Enhanced electrical properties and restrained thermal transport in p- and n-type thermoelectric metal-organic framework hybrids

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Materials

Triphenylene-2,3,6,7,10,11-hexamine 6HCl (HATP6·HCl) was purchased from Shanghai Tensus Biotech CO., LTD. Nickel chloride hexahydrate (NiCl₂·6H₂O), absolute ethanol were purchased from the Energy Chemical company. 22-SWNT (purity >95%) was obtained from the XFNANO company. Concentrated aqueous ammonia (NH₃·H₂O), ethanol, deionized water (H₂O), dimethyl sulfoxide (DMSO), and diethyl ether were purchased from HC Stark (Germany). All the chemicals were used without further purification.

Synthesis of Ni₃(HITP)₂

 $Ni_3(2,3,6,7,10,11$ -hexaiminotriphenylene)₂ ($Ni_3(HITP)_2$) was synthesized by a modified method according to the previously reported literature.¹ A quantity of 95.7 mg of NiCl₂·6H₂O and 141.9 mg of HATP·6HCl were firstly dissolved in 60 mL of deionized water in a 100mL round-bottom flask. After added 1.5 mL of concentrated aqueous ammonia, the mixture was stirred under continuous air bubbling at 65°C with an oil bath. On this basis, the reaction solution was switched to an inert atmosphere (N₂ protection) for another 2 h. The obtained black precipitate was centrifuged in water, ethanol, and acetone. Finally, the solid was dried under a 40°C for further vacuum oven at use. Anal. Calcd for Ni₃(C₁₈H₁₂N₆)_{1.9}·2(C₃H₆O)·2H₂O. Calculated: C, 51.21%; H, 3.73%; N, 19.46%; Cl, 0.00%. Found (%): C, 51.24%; H, 3.78%; N, 19.41%; Cl, <0.02%.

Synthesis of Ni₃(HITP)₂/PEI-CNT

A quantity of CNT and sodium dodecylbenzenesulfonate (SDBS) with a weight ratio of 1:5 was added in dimethyl sulfoxide (DMSO). The mixture was then sonicated for 2h with a pen-type ultrasonicator and 8h with a bath ultrasonicator. Then, a certain amount of PEI (PEI/DMSO at 5.0 wt%) was added to the CNT solution and the solution was stirred for 2h. After that, the as-synthesized Ni₃(HITP)₂ powder was dispersed into the PEI-CNT solution by ultrasonication. Finally, the solid was collected through suction filtration and washed thoroughly by using DMSO and EtOH. All the samples were dried under a vacuum and compressed for further use.

Fabrication of the thermoelectric generator

The prototype TE generator was assembled by alternately connecting eight legs n-type Ni₃(HITP)₂/PEI-CNT₃₀ and eight legs p-type Ni₃(HITP)₂/CNT₃₀ pellets in series. The schematic design of the TEG module in this study was presented in Figure S6. TE generator was tested at different temperature gradient (ΔT) with a Keithley 2401 source meter.

Measurements

Both the electrical conductivity and the Seebeck coefficient reported in this work were measured by using the Netzsch SBA-458 system with Ar (99.999%) gas protection. The electrical conductivity was carried out by the 4-point-measurement method. Two thermocouples and two current pins are in contact with the sample. The sample is located on a sample supporter and in close contact with four probes, with two current pins on the outside and two voltage pins in the middle. While the Seebeck coefficient was calculated by $S = -\Delta V/\Delta T$, where ΔV is the in-plane TE voltage gradient and ΔT is the temperature gradient generated by two micro heaters in both sample directions. For the air stability test, all the samples were stored in the ambient environment after being prepared. The thermoelectric properties of the samples were recorded at regular intervals under the protection of N₂. The thermal conductivity was measured by LFA467 Thermal Conductivity Measurement. All the samples were pressed (D=12.7 mm for the electrical conductivity, Seebeck coefficient, and thermal conductivity measurement) under a pressure of 20 MPa for 15min ($\rho \approx 0.85$ g/cm³ for Ni₃(HITP)₂.

Characterization

X-ray diffraction (XRD) analysis was carried out by Bruker diffractometer (D8-Discover, German), Cu-Kα radiation (0.15418 nm) at a scanning rate of 2° min⁻¹. Scanning Electron Microscope (SEM) images were collected by Gemini SEM 500 scanning electron microscope operating at 10 kV. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Fisher ESCALAB Xi+. Fourier Transform Infrared (FTIR) spectra (KBr pellets) were recorded on a Nicolet 6700 spectrophotometer. Hall measurements were performed according to LakeShore 7707A measured system to obtain the electronic carrier mobility and concentration. With the van der Pauw geometry with 1 cm × 1 cm square samples, sheet resistances, and Hall voltages were measured under 1 T. Samples were degassed for more than 8 h at 80 °C under the vacuum. The thermogravimetric analysis (TGA) was operated on TA Instruments SDT-Q600 with a heating rate of 20 $^{\circ}$ C min⁻¹ under N₂ conditions.



Figure S1. The Grazing-Incidence Wide-Angle X-ray Scattering (GIWAXS) for Ni3(HITP)2 sample. The corresponding scattering profiles in (b) q_{xy} and (c) q_z directions.



Figure S2, FTIR spectra of (a) 2,3,6,7,10,11-hexaaminotriphenylene hexahydrochloride (HATP·6HCI) HATP, Ni₃(HITP)₂, CNT, PEI-CNT and the n-type hybrid Ni₃(HITP)₂/PEI-CNT with CNT concentration of 5 wt.% and 30 wt.% and (b) Ni₃(HITP)₂, CNT and p-type Ni3(HITP)2/CNT hybrids with CNT concentration of 5 wt.% and 30 wt.%.

FTIR spectra of the Ni₃(HITP)₂/PEI-CNT hybrid nanocomposites with a different ratio between the Ni₃(HITP)₂ and CNT show the characteristic peaks of both parent materials, confirming the successful synthesis of the hybrid nanocomposites. Ni₃(HITP)₂ exhibits similar signals for the organic legend HATP, whose characteristic peaks are at 3331 cm⁻¹ (N–H stretch) which shifts to 3428 cm⁻¹ (N-Ni stretch), 2980 cm⁻¹ (C–H stretch of the aromatic rings), 1633 cm⁻¹ (C=C stretch arising from the benzene ring), 1211 cm⁻¹ (C-C stretch) and 1099 cm⁻¹ (C-N stretch).² While the characteristic peaks of C-C stretch around 3433 cm⁻¹ were attributed to CNT. Furthermore, we found that increasing the CNT content in the hybrid nanocomposites, increases the intensities of the CNT-related signals.



Figure S3. The PXRD patterns of HITP, PEI-CNT, Ni3(HITP)2, Ni3(HITP)2/PEI-CNT-SDBS₅, and Ni3(HITP)2/PEI-CNT-SDBS₃₀.

The crystalline structures of the synthesized Ni3(HITP)2/PEI-CNT with different CNT content were determined by XRD Figure S3. The Ni₃(HITP)₂/PEI-CNT hybrid nanocomposites show preservation of the crystallinity of the CNT and Ni₃(HITP)₂ and the relative intensities and position of all the peaks are consistent with that of the standard pattern.¹ All the diffraction signals of the parent materials can be readily indexed, which confirms the synthesis of the nanocomposites.



Figure S4, Theoretical thermal conductivity of a three-dimensional nanotube network is plotted when thermal contact conductance varies from 0.01 to 10 pW/K.



Figure S5, *ZT* of Ni₃(HITP)₂ and its hybrids, Ni₃(HITP)₂/PEI-CNT (red) and Ni₃(HITP)₂/CNT (blue) as a function of CNT concentration at room temperature.



Figure S6 Temperature-dependent ZT of $Ni_3(HITP)_2$ and its hybrids, $Ni_3(HITP)_2/PEI-CNT$ and $Ni_3(HITP)_2$.



Figure S7 Temperature-dependent (a) electrical thermal conductivity; (b) lattice thermal conductivity of $Ni_3(HITP)_2$ and its hybrids, $Ni_3(HITP)_2/PEI$ -CNT and $Ni_3(HITP)_2$.



Figure S8, Temperature-dependent (a) Seebeck coefficient; (b) electrical conductivity CNT and PEI-CNT.



Figure S9, TGA curve for Ni3(HITP)2 in N2 at the rate of 10 °C/min

Thermogravimetric analysis (TGA) of bulk, freshly prepared Ni₃(HITP)₂, shown in Figure S4, suggested that heating at 110 °C would eliminate all water, and samples used for electrical measurements were dried accordingly. The pressed pellets of Ni₃(HITP)₂ were prepared by pressing powder samples under 20 MPa at room temperature for 15 min with a uniaxial hydraulic press. The obtained pellets are circular plates with a diameter of 12.7 mm and thickness ranging from 300 µm to 1 mm. All thermoelectric properties were measured in a vacuum (10⁻⁵ to 10⁻⁴ torr) with the pressed pellets desolvated at 100°C for 15 min.

References

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