

Supporting information

1. Method

1.1 Materials

All chemicals were used without any further purification. Terephthalic acid (H_2BDC), Nickel nitrate hexahydrate $Ni(NO_3)_2 \cdot 6H_2O$, Sodium vanadate ($NaVO_3$) were acquired from Tianjin Yongda Chemical Reagents. *N,N*-Dimethylformamide (DMF) and was purchased from Sinopharm Chemical Reagent Co., Ltd.

1.2. Synthesis of Ni-MOF

The Ni-MOF material was synthesized through an efficient one-step solvothermal method, which offers advantages of mild reaction conditions and high product purity. Specifically, 5.8 mmol (1.686 g) of $Ni(NO_3)_2 \cdot 6H_2O$ and 3.5 mmol (0.581 g) of H_2BDC were precisely weighed and dissolved in 60 mL of DMF to form a homogeneous solution, followed by the gradual addition of 5 mL deionized water and 5 mL absolute ethanol. After vigorous magnetic stirring for 15 minutes, the well-mixed solution was transferred into a 100 mL Teflon-lined stainless steel autoclave. The hydrothermal reaction proceeded at 120°C for 12 h in a constant-temperature oven, followed by natural cooling to ambient temperature. The resulting product underwent three cycles of alternating washing with deionized water and ethanol, before being subjected to vacuum drying at 60°C for 12 h.

1.3. Synthesis of the Ni_xV_y -MOF

Different ratios of Ni_xV_y -MOF were prepared via a one-step solvothermal method. The total molar mass of $Ni(NO_3)_2 \cdot 6H_2O$ and $NaVO_3$ was kept at 5.8 mol. For $Ni_{0.9}V_{0.1}$ -MOF, 5 mmol $Ni(NO_3)_2 \cdot 6H_2O$, 0.8 mmol $NaVO_3$, and 3.5 mmol H_2BDC were dissolved in 60 ml DMF. 5 ml deionized water and 5 ml anhydrous ethanol were added. The mixture was stirred for 15 min and transferred to a 100 ml Teflon-lined autoclave. Reacted in oven at 120°C for 12 h. After natural cooling, the product was washed with deionized water and ethanol 3 times. Dried under vacuum at 60°C.

In addition to the different nickel-vanadium ratios, 4.6mol of nickel nitrate

hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), 1.2mol of sodium vanadate (NaVO_3) and 3.5mol of terephthalic acid (H_2BDC) were dissolved in 60ml of N,N-dimethylformamide (DMF), and then 5ml of deionized water and 5ml of absolute ethanol were added to it. The preparation of $\text{Ni}_{0.8}\text{V}_{0.2}\text{-MOF}$ is the same as the above method.

1.4. Characterization

The morphology, compositions and size of the all samples were investigated using a scanning electron microscope (SEM, HITACHI, SU8010, Japan). Transmission electron microscopy (TEM) images and high-resolution transmission electron microscopy (HRTEM) images were taken on a Tecnai G2 F20 S-Twin electron microscope. The crystal structures of the samples were characterized by an X-ray powder diffractometer (XRD, PANalytical, X'Pert Pro, Netherlands). XPS measurements were performed on a Thermo K-Alpha XPS instrument (Thermo Fisher Scientific, USA).

1.6. Electrochemical measurement

The electrochemical performances of resulting samples were tested by an electrochemical workstation (CHI 660E) in a three-electrode configuration, where resulting products, Pt and Hg/HgO were used as working, counter and reference electrodes, respectively, and 2 M KOH was used as the electrolyte.

Assembly of working electrodes: the synthesised samples, PVDF and super P were mixed and milled in the ratio of 7:2:1, then N-methyl-2-pyrrolidone (NMP) was added to form a slurry. Electrochemical tests including cyclic voltammogram (CV), constant current charge/discharge (GCD) and electrochemical impedance spectroscopy (EIS) were performed on the prepared samples in a three-electrode system. Afterwards, the paste was coated on nickel foam ($1 \times 1 \text{ cm}^2$) and the obtained nickel foam was dried at $80 \text{ }^\circ\text{C}$ for 8 hours. The mass of each electrode was about 0.7 mg.

Based on the charging and discharging times of the GCD curves, the specific capacitance of the test samples was calculated by equation:

$$C_m = \frac{I * \Delta t}{m * \Delta v}$$

where C (F g^{-1}) represents the specific capacity, I (A g^{-1}) represents the current of the

discharge, m (mg) represents the loaded weight of the active material, and Δt (s) represents the time of the discharge.

The energy density (E , Wh kg^{-1}) and power density (P , W kg^{-1}) of the supercapacitor can be calculated in the following equation:

$$E = \frac{1}{2}C\Delta V^2$$

$$P = \frac{E}{\Delta t}$$

C (F g^{-1}) is the mass specific capacitance, ΔV (V) is the voltage window, and Δt is the discharge time.

Table S1. The ratios of $\text{V}^{5+}/\text{V}^{4+/3+}$ and $\text{Ni}^{3+}/\text{Ni}^{2+}$ for the three materials.

Sample	V ⁵⁺ / V ^{4+/3+}	Ni ³⁺ / Ni ²⁺
Ni-MOF	/	1.22
Ni _{0.8} V _{0.2} -MOF	1.28	1.42
Ni _{0.9} V _{0.1} -MOF	1.45	1.69

Table S2. Comparison of Nickel-vanadium metal-organic framework composites as supercapacitor electrodes.

Sample	Capacity (F/g)	Reference
Ni-MOF	318	1
(3D) Ni-MOF	638	2
Cr-doped Ni-MOF	853	3
Mo-doped Ni-MOF	802	4
VNi-MOF NSAs/NF	516.5	5
Ni _{0.9} V _{0.1} -MOF	1182	This work

References

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