of linear response 1×10^{-4} M to 1×10^{-3} M for the determination of sarcosine. This is the first time that a new metal organic framework is served as supercapacitor electrode and sensor.

2. Experimental Section

2.1. Materials and Methods

Nickel nitrate hexahydrate was purchased from J&K Chemical. 2,2'-Biphenyldicarboxylic and 4,4'-bipyridine were purchased from Jinan Henghua Technology company. All reagents used were commercially available and used without further purification. IR of $[Ni_3(BIPY)_3(BPDC)_2(HCOO)_2(H_2O)_2]_n$ (Ni-1;BIPY = 4,4'-bipyridine; BPDC = 2,2'-Biphenyldicarboxylate) was recorded on Affinity-1 FT-IR spectrometer ranging from 200 to 4000 cm⁻¹. Powder X-ray diffraction (PXRD) patterns were carried out through Cu-Karadiation from 5–40°. Thermal gravimetric analysis (TG) was carried out by using aNetzsch STA 449C system with a heating rate of 5 K/min under N₂ protection.

2.2. Synthesis of Ni-1

Firstly, 2,2'- Biphenyldicarboxylic Acid and 4,4'- bipyridine were dissolved in DMA to form 1 mol/L DMA solution, and nickel nitrate hexahydrate was dissolved in water to form 1 mol/L aqueous solution, The above solution 200 μ L:300 μ L:300 μ L and 8 mL H₂O was added to a 25 mL Teflon-lined stainless autoclave, sealed and heated at 160 °C for 72 h, then cooled to room temperature. The green block crystals of **Ni-1** were obtained (yield: 75% based on Ni(II)).

2.3. Single-Crystal Structure Determination

Crystal of **Ni-1** was collected from the mother liquor. Single-crystal data of **Ni-1** were collected on a Rigaku Oxford CCD diffractometer equipped with graphite-monochromatic Mo-K α radiation ($\lambda = 0.71073$ Å) at 293 K. The structure was solved by direct methods, and refined by full-matrix least-square method with the *OLEX-2* program package. The crystallographic data and refinements and the selected bond lengths and angles for **Ni-1** are listed in Tables 1 and 2.

Table 1. Crystal data and structure refinement for Ni-1.

Compound	Ni-1
Chemical Formula	C ₆₀ H ₅₄ N ₆ Ni ₃ O ₁₈
Formula weight	1323.16
Crystal system	Monoclinic
Space group	C2
a (Å)	22.501(2)
b (Å)	11.2879(12)
<i>c</i> (Å)	13.4015(12)
α (°)	90

Compound Ni-1 β (°) 126.099(10) γ (°) 90 V (Å ³) 2750.3(5) Z 2 D_c (g/cm ³) 1.598 μ (mm ⁻¹) 1.101 T (K) 293(2) Wavelength (Å) 0.71073 $F(000)$ 1368.0 Crystal size (mm) 0.20 × 0.19 × 0.12 θ range(°) 7.22 to 59.298 Index ranges $-28 \le h \le 31$ $-15 \le k \le 15$ $-18 \le 1 \le 16$ Reflections collected 11,900 Independent reflections 11,900 [R _{int} = 0.0759, R _{sigma} = 0.1150] Parameters 396 Goodness-of-fit on F^2 0.0769 wR_2 indices [$I > 2\sigma(I)$] 0.1609 R_1 indices [$I > 2\sigma(I)$] 0.1609 R_1 indices [all data] 0.1005 wR_2 indices [all data] 0.1072 Peak and hole (e Å ⁻³) 1.37/-0.95			
$\begin{array}{lll} \beta \left({}^{\circ} \right) & 126.099(10) \\ \gamma \left({}^{\circ} \right) & 90 \\ V \left({}^{A} {}^{3} \right) & 2750.3(5) \\ Z & 2 \\ D_{c} \left({g} {/} {\rm cm} {}^{3} \right) & 1.598 \\ \mu \left({\rm mm} {}^{-1} \right) & 1.101 \\ T \left({\rm K} \right) & 293(2) \\ Wavelength \left({}^{A} \right) & 0.71073 \\ F(000) & 1368.0 \\ {\rm Crystal size (mm)} & 0.20 \times 0.19 \times 0.12 \\ \theta {\rm range}^{\left(\circ \right)} & 7.22 \ {\rm to } 59.298 \\ {\rm Index \ ranges} & -28 \leq {\rm h} \leq 31 \\ -15 \leq {\rm k} \leq 15 \\ -18 \leq {\rm l} \leq 16 \\ {\rm Reflections \ collected} & 11,900 \\ {\rm Independent \ reflections} & 11,900 \\ {\rm Remeters} & 396 \\ {\rm Goodness-of-fit \ on \ F^{2} \\ R_{1} \ indices \left[{I > 2\sigma(I)} \right] & 0.769 \\ wR_{2} \ indices \left[{I > 2\sigma(I)} \right] & 0.105 \\ wR_{2} \ indices \left[{\rm ald \ ata} \right] \\ wR_{2} \ indices \left[{\rm ald \ ata} \right] \\ wR_{2} \ indices \left[{\rm ald \ ata} \right] \\ wR_{2} \ indices \left[{\rm ald \ ata} \right] \\ ext{ and \ hole} \left({\rm e} { {\rm A}^{-3} \right) \\ \end{array}$	Compound	Ni-1	
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$\begin{array}{llllllllllllllllllllllllllllllllllll$	V (Å ³)	2750.3(5)	
$\begin{array}{llllllllllllllllllllllllllllllllllll$	Ζ	2	
$\begin{array}{lll} \mu (\mathrm{mm}^{-1}) & 1.101 \\ 1.101 \\ T (\mathrm{K}) & 293(2) \\ \mathrm{Wavelength}(\mathrm{\AA}) & 0.71073 \\ F(000) & 1368.0 \\ \mathrm{Crystal size}(\mathrm{mm}) & 0.20 \times 0.19 \times 0.12 \\ \theta \mathrm{range}(^{\circ}) & 7.22 \mathrm{to} 59.298 \\ \mathrm{Index ranges} & -28 \leq \mathrm{h} \leq 31 \\ -15 \leq \mathrm{k} \leq 15 \\ -18 \leq 1 \leq 16 \\ \mathrm{Reflections collected} & 11,900 \\ \mathrm{Independent reflections} & 11,900 [\mathrm{R}_{\mathrm{int}} = 0.0759, \mathrm{R}_{\mathrm{sigma}} = 0.1150] \\ \mathrm{Parameters} & 396 \\ \mathrm{Goodness-of-fit on} F^2 & 1.056 \\ R_1 \mathrm{indices}[I > 2\sigma(I)] & 0.769 \\ wR_2 \mathrm{indices}[I > 2\sigma(I)] & 0.1609 \\ R_1 \mathrm{indices}[\mathrm{al data}] & 0.1005 \\ wR_2 \mathrm{indices}[\mathrm{al data}] & 0.1772 \\ \mathrm{Peak and hole}(\mathrm{e} \mathrm{\AA}^{-3}) & 1.37/-0.95 \\ \end{array}$	$D_c (g/cm^3)$	1.598	
T (K)293(2)Wavelength (Å)0.71073 $F(000)$ 1368.0Crystal size (mm) $0.20 \times 0.19 \times 0.12$ θ range(°)7.22 to 59.298Index ranges $-28 \le h \le 31$ $-15 \le k \le 15$ $-18 \le 1 \le 16$ Reflections collected11,900Independent reflections11,900 [R _{int} = 0.0759, R _{sigma} = 0.1150]Parameters396Goodness-of-fit on F^2 1.056 R_1 indices $[I > 2\sigma(I)]$ 0.1609 wR_2 indices [all data]0.1005 wR_2 indices [all data]0.1772Peak and hole (e Å ⁻³)1.37/-0.95	$\mu (\mathrm{mm}^{-1})$	1.101	
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$\begin{array}{ll} -15 \leq k \leq 15 \\ -18 \leq l \leq 16 \\ \\ \text{Reflections collected} & 11,900 \\ \\ \text{Independent reflections} & 11,900 \\ \\ \text{Rameters} & 396 \\ \\ \text{Goodness-of-fit on } F^2 & 1.056 \\ \\ R_1 \text{ indices } [I > 2\sigma(I)] & 0.0769 \\ \\ wR_2 \text{ indices } [I > 2\sigma(I)] & 0.1609 \\ \\ R_1 \text{ indices [all data]} & 0.1005 \\ \\ wR_2 \text{ indices [all data]} & 0.1772 \\ \\ \text{Peak and hole (e Å^{-3})} & 1.37/-0.95 \\ \end{array}$	Index ranges	$-28 \le h \le 31$	
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wR_2 indices [all data] 0.1772 Peak and hole (e Å ⁻³) 1.37/-0.95	R_1 indices [all data]	0.1005	
Peak and hole (e Å ⁻³) $1.37/-0.95$	wR_2 indices [all data]	0.1772	
	Peak and hole (e Å ⁻³)	1.37/-0.95	

Table 1. Cont.

Table 2. Selected Bond lengths [Å] and Angles [deg] for Ni-1.

Ni1- O1 = 2.029(7)	Ni2- O3 = 2.078(8)
Ni1- $O7 = 2.048(6)$	Ni2- O3 2 = 2.078(8)
Ni1- N2 = $2.090(12)$	Ni2- N3 = 2.098(15)
Ni1- O5 1 = 2.091(6)	Ni2- O2 2 = 2.118(7)
Ni1- N1 = $2.113(12)$	Ni2 - O2 = 2.118(7)
Ni1- $O5 = 2.120(6)$	Ni2- N4 = $2.127(15)$
O1-Ni1-O7 98.1(3)	O3-Ni2-O3 ² 176.6(5)
O1-Ni1-N2 84.6(3)	O3-Ni2-N3 88.3(3
O7-Ni1-N2 87.3(4)	O3 ² -Ni2-N3 88.3(3)
O1-Ni1-O5 ¹ 93.2(3)	O3-Ni2-O2 ² 99.7(3)
O7-Ni1-O5 ¹ 168.4(3	$O3^{2}-Ni2-O2^{2}$ 80.4(3)
N2-Ni1-O5 ¹ 91.2(4)	N3-Ni2-O2 ² 91.0(2)
O1-Ni1-N1 92.0(4)	O3-Ni2-O2 80.4(3)
O7-Ni1-N1 90.8(4)	O3 ² -Ni2-O2 99.7(3)
N2-Ni1-N1 175.9(3)	N3-Ni2-O2 91.0(2)
O5 ¹ -Ni1-N1 91.3(4)	O2 ² -Ni2-O2 178.0(5)
O1-Ni1-O5 168.3(3)	O3-Ni2-N4 91.7(3)
O7-Ni1-O5 92.6(3)	O3 ² -Ni2-N4 91.7(3)
N2-Ni1-O5 91.1(4)	N3-Ni2-N4 180.0
O5 ¹ -Ni1-O5 76.0(3)	O2 ² -Ni2-N4 89.0(2)
N1-Ni1-O5 92.6(4)	O2-Ni2-N4 89.0(2)

Symmetry transformations used to generate equivalent atoms: $^{1} 1 - X$, +Y, -Z; $^{2} 1 - X$, +Y, 1 - Z.

2.4. Fabrication of Working Electrode

80% of Ni-1, 10% of acetylene black and 10% of PVDF were mixed in N-methyl pyrrolidone (NMP) until a homogeneous slurry was obtained, which was then applied to Ni foam and dried at 60 °C in the air. Electrochemical sensing tests were performed using the glassy carbon electrode (GCE, model CHI104, 3 mm in diameter). Prior to the tests, it was polished with 0.05 μ m alumina, followed by ultrasonicated in 50% HNO₃,

absolute ethanol and distilled water mixture for 30 at each step. Two milligrams of MOF was dispersed in 1 mL of DMF ultrasonically. Five microliters of this suspension was dropped onto the GCE surface to obtain a **Ni-1** based working electrode (NHCPs-GCE).

2.5. Electrochemical Measurements

All the electrochemical measurements were conducted on an electrochemical workstation (CHI760E). In a three-electrode system, the **Ni-1** was used as the working electrode, with Pt plate as the counter electrode, Hg/HgO as the reference electrode, and 6 M KOH as the electrolyte, respectively.

3. Results and Discussion

3.1. Structure Description

The Compound **Ni-1** shows two-dimensional structure and belongs to C_2 space group. The asymmetric unit contains one and a half nickel (II) centers, one bridging BPDC^{2–} group, one and a half BIPY, one formic acid group, and one water molecule. As shown in Figure 1, the Ni^{2+} are six-coordinated by four O atoms and two N atoms. In coordination mode of Ni(1), N1, and N2 come from two bipyridine molecules, O1 is from biphenyl dicarboxylic acid molecules, O6 and O6d are from two formic acid molecules, and O5 is from water molecules. Formic acid comes from the decomposition of solvent molecules. In coordination mode of Ni(2), N3 and N4a are from two bipyridine molecules, O2, O3, O2c, and O3c come from two BPDC²⁻ group (Figure 1). As a bridging ligand, two N atoms in pyridine participate in the coordination, and only three oxygen atoms of BPDC²⁻ group are involved in the coordination. It is interesting that in this structure, the conformation of the bipyridine molecule in which N1 is located is quite different from that of N3 (Figure 2). The bipyridine molecule in which N3 is located has a symmetry plane, and the two planes of N3 and N4 form a certain angle of 38.60(9)°, which is close to the normal bipyridine molecular structure, while the bipyridine molecule of N1is relatively deformed (without plane of symmetry), N1 and N2 the two planes rotate to the same plane through the δ bond between C17 and C18 (the angle is 14.89°). Although this conformation is not a stable conformation of the bipyridine molecule, the structure δ -bond rotation precisely enhances the relationship between pyridine rings π - π accumulation. In this two-dimensional structure, the bipyridine molecule where N1 resides forms a straight chain with Ni1 via a coordination bond. Similarly, the bipyridine molecule in which N2 resides forms another straight chain with Ni2 via a coordination bond. The Ni(1) chain and the other Ni1 chains are connected by O6 atom in two coordinated formic acid molecules. After connecting with Ni1 chain, Ni1 is coordinated with Ni2 chain via O atom of Biphenyldicarboxylic Acid Molecule. Finally, a two-dimensional layered structure is formed by O-coordination and π - π stacking (Figure 3)



Figure 1. Coordination mode of Ni-1. Symmetric code: a(x, -1 + y, z), b(x, 1 + y, z), c(1 - x, y, 1 - z), d(1 - x, y, -z).

Figure 2. Conformations of two bipyridine molecules.



Figure 3. 2D structure in the a direction of Ni-1.

3.2. Purity and Thermal Stability

In order to explore the properties of Ni-1, the purity and thermal stability of the material were investigated. Figure 4a shows the PXRD patterns of the Ni-1, The PXRD patterns of Ni-1 showed the diffraction peaks corresponding to the simulated Ni-1 pattern. FT-IR spectrum of Ni-1 showed bands at 1610 and 1493 cm⁻¹, which correspond to bending and stretching of C = O (Figure 4b), while peaks at 1305 and 1542 cm⁻¹ were ascribed to the pyridine bending. The Ni-1 thermal stability was analyzed by the thermogravimetric analysis (TGA) performed in the 50–800 °C range under N₂ (see Figure 4c). The first weight-loss stage occurred at 100–350 °C due to the loss of weakly bonded water and DMA solvent molecule. The second weight-loss step occurred at 350–400 °C due to the decomposition of the organic ligand in the MOF.



Figure 4. (a) PXRD patterns of simulated and the synthesized **Ni-1**; (b) FT-IR spectra of **Ni-1**; (c) Thermogravimetric analysis of **Ni-1**.

3.3. Investigation of Electrochemical Properties

CV curves of the Ni-1 supercapacitor electrode were recorded at 10–100 mV/s scan rates at 0–0.6 V showed faradaic redox peaks (see Figure 5a), which is indicative of the Faradaic behavior. As the scan rate was increased, no changes in the redox peaks were detected, which indicates excellent rate capability of the Ni-1 based electrode. The GCD test showed that the specific capacitances of the Ni-1 based electrodes were equal to 667, 334, 300, 267, and 240 F/g at 1, 2, 5, 8, and 10 A/g current densities, respectively (see Figure 5b). EIS tests showed straight curves in the low-frequency region (see Figure 5c), which indicates very low diffusion resistance and fast ion diffusion of electrolyte in the Ni-1 based electrode. Such excellent electrochemical properties are very beneficial for excellent capacitive performance. Analysis of the EIS curve in the high-frequency region revealed low resistance (Rs), judging by the small intercept of the arc with the real axis. Thus, the Ni-1 based electrode possessed low intrinsic and ionic resistances as well as excellent contact resistance with the current collector. The retention rate is up to 82% after 5000 cycles at a current density of 1 A/g, which indicates good cycling performance and stability. The capacitance in comparison with those reported ones is depicted in Table 3.



Figure 5. (a) CV curves at different scan rates from 2 mV/s to 100 mV/s and (b) GCD curves at different current densities from 1 to 10 A/g. (c) Electrochemical impedance spectra of Ni-1. (d) Cyclic stability of Ni-1 up to 5000 cycles.

Chemical Compound	Performance	Ref.
$[Co_3(\mu_3-OH)(L)_2(H_2O)_3]^-$	300 F/g	[35]
Co-MOF	206 F/g	[36]
$[Zn_3(NIPA)_3(1,3-dpp)(H_2O)_2 \cdot H_2O]n$	22.8 F/g	[37]

Table 3. Comparation of Ni-1 and other materials.

3.4. Selectivity and Stability of the Sensor

The selectivity of the Ni-1/GCE-based electrode was tested under the presence of 1.0 mM species (Streptomycin, Erythromycin, Norfloxacin, Tetracycline, Tryptophan) with 0.1 M KOH as an electrolyte. The presence of the compounds did not affect the performance of our electrode (see Figure 6b), which indicates excellent anti-interference properties of our Ni-1/GCE.

Figure 6c exhibits the DPV curves of the Ni-1/GCE (recorded at 0.2–0.6 V/s scan rate and 0.2–0.6 V range in 0.1 M KOH) under the presence of 1×10^{-4} – 1×10^{-3} M of sarcosine. The peak current rose linearly (with the correlation coefficient R² = 0.9981, see Figure 4c) as the sarcosine content in the solution was increased, which indicates excellent sensitivity of the electrode. This linear relationship could be expressed as I (A) = 0.95044 × -1.4326. The shelf life of the Ni-1 based GCE was examined by its response (measured every two days) during its storage at 2 °C for two weeks. Our sensor demonstrated the same current after 10 days of storage (see Figure 6e,f), which suggests its excellent storage stability and post-storage performance.





Streptomycin Erythromycin Norfloxacin Tetracycline Tryptophan

Figure 6. Cont.



Figure 6. (a) CV curves of bare GCE and **Ni-1**/GCE (b) The ratios of current peak intensities of in KOH electrolyte solutions after the respective additions of different interferences with a coexisting concentration of 1.0 mM sarcosine (c) DPV curves of the **Ni-1**/GCE with successive additions of sarcosine in 0.1 M KOH, and (d) peak current versus sarcosine concentration plot showing a linear relationship (e,f) peak current of the electrode after two weeks.

4. Conclusions

We developed a novel Ni²⁺-containing metal-organic framework (Ni-MOF) material, which was then used as an active material for sarcosine sensing and for a high-performing supercapacitor (with excellent capacitance 667 F/g at 1 A/g and long-term cycling stability 82% after 5000 cycles). In fact, the sensor was very sensitive to sarcosine (with a low detection limit), and its response was linear relative to the increasing sarcosine contractions. Sarcosine was even detected when other interfering substances (such as Streptomycin, Erythromycin, Norfloxacin, Tetracycline, Tryptophan) were present. Our results strongly indicate that the Ni-MOFs are aspiring materials for next-generation supercapacitors and sensors.

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