Supporting Information
Constructing interfacial potential barrier via a gradient configuration: an effective method to enhance energy-filtering effect

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Fig. S1 N₂ adsorption–desorption isotherms of 35 % TiO₂-65 % CF.

Figure S2 (a) TGA of 35 % TiO₂-65% CF, 25 % TiO₂-75% CF and 15 % TiO₂-85% CF. (b) FTIR of 35 % TiO₂-65% CF.

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Figure S3 Raman spectrum and XRD pattern of TiO$_2$ film before and after 700 K sintering treatment.

Figure S4 TEM image of 4% PVP-96% MWCNT.
Figure S5 SEM image of 45% TiO$_2$-55% CF.

Figure S6 SEM image of 20% PANI-80% (35% TiO$_2$-65% CF).

Figure S7 (a) $\sigma$ and (b) $S$ for 20% PANI-80% (35% TiO$_2$-65% CF) and 50% PANI-50% (35% TiO$_2$-65% CF).
Fig. S8 Ratio of electrical conductivity of the 20 % PANI-80 % (35 % TiO₂-65 % CF) to its initial values with bending cycles and (b) exposure time under 373 K/80 % humidity conditions.

Extended discussions

Extended discussions 1 Material preparation and performance characterization

Preparation of carbon nanotube network
The multi-wall carbon nanotube network (CF) is prepared by a chemical vapor deposition method. And then, a 30 min ultrasonic cleaning using the HCL solution (4mol/L) is performed to remove the residual metal catalyst. Subsequently, a 700 K sintering treatment with the period of 0.5 h is also employed to remove the residual catalyst. Finally, the CF is naturally dried under the vacuum environment for 24 h. The as-prepared CF shows a porous morphology with the character thickness of about 15 μm.

Preparation of PVP-CF
The CF is soaked in the 200 ml Polyvinyl Pyrrolidone (PVP) solution, and ultrasonically disperses for 24 h. Four kinds of PVP solution with different concentration (3, 6, 9 and 12 mg/L) is used to adjust the content of PVP layer on the CF. And then, a vacuum-assisted extraction filtration process is performed to collect the PVP-CF by using the 200 nm cellulose acetate membrane. Subsequently, the free PVP is removed by a repeated alcohol washing.
**Preparation of TiO$_2$-CF**

The titanium isopropylate solution (5 mL) is added into the alcohol (45 mL) and nitric acid (15 mL) mixed solution (Ph=2) and mechanical stirring for 60 mins to get a titanium isopropylate mixed solution. The TiO$_2$ content is controlled by regulating the volume of titanium isopropylate mixed solution. Herein, the titanium isopropylate mixed solution with volume of 8 11, 14 and 17 mL is employed in hydrothermal reaction. Subsequently, put the 5 g PVP-CF into the mixed solution and mechanical stirring for 180 min. After a completely cleaning by alcohol, a hydrothermal method with the temperature and period of 700 K and 30 min is employed to make TiO$_2$ grow on the CF and remove the PVP component.

**Preparation of PANI-(TiO$_2$-CF)**

PANI powder is prepared by the chemical polymerization of aniline monomers with hydrochloric acid (HCl) and ammonium persulfate (APS) as the dopant and the oxidant. The resulting PANI powder is soaked in 1 M ammonia solution and stirred for 48 h at 300 K to prepare the emeraldine-based PANI. The resulting solution is filtered and washed with deionized water and ethanol, and naturally dried in a vacuum environment for 24 h. The as-synthesized PANI powder is doped with camphorsulfonic acid (CSA) by a solid state reaction at a mole ratio of 1:0.6. The as-prepared 2g or 4g CSA-doped PANI is completely dissolved in 300 ml m-cresol by continuously mechanical stirring for 24 h. And then, 20 g of TiO$_2$-CF is added to the solution and stirred for 6 h to fabricate the PANI-(TiO$_2$-CF). The resulting solution is filtered and washed with deionized water and ethanol, and naturally dried in a vacuum environment for 12 h.

**Morphology characterization**

Field-emission scanning electron microscopy (FE-SEM, GeminiSEM 500) with energy dispersive X-ray spectroscopy (EDS) and high-resolution transmission electron microscopy (HRTEM) (HRTEM, JEOL JEM-F200) with selected-area electron diffraction (SAED) are carried out to determine the microstructures of the
materials. The crystal structure is identified by the X-ray diffraction (XRD, Bruker D8 ADVANCE) using Cu Kα radiation (0.154056 nm) with the a scan rate of 1°/s in the 2θ range of 10-90°. X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) (PHI-5000 VersaProbe, ULVAC-PHI) using a monochromatic Al Kα and He source are performed to obtain chemical information and work function of the samples. The Fourier-transform infrared (FT-IR, Bio-Rad FTS-1465) spectra are investigated with an average of 32 scans in the 400–2000 cm⁻¹ spectral region. Thermogravimetric analysis (TGA, TGA-2050, TA Instruments) is used to examine the thermal degradation of the samples under a N₂ atmosphere at a heating rate of 10 K min⁻¹. Electron paramagnetic resonance (EPR) measurement is performed with a Bruker EMX-6/1 spectrometer at 9.424 GHz (120 K) or 9.868 GHz (300 K) using a 100 kHz field modulation and a 0.5 G standard modulation width.

**Thermoelectric characterization**

The in-plane \( k \) is measured by both the 3 \( \omega \) method and laser flash method. Here, we propose a specific case for the \( k \) measurement of CF by the 3 \( \omega \) method. The freestanding CF is firstly placed on the Si substrate. And then, the SiNₓ with the thickness of 100 nm is deposited on the film by the PECVD as the insulating layer. Finally, the platinum lines with length (\( l \)) of 3 mm, width (\( a \)) of 500 μm and 20 μm, thickness of 200 nm are patterned on the SiNₓ layer by using photolithography method (SUSS MA-6 Mask Aligner) as the heater. The schematic diagram for the 3\( \omega \) measurement system is shown in Fig. S9.

![Figure S9 Schematic diagram for the thermal conductivity measurement by the 3\( \omega \) method.](image-url)
When using the 500 μm platinum line to heat the sample, the thermal conduction is quasi-one dimensional along the cross-plane direction due to the width of heater is quite larger than the thickness of sample. The cross-plane thermal conductivity \( k_\perp \) of the film is calculated by,

\[
k_\perp = \frac{P h_f}{a l \Delta T_f}, \tag{S1}
\]

where \( P \) is the power dissipations of the sample. \( h_f \) is the sample thickness. \( l \) is the length of the platinum line. \( \Delta T_f \) temperature degradation in sample, which could be calculated as follows,

\[
\frac{\Delta T_f}{P} = \frac{\Delta T_s}{P_s} - \frac{\Delta T_r}{P_r}, \tag{S2}
\]

where \( \Delta T_f \) is the temperature drop in the sample. \( \Delta T_s \) and \( \Delta T_r \) are the temperature oscillations of the platinum line heaters on the sample group and reference group. \( P_s \) and \( P_r \) are the corresponding power dissipations. The \( \Delta T_s \) and \( \Delta T_r \) are determined by

\[
\Delta T_s or r = 2R \frac{dT V_{3\omega}}{dR V_{1\omega}}, \tag{S3}
\]

where \( R \) and \( \frac{dR}{d\theta} \) are the resistance and temperature coefficient of resistance of the platinum heater line. \( V_{3\omega} \) and \( V_{1\omega} \) are the third and first harmonic voltages.

When using the 20 μm platinum line, which is nearly comparable to the thickness of sample, the heat transports along both cross-plane and in-plane direction. The temperature degradation relates to the narrow (\( \Delta T_{2D} \)) and wide (\( \Delta T_{1D} \)) platinum line are shown as follows

\[
\frac{\Delta T_{2D}}{\Delta T_{1D}} = \left( \frac{k_\perp}{k_\parallel} \right)^{1/2} \frac{a}{h_f} \frac{K(\beta)}{K'(\beta)}, \tag{S4}
\]

where \( k_\parallel \) is the in-plane thermal conductivity. \( K(\beta) \) is the complete elliptical integral of the first kind, and \( K'(\beta) \) is corresponding complementary integral. The \( \beta \) is given by,

\[
\frac{1}{\beta} = \cosh \left[ \frac{\pi a}{4 h_f} \left( \frac{k_\perp}{k_\parallel} \right)^{1/2} \right], \tag{S5}
\]

The detailed data in thermal conductivity measurement of CF is exhibited in Fig.
S10. The measured \( k_\perp \) is 0.024 W m\(^{-1}\) K\(^{-2}\). The ratio of \( \Delta T_{1D}/\Delta T_{2D} \) is 0.56 and fits to equation S4, the \( k_\parallel/k_\perp \) is 1.46. Thus, the \( k_\parallel \) is 0.035 W m\(^{-1}\) K\(^{-2}\).

Figure S10 Thermal conductivity measurement of CF. (a) Temperature coefficient of resistance of the platinum line. (b) Temperature oscillation amplitudes of 500 μm platinum line in the \( \Delta T_{1D} \) measurements. (c) Temperature oscillation amplitudes of 20 μm platinum line in the \( \Delta T_{2D} \) measurements. (d) Relationship between \( \Delta T_{1D}/\Delta T_{2D} \) and \( k_\parallel/k_\perp \) as described in Eq. (S4).

For the flash method, the in-plane \( k \) is measured by a commercial device (LFA 467, NETZSCH, Germany), based on the \( k = \alpha \rho C_p \), where \( \alpha \) is the thermal diffusivity, \( \rho \) is the density of the material and \( C_p \) is the specific heat. The in-plane \( \alpha \) is measured by a commercial device (LFA 467, NETZSCH, Germany), the \( C_p \) is obtained through the differential scanning calorimetry (NETZSCH, Germany) analysis, in which the sample is heated from 20 to 120 °C at a rate of 10 °C min\(^{-1}\) in a N\(_2\) atmosphere.

The in-plane electrical resistivity of the composite is measured by a classical four-point probe method (Keithley 2400 source meter). The Carrier concentration (n) and the Hall carrier mobility (\( \mu \)) are measured by Hall measurement (Nanometrics...
The Seebeck coefficient is measured using lab-made equipment as schematically illustrated in Fig. S11. The hot and cold end copper bars are both heated up steadily and a constant temperature gradient $\Delta T$ is established along the in-plane direction of the sample. The potential difference $\Delta V$ is measured by a Keithley 2182 voltmeter with two Pt wires welded to the hot and cold end copper bar. The Seebeck coefficient is obtained by the equal $S = -\Delta V/\Delta T$. In addition, the $S$ is also tested by the commercial instrument ZEM-3 to confirm the accuracy of our measurement. Selecting the constantan as the reference samples, $S$ of -36.6 $\mu$V K$^{-1}$ is obtained by the ZEM-3 and $S$ of -35.8 $\mu$V K$^{-1}$ is obtained by our instrument, illustrating a relative error (2.18 %) less than 3 %.

![Fig. S11 Schematic diagram for the Seebeck coefficient measurement apparatus.](image)

**Extended discussions 2 Parallel and series connected model**

Electric conductivity predicted by parallel model

$$\sigma_{\text{parallel}} = \sigma_{\text{TiO}_2} x + \sigma_{\text{CF}} (1 - x), \quad (S6)$$

Electric conductivity predicted by series model

$$\sigma_{\text{series}} = \frac{\sigma_{\text{TiO}_2} \sigma_{\text{CF}}}{\sigma_{\text{TiO}_2} (1 - x) + \sigma_{\text{CF}} x}, \quad (S7)$$

Seebeck coefficient predicted by parallel model

$$S_{\text{parallel}} = \frac{S_{\text{TiO}_2} \sigma_{\text{TiO}_2} x + S_{\text{CF}} \sigma_{\text{CF}} (1 - x)}{\sigma_{\text{TiO}_2} x + \sigma_{\text{CF}} (1 - x)}, \quad (S8)$$

Seebeck coefficient predicted by series model
\[ S_{\text{series}} = \frac{S_{\text{TiO}_2} \sigma_{\text{CF}} x + S_{\text{CF}} \sigma_{\text{TiO}_2} (1 - x)}{\sigma_{\text{CF}} x + \sigma_{\text{TiO}_2} (1 - x)}, \]  
\text{(S9)}

Thermal conductivity predicted by parallel model

\[ k_{\text{parallel}} = k_{\text{TiO}_2} x + k_{\text{CF}} (1 - x), \]  
\text{(S10)}

Thermal conductivity predicted by series model

\[ k_{\text{series}} = \frac{k_{\text{TiO}_2} k_{\text{CF}}}{k_{\text{TiO}_2} (1 - x) + k_{\text{CF}} x} \]  
\text{(S11)}

where, the subscripts of parallel or parallel represent the parameters calculated based on the parallel and series connected model. \( x \) is the volume fraction of TiO\(_2\) component.

**Extended discussions 3**

He I \((h\nu=21.2 \text{ eV})\) is used as the energy source for the UPS measurements, and the UPS data of the A-R mixed phase, anatase phase and MWCNT are shown in Figs. S12 (a), (b) and (c). The relationship between cutoff energy \((E_{\text{cutoff}})\) and Lowest Unoccupied Molecular Orbital (HOMO) can be expressed as shown in the following equations

\[ \Phi = h\nu - (E_{\text{cutoff}} - E_f), \]  
\text{(S12)}

The Fermi level \((E_f)\) is placed below the vacuum level \((E_v)\) by the magnitude of the \(\Phi\) and the valence band edge is then placed below the \(E_f\) by the magnitude of the HOMO. We also use Tauc plots to determine the bandgap \((E_g)\) of each component as shown in shown in Figs. S12 (d), (e) and (f). By combing the \(E_g\) with the HOMO, the conduction band edge \((E_c)\) and the electron affinity \((\chi)\) are also derived, thereby completing the band structure.
Fig. S12 UPS results of the onset and cutoff energy boundaries of (a) A-R mixed phase, (b) anatase phase and (c) MWCNT. Tauc plots for (d) A-R mixed phase, (e) anatase phase and (f) MWCNT. The inset shows the corresponding optical reflectance spectra.