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Synergistic high entropy alloy-polymer interfaces: A leap in solid-state cooling

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The electrocaloric effect research field faces critical challenges, including enhancing material performance under low electric fields, improving device efficiency, and addressing practical application issues such as system integration and stability. Recently, Cai et al. achieved a 55 $Jkg^{-1}K^{-1}$ electrocaloric entropy change at 80 MV/m via integrating high-entropy-alloy magnetic nanoparticles into electrocaloric polymers. This interface-engineered composite enhances entropy while decoupling thermal and mechanical drives, enabling efficient solid-state refrigeration.

The advancement of solid-state cooling technologies, such as electrocaloric (EC), magnetocaloric, and elastocaloric systems, has emerged as a critical pathway to address energy sustainability and environmental concerns.[1–3] Among these, EC cooling distinguishes itself through unique advantages: unlike magnetocaloric systems, which require bulky electromagnets, or elastocaloric devices, which depend on mechanical stress cycles, EC technology utilizes electric fields to drive entropy changes, offering superior compactness, rapid response, and precise thermal management.[2] These characteristics make EC materials ideally suited for applications in miniaturized electronics, medical devices, and integrated circuits that require precise localized temperature control, which has led to growing research interest in this field. Recent advances have highlighted strategies such as defect modification, interface optimization, supercritical transitions, high-entropy engineering, and nanocomposite design to enhance the electrocaloric effect.[4–6] These material innovations, coupled with novel device architectures, are accelerating the commercialization of EC technology for sustainable cooling solutions.

Despite significant progress in EC materials, the practical deployment of electrocaloric (EC) refrigeration is constrained by several critical bottlenecks: high electric fields required to achieve substantial entropy changes (ΔS) and inadequate thermal management due to low thermal conductivity and polarization fatigue under cyclic loading. Additionally, the integration of mechanical cycling units into EC coolers often results in complex device designs that do not directly contribute to the EC effect, increasing the overall system complexity and reducing energy efficiency.[4] In a recent study published in *Cell Reports Physical Science*, Cai et al. (2025) address these challenges by integrating high-entropy alloy (HEA) magnetic nanoparticles (MNPs) into relaxor ferroelectric polymers P(VDF-TrFE-CFE), achieving a record-breaking ΔS of 55 J $kg^{-1}K^{-1}$ at 80 MV/m while enabling magnetic-field-driven actuation of the cooling cycle.[7] This dual-functional design, reminiscent of the Gd-Co-Al nano-glass-hydride approach that combines giant magnetocaloric effects with mechanical robustness,[3] not only enhances the EC effect but also simplifies device architecture, marking a pivotal leap toward practical solid-state refrigeration.

Among others, relaxor ferroelectric polymers offer distinct advantages for electrocaloric applications, primarily due to their large electrocaloric response, mechanical flexibility, and ease of processing.[2,8] When it comes to enhancing EC properties, nanocomposites have proven to be a highly effective approach to combine the beneficial properties of both organic (polymers) and inorganic (ceramics) materials.[8–10] For instance, introducing ceramic-based 3D frameworks or boron nitride nanosheets into relaxor ferroelectric polymer matrices can not only improve their electrocaloric performance but also significantly increase their thermal conductivity.[4,10] The use of barium strontium titanate nanowires as fillers in the polymer matrix results in a large ECE (ΔT = 19.5 K at 100 MV/m). The nanowire morphology increases interfacial areas and enhances dielectric properties, resulting in superior electrocaloric performance.[9] However, current nanocomposite additions don't serve as driving units to substitute the extra accessories in EC devices.

Cai et al. take a divergent approach by embedding FeCoNiCuVMn HEA nanoparticles—encapsulated in graphitic shells (MNP@C)—into the polymer matrix, denoted as MNP@C/TP. The HEA's unique multi-element composition ensures strong magnetization, low hysteresis, and high resistivity, while the carbon shell facilitates hydrogen bonding with the polymer, enhancing interfacial polarization and dipolar response in the MNP@C/TP (Figures 1A and 1B). This interface-driven strategy disrupts the polymer's long-range crystalline order, creating nanoscale polar domains that lower the energy barrier for polarization switching. The result is a 2.4-fold increase in ΔS (55 vs. 23 J $kg^{-1}K^{-1}$) and a 250% volumetric enhancement efficiency—a 10-fold improvement over prior nanocomposite designs.

The team's success hinges on precision interfacial engineering of the HEA-polymer interface. By employing the arc-discharge synthesis method, they were able to produce core-shell nanoparticles with a 24.5 nm HEA core and a 2.7 nm graphitic shell. These

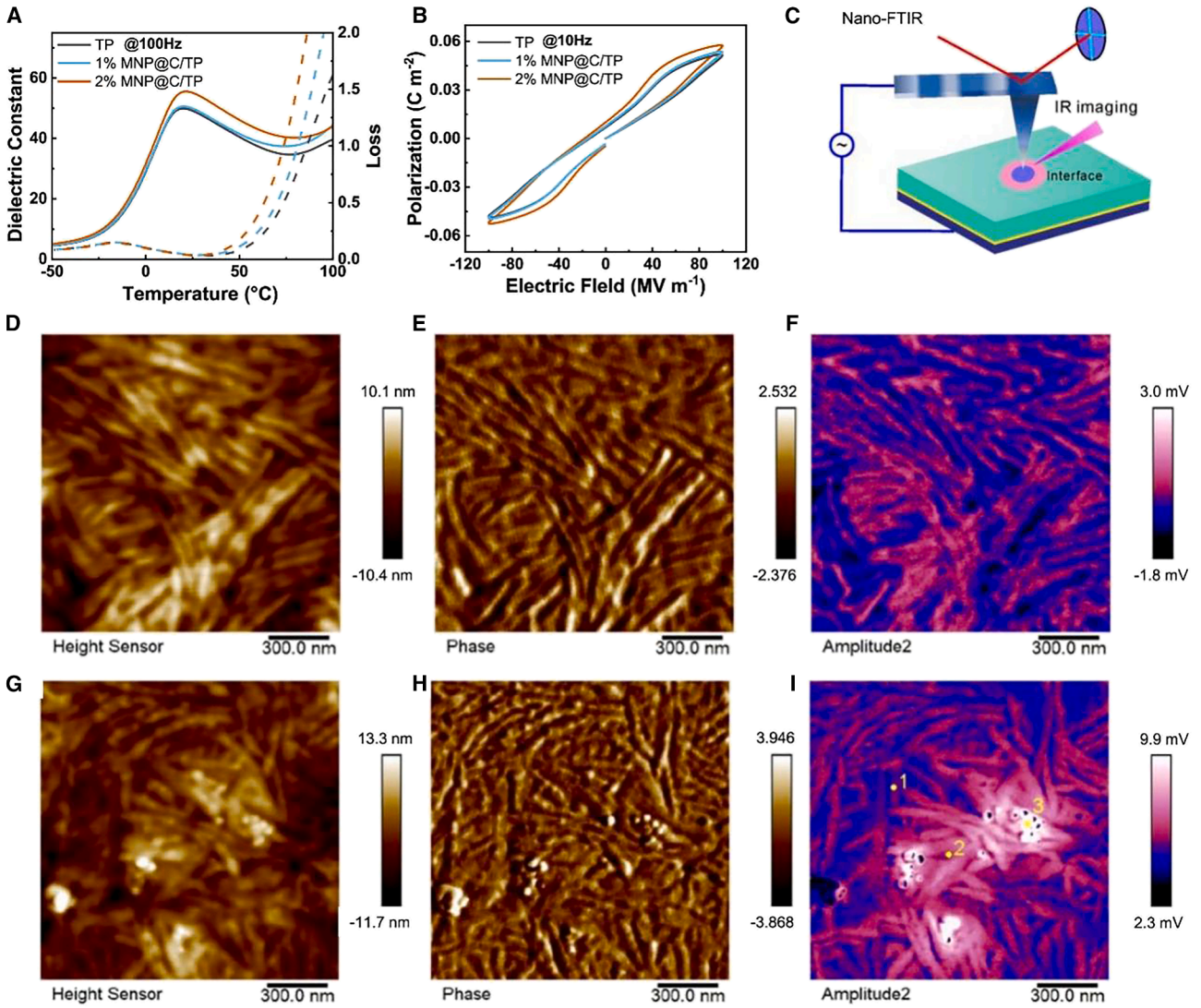

Figure 1. Enhanced dipolar response through the interface effect in MNP@C/TP nanocomposites

(A and B) Temperature dependence of dielectric constant (A) and bipolar polarization-electric field loops (B) of TP, 1% MNP@C/TP NCs, and 2% MNP@C/TP nanocomposites.

(C) Schematic of AFM-IR spectroscopy characterization of MNP@C/TP nanocomposites.

(D–I) Topography images (D and G), phase images (E and H), and IR absorbance (around TTTT characteristic vibrations) intensity images (F and I) of TP and MNP@C/TP nanocomposites, respectively.

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nanoparticles feature a uniform distribution of elements throughout their structure, which are mixed into a solid solution through the arc-discharge process. This precise control and uniformity are crucial for optimizing the performance of the composite material MNP@C/TP. The carbon shell not only stabilizes the MNPs but also promotes physical interactions with the polymer matrix, as evidenced by atomic force microscopy-infrared (AFM-IR) spectroscopy (Figure 1). Nanoscale mapping revealed heightened IR absorbance at interfacial regions (Figures 1H and 1I), indicating localized polar phase formation near MNP@C surfaces. These polar nuclei act as seeds for electric-field-induced phase transitions, significantly amplifying the EC response. *In situ* synchrotron X-ray diffraction further illuminated the structural dynamics. Under an 80 MV/m field, the HEA nanocomposite exhibited a 32.3% polar phase fraction—nearly double that of the pristine polymer (17.5%)—correlating directly with its superior ΔS. Small-angle X-ray scattering (SAXS) confirmed the disruption of long-range polymer crystallinity, which facilitates rapid polarization switching with minimal hysteresis.

Beyond material enhancement, the study introduces a transformative device concept: magnetic-field-driven EC heat pumps. Traditional EC coolers rely on external actuators (e.g., motors) to cycle the EC layer between hot and cold

reservoirs, adding complexity and energy loss. By contrast, the HEA nanocomposite's inherent magnetism enables direct actuation via alternating magnetic fields. The prototype device features a polymer film that adheres to a copper heat exchanger under a magnetic field (35 mT) and detaches when the field is removed, driven by gravity and the magnetic field below the lower copper plate. Synchronizing the electric and magnetic field cycles enables continuous heat pumping, as confirmed by measurements of heat flux. Remarkably, the EC performance remains stable under operational fields, with no significant leakage current or dielectric breakdown—a critical advantage over conventional metal-polymer composites.

Remarkably, the HEA-polymer nanocomposite exhibits an electrocaloric entropy change as high as 55 J $kg^{-1}K^{-1}$ at an electric field of 80 MV/m. This outstanding performance significantly surpasses that of current state-of-the-art electrocaloric polymers and ceramic-polymer hybrid materials. Moreover, its electrocaloric strength ($\Delta S/\Delta E$) reaches an impressive 0.69 J $kg^{-1}K^{-1}MV^{-1}m$, which is far superior to earlier nanocomposites, such as those filled with boron nitride (BN) that typically have an electrocaloric strength of around 0.3 J $kg^{-1}K^{-1}MV^{-1}m$. The incorporation of magnetic actuation not only enhances the device's functionality but also significantly reduces its complexity. It eliminates the need for auxiliary motors, thereby enabling the development of more compact and energy-efficient designs.

This study represents a significant breakthrough in the field of EC materials and devices. From a technical perspective, the integration of HEA magnetic nanoparticles into EC polymers offers a novel approach for enhancing EC performance while simplifying device design. In terms of applications, this work paves the way for the development of more efficient and compact EC cooling devices, which could have a broad impact on various industries, from consumer electronics to precision temperature control systems.

Although this study represents a significant advancement, concerns remain regarding scalability and stability. The 2wt % MNP@C loading is crucial for preventing dielectric losses, which restricts additional increases in ΔS. Subsequent research might investigate shell engineering techniques to stabilize higher concentrations of fillers and/or refine the composition and structure of the HEA nanoparticles, thereby aiming to attain superior electrocaloric (EC) performance. Long-term cycling stability under combined electric/magnetic fields also warrants investigation, as interfacial degradation could diminish performance. Exploring novel multiphase nanocomposites and gradient-composition materials through defect/interface engineering, entropy modulation (via cationic disorder or configurational entropy), and phase-transition control (multistage/continuous transitions), synergized with computational tools like phase-field modeling and machine learning for accelerated materials discovery, could provide new pathways to enhance the EC effect. Besides, the successful demonstration of a magnetic-field-driven EC heat pump also suggests the possibility of developing multi-functional EC devices that can respond to multiple external stimuli, such as electric, magnetic, and thermal fields.

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DECLARATION OF INTERESTS

The authors declare no competing interests.

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