Phthalocyanine-Based 2D Conjugated Metal-Organic Framework Nanosheets for High-Performance Micro-Supercapacitors

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1. Introduction

2D conjugated metal-organic frameworks (2D c-MOFs) are emerging as a novel class of conductive redox-active materials for electrochemical energy storage. However, developing 2D c-MOFs as flexible thin-film electrodes have been largely limited, due to the lack of capability of solution-processing and integration into nanodevices arising from the rigid powder samples by solvothermal synthesis. Here, the synthesis of phthalocyanine-based 2D c-MOF (Ni$_3$(CuPc(NH)$_8$)$_3$) nanosheets through ball milling mechanical exfoliation method are reported. The nanosheets feature with average lateral size of $\approx 160$ nm and mean thickness of $\approx 7$ nm ($\approx 10$ layers), and exhibit high crystallinity and chemical stability as well as a p-type semiconducting behavior with mobility of $\approx 1.5$ cm$^2$ V$^{-1}$ s$^{-1}$ at room temperature. Benefiting from the ultrathin feature, the nanosheets allow high utilization of active sites and facile solution-processability. Thus, micro-supercapacitor (MSC) devices are fabricated mixing Ni$_3$(CuPc(NH)$_8$)$_3$ nanosheets with exfoliated graphene, which display outstanding cycling stability and a high areal capacitance up to 18.9 mF cm$^{-2}$; the performance surpasses most of the reported conducting polymers-based and 2D materials-based MSCs.

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Herein, we report the synthesis and delamination of a novel phthalocyanine-based layer-stacked 2D ε-MOF \(\text{Ni}_2[\text{CuPc(NH)}_8]\) with Ni-bis(o-diiminobenzosemiquinonate) redox active centres into nanosheets. The highly crystalline bulk samples with the domain size of \(\approx 200\) nm were prepared by solvothermal synthesis, and presented high specific surface area up to \(690\) m\(^2\) g\(^{-1}\) and high chemical stability in acid/alkaline aqueous solution and other polar solvents. Subsequently, NaCl-assisted ball milling was performed for the mechanical exfoliation of the bulk crystals into nanosheets. The achieved 2D ε-MOF nanosheets feature with average lateral size of \(\approx 160\) nm and mean thickness of \(\approx 7\) nm (corresponding to \(\approx 10\) layers), which can be homogeneously dispersed in DMF for more than 6 months. The conductivity of the 2D ε-MOF nanosheets was determined as 0.01 S m\(^{-1}\) based on a van der Pauw pattern. The Hall effect measurement revealed a p-type semiconducting behavior with mobility of \(\approx 1.5\) cm\(^2\) V\(^{-1}\) s\(^{-1}\) at room temperature. Benefiting from the intrinsic conductivity and porosity, high crystallinity, and ultrathin feature that allows high exposure of active sites and fast ion diffusion as well as facile film processability of the nanosheets samples, MSC devices were fabricated based on Ni\(_2[\text{CuPc(NH)}_8]\)/graphene hybrids, which exhibited outstanding cycling stability and a high areal capacitance up to \(18.9\) mF cm\(^{-2}\). The achieved areal capacitance is superior to most of the reported conducting polymers and 2D materials for MSCs (Table S1, Supporting Information). Our work opens up an avenue on the top-down scalable synthesis of conductive 2D ε-MOF nanosheets toward energy storage applications with high performance.

2. Results and Discussion

2.1. Synthesis and Characterization of Bulk Crystals of Ni\(_2[\text{CuPc(NH)}_8]\)

The bulk Ni\(_2[\text{CuPc(NH)}_8]\) was synthesized through the coordination reaction between 2,3,9,10,16,17,23,24-octaaminophthalocyaninato copper [II] (OAPcCu) ligand (Figure 1a) and Ni(NO\(_3\))\(_2\) \(\cdot\) 6H\(_2\)O in dimethyl sulfoxide (DMSO) at \(60^\circ\) C with the existence of NH\(_3\) \(\cdot\) H\(_2\)O. The achieved Ni\(_2[\text{CuPc(NH)}_8]\) is black powder sample comprising aggregated crystals featuring with Ni-bis(diimine) linkages, which are the known redox active centres for energy storage.\(^{[5b,c]}\) The powder X-ray diffraction (XRD) pattern with Cu K\(_\alpha\) radiation (\(\lambda = 1.54\) Å) of the as-prepared bulk Ni\(_2[\text{CuPc(NH)}_8]\) exhibited peaks at \(2\theta = 4.91^\circ\), 7.01°, 9.89°, 14.81°, 15.63°, 19.80°, 22.17°, and 27.51°, assignable to (100), (110), (200), (210), (300), (310), (400), (420), and (002) lattice planes, respectively, indicative of long-range order within the ab-plane with a center-to-center (neighbouring Cu···Cu) distance of 18.0 Å (Figure 1b, black line and Figure S1, Supporting Information). The broad peak at 27.51°—that is common in

![Figure 1. Characterizations of bulk Ni\(_2[\text{CuPc(NH)}_8]\)](https://www.afm-journal.de)
layered 2D framework materials—suggests less coherence of the stacked Ni$_2$[CuPc(NH)$_8$]$_3$ layers in the out-of-plane direction and corresponds to an interlayer distance of 3.24 Å. Additionally, we performed structural modeling with several possible interlayer arrangements (Figure 1c and Figure S2, Supporting Information) by density functional theory (DFT) method. As shown in Figure 1b, the experimental XRD pattern rules out the AA-eclipsed, AA-inclined as well as AB stacking, and can be reproduced well with AA-serrated geometry, which is energetically most favored (Table S2, Supporting Information). Therefore, the peak at 2751° is assigned to the (002) lattice plane and Ni$_2$[CuPc(NH)$_8$] can be fully defined by square unit cells with $a = b = 18.0$ Å. Field-emission scanning electron microscopy indicated that this MOF presented stacked sheet-like morphologies, where the size of sheets was estimated as 100–300 nm (Figure 1d and Figure S3, Supporting Information). Corresponding energy-dispersive X-ray (EDX) spectroscopy evidenced the uniform element distribution of C, N, Cu, and Ni (Figure S4, Supporting Information). Transmission electron microscopy (TEM) imaging showed the layer-stacked crystallites (Figure 1e and Figure S5, Supporting Information). Fast Fourier transform (FFT) analysis confirmed the (100) crystallographic plane, which agrees well with the XRD result.

Fourier-transform infrared (FT-IR) spectroscopy revealed the disappearance of the N–H stretching vibration band from the monomer OAPcCu in the Ni$_2$[CuPc(NH)$_8$]$_3$ (Figure S6, Supporting Information), which further demonstrated the successful coordination polymerization. The porosity of Ni$_2$[CuPc(NH)$_8$]$_3$ was evaluated by low-pressure CO$_2$ adsorption at 195 K (Figure S7a, Supporting Information), which showed a type I isotherm and a BET surface area of 659 m$^2$ g$^{-1}$. According to the quench solid DFT, the average pore size was calculated as 0.9–1.7 nm. Analogous to CO$_2$, nitrogen adsorption at 77.3 K revealed similar behavior with surface area of 659 m$^2$ g$^{-1}$ and pore size of 0.6–1.5 nm (Figure S7b, Supporting Information). Thermogravimetric analysis (TGA) exhibited no significant weight loss at temperature up to 310 °C in argon (Figure S8, Supporting Information). To determine the chemical stability of Ni$_2$[CuPc(NH)$_8$]$_3$, various organic solvents and aqueous solutions, including DMF, ethanol, water, 1 M KOH, and 1 M HCl were examined; the related XRD patterns demonstrated the integrity of its crystalline structure after immersing for 24 h at room temperature (Figure 1f). Notably, the (100) and (002) peaks were shifted from 4.91° and 2751° to 5.58° and 2706° after soaking in 1 M HCl, respectively, which is attributed to the protonation of imine units in MOFs.

### 2.2. Ni$_2$[CuPc(NH)$_8$]$_3$ 2D $\sigma$-MOF Nanosheets

Ball milling has been demonstrated as an efficient top-down synthetic strategy for preparing graphene, 2D carbon nitrides, and 2D transition metal dichalcogenides nanosheets. Using the low energy ball milling method, the well-defined bulk Ni$_2$[CuPc(NH)$_8$]$_3$ crystals were mechanically exfoliated into nanosheets with 40–50% yield. During the exfoliation, the addition of NaCl as controlling agent played a key role in inserting into the layers, reducing the shear forces and mildly separating the stacked MOF layers (Figure 2a), which resulted in larger-sized nanosheets compared with the contrast flakes obtained in the absence of NaCl. The resultant nanosheets can be homogeneously dispersed in DMF for more than 6 months after mild sonication (Figure 2b and Figure S9, Supporting Information).

Figure 2c shows the XRD pattern of the MOF nanosheets, which present intensive (100) and (002) diffraction peaks. Notably, the shift of the (002) peak from 27.51° to 26.74° correlates with an increase in the c parameter from 3.24 Å to 3.33 Å, indicative of swollen layers after delamination by the milling process. SEM and TEM images (Figure 2d and Figure S10, Supporting Information) reveal thin nanosheets with size distribution ranging from 50 to ~600 nm. Based on the statistical analysis of 220 individual nanosheets, the average size was estimated to be ~160 nm (Figure S11, Supporting Information). High resolution TEM image unambiguously confirmed the square unit cells at the molecular level with lattice parameter of $a = b = 1.7$ nm in the nanosheets (Figure 2e). Atomic force microscopy (AFM) images revealed the mean thickness of the nanosheets as ~7 nm, corresponding to ~10 layers of Ni$_2$[CuPc(NH)$_8$]$_3$ (Figure 2f).

After exfoliation, the composition in the nanosheet samples was remained, as suggested by FT-IR spectroscopy characterizations (Figure S12, Supporting Information). The survey spectrum by X-ray photoelectron spectroscopy further revealed the presence of C, N, Cu, Ni, and O elements (Figure S13, Supporting Information). Deconvolution of the N(1s) and Ni(2p) signals showed three types of N (N$_{CN}$, N$_{CN}$ and N$_{CN}$) atoms. No other counter ions could be detected, which reveals that Ni$_2$[CuPc(NH)$_8$]$_3$ is a charge-neutral material. To investigate the charge transport property, macroscopic conductivity measurement was applied in a van der Pauw configuration on the assembled nanosheets (Figure S14, Supporting Information). Linear current–voltage ($I$–$V$) curves confirm the ohmic contact during the whole measurement (Figure S15, Supporting Information); temperature ($T$)-dependent measurement indicated a semiconducting non-linear drop of conductivity ($\sigma$) upon cooling from 310 to 100 K (Figure 2g). Based on the above data, we obtained a conductivity of $\approx$0.01 S m$^{-1}$ at 300 K. As shown in the inset of Figure 2g, the plot of $\sigma$ versus $T^{-1/4}$ over the measured temperature region can be well fitted to the Motz variable range hoping (Mott–VRH) model ($\sigma(T) = \sigma_0 \exp[-(\frac{T}{T_0})^{1/4}]$), which describes the temperature dependence of hopping conductivity in the polycrystalline nanosheets. Hall effect measurement was applied under a magnetic field (~4 to 4 T) perpendicular to the sample plane at 300 K. Ni$_2$[CuPc(NH)$_8$]$_3$ nanosheets exhibit a linear relationship of Hall resistance to the magnetic field (Figure 2h); moreover, the polarity indicates a p-type semiconducting behavior with carrier (holes) density of $\approx$6 x 10$^{14}$ cm$^{-3}$ and mobility of 1.6 ± 0.2 cm$^2$ V$^{-1}$ s$^{-1}$.

### 2.3. Ni$_2$[CuPc(NH)$_8$]$_3$-Based MSCs

Benefiting from the intrinsic conductivity and porosity, high crystallinity, and ultrathin feature that provide sufficient accessible active sites and fast ion diffusion as well as facile film processability, 2D $\sigma$-MOF nanosheets hold great potential application in flexible energy storage devices. As a proof of concept,
Ni$_2$[CuPc(NH)$_8$] nanosheets were mixed with electrochemically exfoliated graphene (EG, conductive platform, exfoliation details seen in Supporting Information) nanosheets (in different mass ratios) and filtered subsequently with a home-made mask into interdigital electrodes for flexible MSCs (Figure 3a,b and Figures S16 and S17, Supporting Information). The electrochemical behavior of MSCs based on pure EG thin film and Ni$_2$[CuPc(NH)$_8$]/EG-x (x represents the mass ratio of graphene/Ni$_2$[CuPc(NH)$_8$]) were investigated firstly by cyclic voltammetry (CV) measurement. It is clearly shown that the integral area of CV curve for Ni$_2$[CuPc(NH)$_8$]/EG-2 based MSC (abbreviated as Ni$_2$[CuPc(NH)$_8$]/EG-2) presents the maximum value compared with other fabricated devices (Figure 3c). Therefore, the weight ratio of graphene/Ni$_2$[CuPc(NH)$_8$] = 2 was found to be the optimized one for the construction of Ni$_2$[CuPc(NH)$_8$]/EG-based MSC electrode. The CV profiles of Ni$_2$[CuPc(NH)$_8$]/EG-2 display the nearly rectangular shape at scan rates from 2 to 50 mV s$^{-1}$ (Figure 3d), resulting from the high specific surface area and well-defined structure of Ni$_2$[CuPc(NH)$_8$]. In addition, the capacitive behavior of Ni$_2$[CuPc(NH)$_8$]/EG-2 was investigated through galvanostatic charge–discharge (GCD) measurement at various current densities of 0.04–0.4 mA cm$^{-2}$ (Figure 3e).

Based on the optimized conditions, Ni$_2$[CuPc(NH)$_8$]/EG-2 delivered an areal capacitance of 18.9 mF cm$^{-2}$ at a current density of 0.04 mA cm$^{-2}$ (Figure 4a), which is higher than those of recently reported conducting polymers-based and 2D materials-based MSCs (Table S1, Supporting Information), such as...
as benzene-bridged polypyrrole (0.35 and 0.95 mF \( \text{cm}^{-2} \)),[14] azulene-bridged coordination polymer (0.1 mF \( \text{cm}^{-2} \)),[15] graphene/carbon nanotube (CNT) (6.1 and 2.16 mF \( \text{cm}^{-2} \)),[16] thiophene/graphene (3.9 mF \( \text{cm}^{-2} \)),[17] phosphorene/graphene (9.8 mF \( \text{cm}^{-2} \)),[18] 2D c-MOF/graphene (LSG/Ni-CAT MOF, 15.2 mF \( \text{cm}^{-2} \)),[19] covalent organic framework/CNT (15.2 mF \( \text{cm}^{-2} \)) and \( \text{V}_2\text{O}_5 \)/graphene (3.9 mF \( \text{cm}^{-2} \)).[21] Moreover, this device exhibited excellent cycling stability with 91.4% of capacitance retention after 5000 charge/discharge cycles (Figure 4b). The cycling stability agrees well with the absence of any morphological changes during the cycling processes. After the cycling measurements, only slight increase in the equivalent series resistance was observed (Figure S18, Supporting Information), which might be resulted from the solvent evaporation of the electrolyte. To further demonstrate the overall performance of \( \text{Ni}_2[\text{CuPc}(\text{NH})_8] \)/EG-2, Ragone plots were presented in Figure 4c. Notably, our fabricated MSCs delivered an ultrahigh areal power density of 168 mW cm\(^{-2}\) at 1.1 \( \mu \text{Wh cm}^{-2} \), which is comparable to those of recently reported graphene-based MSCs.[16,20,29] conducting polymer-based MSCs,[21] and carbon-based MSCs.[14] In addition, \( \text{Ni}_2[\text{CuPc}(\text{NH})_8] \)/EG-2 also provided high areal energy density of 1.7 \( \mu \text{Wh cm}^{-2} \) at 16 mW cm\(^{-2}\), which is superior to that of carbon-based MSCs (0.1–1 \( \mu \text{Wh cm}^{-2} \)).[16,24]

On the other hand, flexibility and variable working window are crucial for portable and wearable energy storage devices. As depicted in Figure 4d,e, no obvious change of CV curves was observed at different bending angles, highlighting the excellent mechanical flexibility and electrochemical stability of the device. Even alternating the flat and bent states, our \( \text{Ni}_2[\text{CuPc}(\text{NH})_8] \)/EG-2 based MSCs maintained 86.2% of their initial performance after 3000 cycles (Figure 4f). Moreover, different working windows and prolonged discharging time could be achieved by the series or parallel connection of as-fabricated MSCs, demonstrating the good integration capability (Figure S19, Supporting Information).

3. Conclusion

In summary, we demonstrated the efficient synthesis and delamination of phthalocyanine-based 2D c-MOF \( \text{Ni}_2[\text{CuPc}(\text{NH})_8] \) into ultrathin nanosheets by top-down ball milling exfoliation. The ultrathin \( \text{Ni}_2[\text{CuPc}(\text{NH})_8] \) nanosheets possess intrinsic conductivity, porosity and high crystallinity as well as high chemical stability. For the utilization as energy storage material, the \( \text{Ni}_2[\text{CuPc}(\text{NH})_8] \) 2D c-MOF based MSC device exhibited outstanding mechanical flexibility, cycling stability, and a high areal capacitance of 18.9 mF \( \text{cm}^{-2} \). Our work provides a guideline for the top-down exfoliation of 2D c-MOF nanosheets and sheds light on realizing their function in flexible MSCs. By further modifying the chemical structures with redox active sites and improving the crystallinity and porosity as well as conductivity, we highlight the great potential of 2D c-MOFs for developing flexible electronic devices.
4. Experimental Section

Synthesis of Bulk Ni$_2$[CuPc(NH)$_8$] 2D c-MOF: All chemicals were purchased from commercial suppliers and used without further purification. 2,3,9,10,16,17,23,24-octaamino-phthalocyaninato copper (II) (OAPcCu) was synthesized according to the known procedure.$^{25}$ OAPcCu (5.00 mg) was dissolved in dimethyl sulfoxide (DMSO, 3 mL) and ammonia solution (50% v/v, 0.1 mL). The mixture was stirred at 60 °C in a sand bath under air. Then Ni(NO$_3$)$_2$·6H$_2$O (3 mg) in DMSO (1 mL) and ammonia solution (50% v/v, 0.1 mL) was added at this temperature. The reaction mixture was stirred for 30 min and stand for 8 h at 60 °C. After cooling to room temperature, the obtained solids were filtered, washed with N,N-dimethylformamide (DMF), H$_2$O, and acetone, respectively. The solids were stirred in deionized water (20 mL) for 6 h. After cooling to room temperature, the obtained solids were filtered, washed with N,N-dimethylformamide (DMF), H$_2$O, and acetone, respectively. Then Ni(NO$_3$)$_2$·6H$_2$O (3 mg) in DMSO (1 mL) and ammonia solution (50% v/v, 0.1 mL) was added at this temperature. The reaction mixture was stirred for 30 min and stand for 8 h at 60 °C. After cooling to room temperature, the obtained solids were filtered, washed with N,N-dimethylformamide (DMF), H$_2$O, and acetone, respectively. The solids were stirred in deionized water (20 mL) for 6 h, and water was exchanged 6 times. Bulk Ni$_2$[CuPc(NH)$_8$] 2D MOF was collected by filtration, washed with acetone, and dried under vacuum at 100 °C overnight as black powder.

Synthesis of Ni$_2$[CuPc(NH)$_8$] Nanosheets: To Ni$_2$[CuPc(NH)$_8$] (0.1 g) and NaCl (1 g) in a 45 mL grinding bowl, steel balls (50 g) were added under argon. Milling was performed for 6 h at 100 rpm. After delamination, the nanosheets were washed with deionized water for 6 times and then DMF by centrifugation (5000 rpm, 5 min). The resultant material was dispersed into DMF by mild sonication for 15 min in an ice bath. After centrifugation at 2000 rpm for 10 min to remove thick-layered flakes, homogeneous Ni$_2$[CuPc(NH)$_8$] dispersion was obtained and used for characterization as well as device fabrication.

Ni$_2$[CuPc(NH)$_8$]/Graphene Hybrid and Device Fabrication: EG dispersion (≈0.3 mg mL$^{-1}$) and Ni$_2$[CuPc(NH)$_8$] dispersion (≈0.3 mg mL$^{-1}$) in DMF were mixed with different volume ratios and sonicated for 10 min. A home-made mask with 8 interdigital fingers (width of 1 mm, length of 10 mm, and interspace of 1 mm) was covered on the polyvinylidene fluoride (PVDF, 0.2 μm, 47 mm in size) membrane filter. Then, the mixture was dropped into the channels of the mask and vacuum-filtrated to obtain the hybrid film with interdigital pattern. Immediately, the resultant mid-wet pattern was directly transferred onto a flexible polyimide (PI) substrate. Afterwards, PVA/LiCl gel electrolyte (1 mL) was drop-casted onto the surface of interdigital electrode and solidified overnight. Finally, all solid-state Ni$_2$[CuPc(NH)$_8$]/EG-based in-plane MSCs were fabricated. For comparison, the EG film-based MSCs were prepared under the similar experimental condition without adding MOF. The PVA/LiCl gel electrolyte was prepared by mixing PVA (molecular weight 85 000-124 000, 2 g) and LiCl (4.24 g) in deionized water (20 mL), and heated at 85 °C until forming a clear solution.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

2D conjugated metal-organic frameworks, energy storage, microsupercapacitor, milling exfoliation, ultrathin nanosheets

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