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Heterostructures: new opportunities for functional materials

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ABSTRACT

Heterostructures with large microstructural heterogeneities have been introduced in structural materials for superior strength-ductility combinations, but their effects on functional properties remain little explored. Here I highlight the enormous potential of heterostructures to resolve conflicting properties in functional materials. The challenges, strategies and prospects of heterostructured functional materials are discussed. Rational design of heterostructures will open up new opportunities for creating functional materials with unprecedented performance or new functionalities. This Perspective aims to draw the attention of scientific community to the emerging heterostructured functional materials and to trigger intense fundamental and applied researches on this topic.



IMPACT STATEMENT

The performance of functional materials could be significantly enhanced through engineering heterostructures, and the combination of heterostructures and hybrid materials will open up new opportunities for functional materials.

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KEYWORDS

Heterostructures; heterostructured functional materials; hybrid and heterostructure; heterogeneous structured materials; microstructural control

Background

The performance of polycrystalline materials is closely related to their grain sizes. With decreasing grain sizes, the strength or hardness of a material increases, while its ductility decreases [1]; similarly, the coercivity of a magnetic material—the reverse-field strength needed to reduce its magnetization to zero—increases with decreasing grain sizes [2]. Traditionally, the grain sizes of a material are turned by composition designs. For example, the addition of Nb, V and Ti elements plays a key role for grain refinement (1–5 μm) in microalloyed steels [3], and a mixed addition of Nb and Cu leads to ultra-fine nanograins ($\sim 10\text{ nm}$) in Fe-Si-B-Cu-Nb alloys [4]. However, the grain refinement induced by composition design is usually homogeneous. In such homogeneous structures, the enhancement of strength is always at the expense of ductility [5]. The trade-off between the strength and ductility becomes a fundamental challenge in creating high-performance structural materials [6].

To address this issue, heterostructures with large microstructural heterogeneities were introduced in structural materials [5,7–9], such as bimodal grains [10], gradient grains [11–13], gradient nanotwins [14], nanolaminar [15] and heterogeneous laminae [7]. Such heterostructures were created through developing advanced processing technologies without the variation of composition, including severe plastic deformation, surface grinding or rolling, and electrodeposition. The resulting heterostructured materials exhibit excellent mechanical properties, e.g. the strength-ductility synergy and enhanced fatigue properties and wear resistance [5–9]. Naturally, an intriguing question arises: Can such heterostructures be used to create advanced functional materials? To date it remains little explored.

In this Perspective, I will start with typical functional materials whose performance is inherently inhibited by the requirements on conflicting properties and subsequently, with recent advances, highlight the enormous

potential of heterostructures to achieve the competing properties simultaneously. Next, I will consider the challenges and strategies for the development of heterostructured functional materials. Finally, I will discuss the prospects of heterostructured functional materials, and highlight new opportunities for achieving unprecedented performance or functionalities through engineering heterostructures in a hybrid system comprising two or more constituents.

Emerging examples of heterostructured functional materials

Although heterostructures have been initially studied in structural materials [5–9], recent advances demonstrate that such structures hold great promise for realizing unprecedented functional properties via breaking trade-offs between competing properties that are unsolvable to homogeneous structures, as follows.

Heterostructured permanent-magnet materials

Permanent magnets that can interconvert mechanical power and electricity are critical energy-conversion materials [16]. They have key applications in electric cars, wind power generators, and computer hard-disk drives.

The performance of permanent magnets is judged by the figure of merit—the energy product $(BH)_{\max}$. The energy product of a magnet depends on the area of its hysteresis loop (Figure 1), where obtaining a large energy product requires both high magnetization and large coercivity [17]. Unfortunately, like the strength and ductility

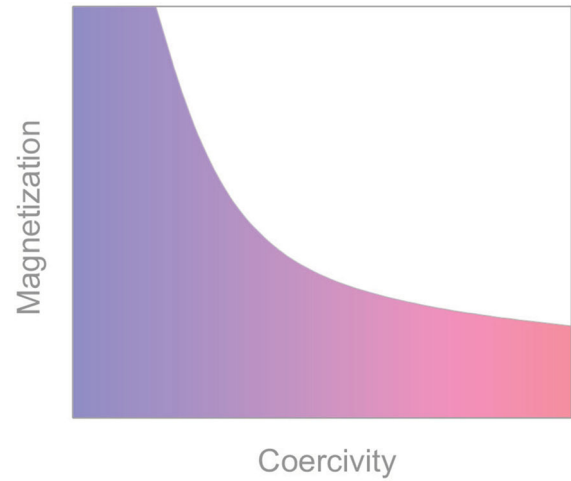


Figure 2. Schematics of the trade-off between the magnetization and coercivity of permanent magnetic materials.

in structural materials, there is a trade-off between the magnetization and coercivity (Figure 2), which results from an inherently inverted relationship between the magnetization M_s and anisotropy H_a that determines the physical limit of coercivity [18]:

$$H_a = \frac{2K_1}{\mu_0 M_s} \quad (1)$$

where K_1 is the magnetocrystalline anisotropy constant, and μ_0 is the magnetic constant.

As a result, how to *simultaneously* obtain high magnetization and large coercivity becomes a key scientific problem and a fundamental challenge toward increasing the energy products of permanent-magnet materials.

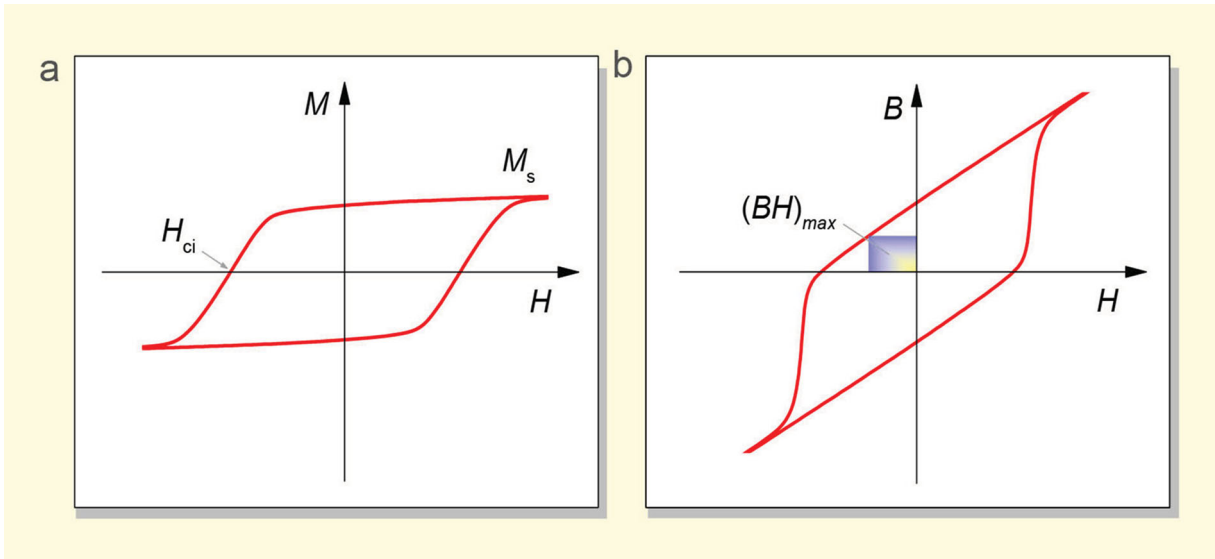


Figure 1. Typical hysteresis loops for a permanent-magnet material. The response of a magnet to an applied field (H) is shown in terms of its magnetization M (a) and magnetic induction or flux density B (b), where $B = H + 4\pi M$. The coercivity of a magnet is defined in (a) and is a factor in the figure of merit of permanent magnets—the energy product $(BH)_{\max}$ (shaded area in b).

Recently, a conceptual strategy has been proposed to break the trade-off between magnetization and coercivity [19,20]. The basic idea is to introduce a heterostructure in permanent magnetic materials, in which one type of structures contribute to high magnetization via both the exchange coupling between soft- and hard-magnetic nanograins and the alignment of hard-magnetic phase, and the others contribute to large coercivity through impeding magnetization reversal. With this strategy, great advances have been achieved toward high energy products in nanostructured magnets [19,20]. The resulting heterostructured magnets with NdFeB nanograin layers in a SmCo/FeCo nanostructured matrix exhibit an enhanced coercivity without reducing the remanence

(B_r) (Figure 3) [20], as compared to their corresponding homogeneous magnets, yielding a large energy product of 31 MGOe that outperforms the existing SmCo-based hybrid nanostructured magnets and defeats, for the first time, the corresponding pure rare-earth magnets (Figure 3(c)). The achieved energy product is comparable to that (28–33 MGOe) of pure commercial SmCo magnets but with reduced rare-earth metals of 20–30 wt.%.

A core/shell-like $\text{Nd}_2\text{Fe}_{14}\text{B}/\alpha\text{-Fe}$ heterostructured magnet also exhibits a superior combination of the remanence and coercivity as compared to the homogeneous structured counterparts (Figure 4) [21], yielding a record-high energy product of 25 MGOe for *isotropic* permanent magnets.

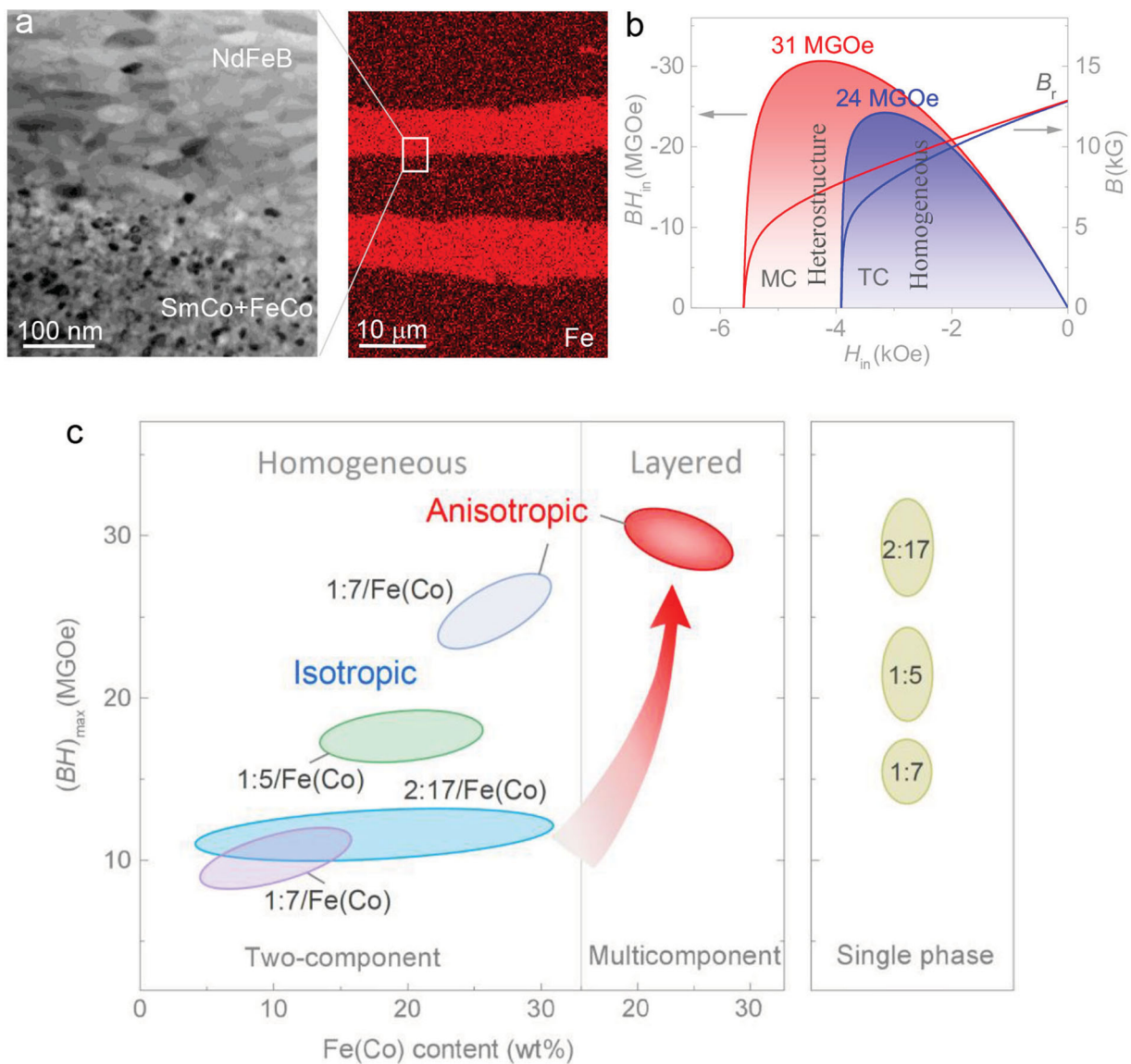


Figure 3. Microstructure (a) and magnetic properties (b) of layered (SmCo + FeCo)/NdFeB heterostructured magnets. (c) Comparison of energy product for layered heterostructured magnets, homogeneous structured SmCo-based hybrid magnets, and pure SmCo rare-earth magnets including SmCo_5 (1:5), SmCo_7 (1:7) and $\text{Sm}_2\text{Co}_{17}$ (2:17) magnets.

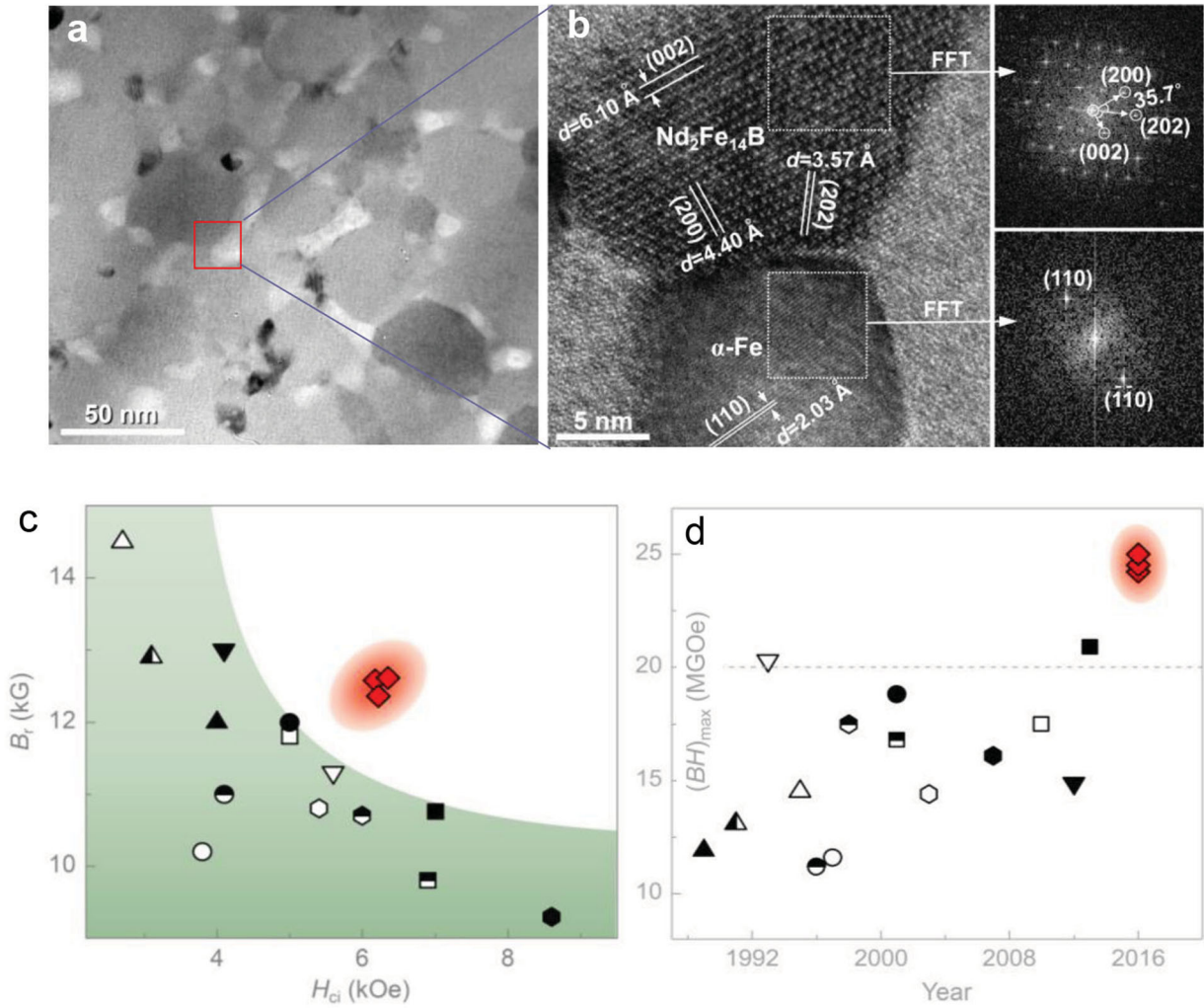


Figure 4. Bright-field TEM (a) and HRTEM (b) images of a core/shell-like $\text{Nd}_2\text{Fe}_{14}\text{B}/\alpha\text{-Fe}$ heterostructured magnet. (c) The trade-off between the remanence (B_r) and coercivity (H_{ci}) of isotropic $\text{Nd}_2\text{Fe}_{14}\text{B}/\alpha\text{-Fe}$ nanocomposite magnets. The data marked with the red color are for core/shell heterostructured magnets. (d) Typical energy products of isotropic $\text{Nd}_2\text{Fe}_{14}\text{B}/\alpha\text{-Fe}$ nanocomposite magnets in the development history.

It is anticipated that even higher energy products could be realized through further engineering heterostructures to effectively align hard-magnetic nano-grains and to enhance domain-wall pinning.

Heterostructured thermoelectric materials

Thermoelectric materials are emerging energy-conversion materials that enable the conversion between thermal energy and electricity [22], providing potential solutions to the environmental and energy problems currently faced by the world.

The figure of merit of a thermoelectric material is defined as ZT [22],

$$ZT = \frac{\alpha^2 \sigma T}{\kappa} \quad (2)$$

where α is the Seebeck coefficient (i.e. the thermopower), σ is the electrical conductivity, κ is the thermal conductivity, and T is the temperature.

Obtaining a large ZT value requires large α , high σ , and low κ . Unfortunately, there is trade-off between the α and σ ; in addition, the requirement on high σ and low κ often conflicts (Figure 5) [22]. Both issues constitute fundamental challenges in realizing high- ZT thermoelectric materials.

Nevertheless, a large ZT value can be realized through rational design of microstructure and band structure. In this respect, heterostructures show a promising approach to lowering the thermal conductivity. The basic idea is as follows. Thermal vibration of atoms in a solid creates displacements from their equilibrium positions, yielding a set of vibrational waves with different wavelengths—phonons. These phonons are heat carriers that

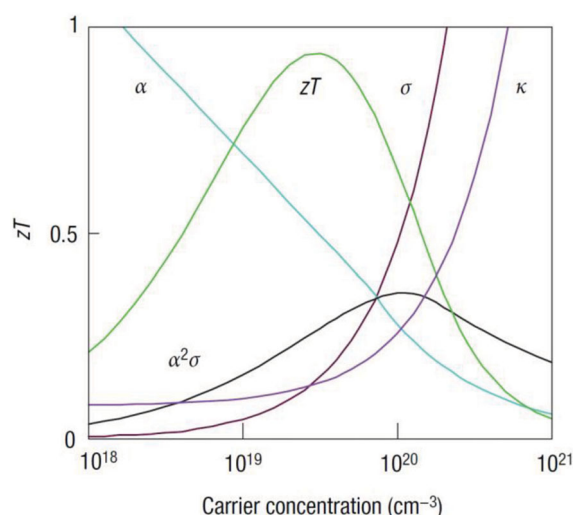


Figure 5. Carrier-concentration dependence of zT value, Seebeck coefficient α , electrical conductivity σ , thermal conductivity κ , and thermoelectric power factor $\alpha^2\sigma$. Maximizing the zT involves a compromise of conflicting properties—the α and the σ , as well as high σ and low κ .

propagate through the lattice, contributing to the lattice thermal conductivity. They can be effectively scattered at all-scale crystal defects: Atomic-scale point defects for short-wavelength phonons, the interfaces of nanoscale precipitate for medium-wavelength phonons, and the boundaries of mesoscale grains for long-wavelength phonons. Therefore, an all-scale heterostructure enables a significant reduction of the thermal conductivity.

The pioneering work on heterostructured thermoelectrics is the generation of micro and nanostructures in the PbTe-SrTe(4 mol%) doped with 2 mol% Na [23], where the nanoscale precipitate phase (SrTe) has a coherent interface with the matrix (Figure 6). The resulting heterostructure exhibits the maximum reduction in lattice thermal conductivity and thus achieve a high thermoelectric performance: A large zT value of 2.2 at 915 K beyond the reach (1.5–1.8) of existing nanostructured thermoelectrics (Figure 7).

Such heterostructure strategy has also been applied to other thermoelectric materials [24], including PbTe-MgTe, PbTe-MTe ($M = \text{Ca, Ba}$), GePbTe-BiTe, CeFeSb-FeSb, AgSbSe-ZnSe, AgCrSe-CuCrSe, and BiTe-Ag. Interestingly, the BiSbTe heterostructured material exhibits both high thermoelectric and mechanical properties simultaneously [25].

The grain or phase interfaces of heterostructured materials also increase the scattering of charge carrier, leading to low carrier mobility. To maintain high electrical conductivity while reducing the lattice thermal conductivity, a coherent interface is necessary that facilitates charge transport [24,26] but strongly blocks phonon propagation.

Heterostructured catalytic materials

Porous materials, as catalytic materials, hold great promise for energy conversion and storage [27] and thus can serve as a solution to the current energy crisis we face. Obtaining superior catalytic performance in these materials requires both high mobility of reactants (i.e. enhanced mass diffusion) and many catalytic active sites. However, such requirements often conflict in ordinary porous catalysts. For example, the catalysts with macropores or mesopores (pore diameter > 100 nm) facilitate the mobility of reactants but lack enough active sites due to their low specific surface area, while those with nanopores (pore diameter ≤ 100 nm) can provide many active sites due to high specific surface area, but have poor reactant mobility. This trade-off is a challenge for enhancing the catalytic activity of porous materials.

A heterostructure strategy has been devised to overcome this challenge, through creating a material that contains both meso- and nanopores [27]. Such structures have a synergy between the mobility and active sites. The resulting ordered meso-nanoporous metal-organic framework single crystals, with an average diameter of ~ 270 nm for mesopores and ~ 0.8 nm for nanopores, exhibit higher catalytic performance and improved recyclability than their counterparts with homogeneous pores (Figure 8).

Challenges and strategies

Despite the exciting performance and extraordinary potential of heterostructured functional materials, great challenges remain for their fabrication and microstructural control. Moreover, understanding the effect of heterostructuring on functional properties and establishing structure–property relationships also provide new challenges for experimental and theoretical studies as follows.

Processing techniques

To date many deformation approaches have been devised to generate heterostructures in structural materials. However, these methods are generally inappropriate for functional materials that usually consist of intermetallic and/or inorganic compounds and thus cannot survive from severe plastic deformation.

To address this issue, new innovations in processing techniques are required. For example, a strong-constraint deformation that enables the plastic deformation of brittle materials could be promising for yielding heterostructured functional materials. Moreover, non-deformation strategies such as electrodeposition and structural phase transition in a temperature gradient

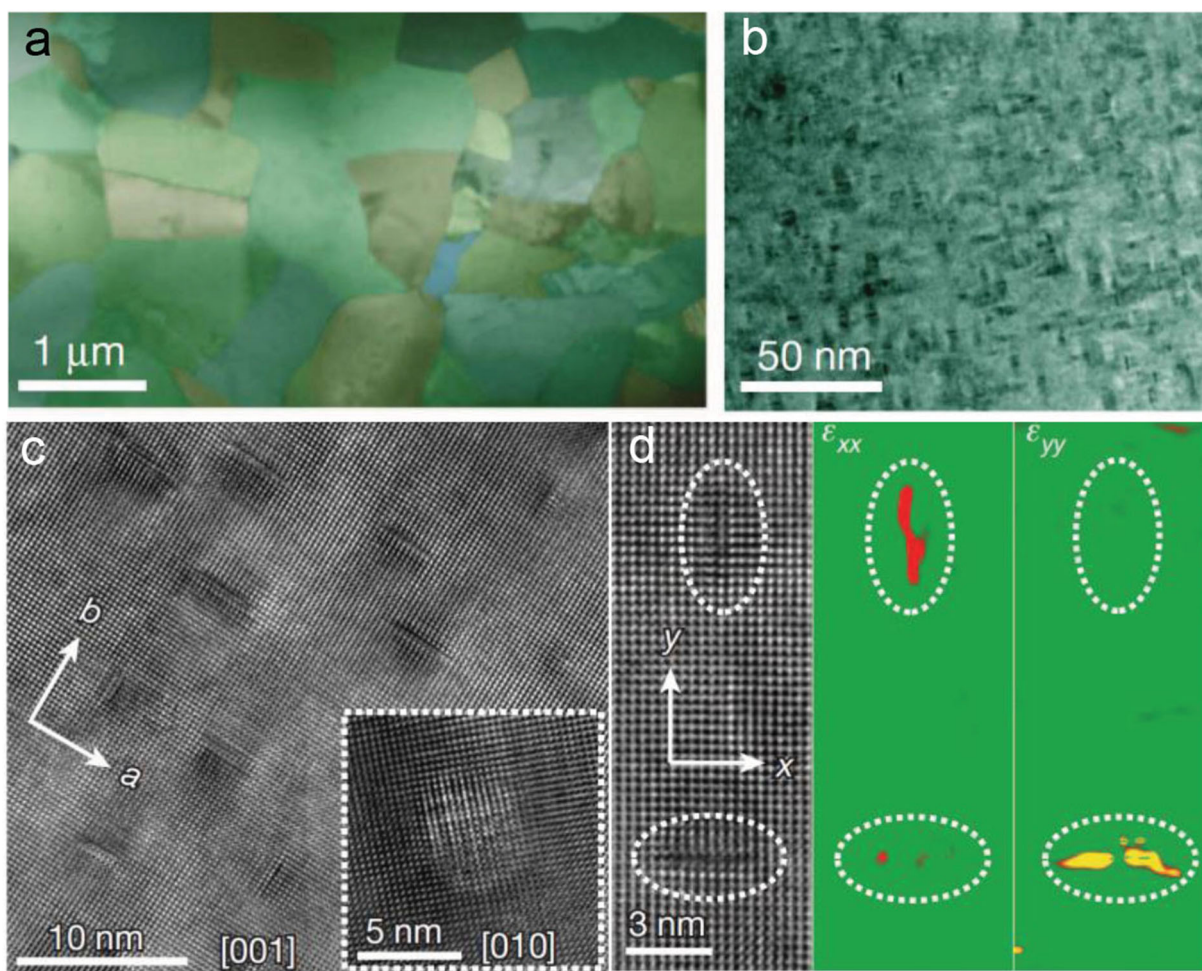


Figure 6. PbTe–SrTe(4 mol%) heterostructured thermoelectric materials doped with 2 mol% Na. Bright-field TEM images showing mesoscale grains (a) and nanoscale precipitates (b) in the material. (c) HRTEM image depicting some perpendicular or parallel platelet-like precipitates. The inset shows a small spherical precipitate with a coherent interface with the matrix. (d) Lattice image (the left panel) and strain maps.

could hold great promise for creating gradient structures in functional materials. Complex heterostructures, e.g. core/shell structures, could also be realized in 3D functional materials through precise control over crystal nucleation and growth processes in phase transitions.

In contrast to existing single-phase heterogeneous structural materials, producing a hybrid and heterostructured functional material might require a complex processing technique, such as a hybrid method that combines the advantages of different approaches. Moreover, an approach with scale-up capability is also required to put this new class of materials in practical applications.

Microstructural control

Fulfilling the remarkable potential of heterostructured functional materials requires precise control over their

microstructure, that is, creating heterostructures with the desired structure. To meet this challenge, some issues have to be addressed.

Aligning grains at the nanoscale: Obtaining specific crystallographic orientations is critical for high-performance functional materials including magnetic, ferroelectric, thermoelectric and catalytic materials. But aligning grains at the nanoscale remains a formidable challenge in bulk materials, due to strong interactions between nanoparticles or the difficulty in activating dislocations in nanograins.

To address this issue, a conceptual strategy is proposed in this Perspective that utilizes strain-energy anisotropy to align nanoscale grains. For a solid-state phase transformation under high pressure thermal compression (HPTC), where the spherical nucleus with a radius r forms for a new phase and suffers from an elastic strain induced by the HPTC, the total free energy change (ΔG)

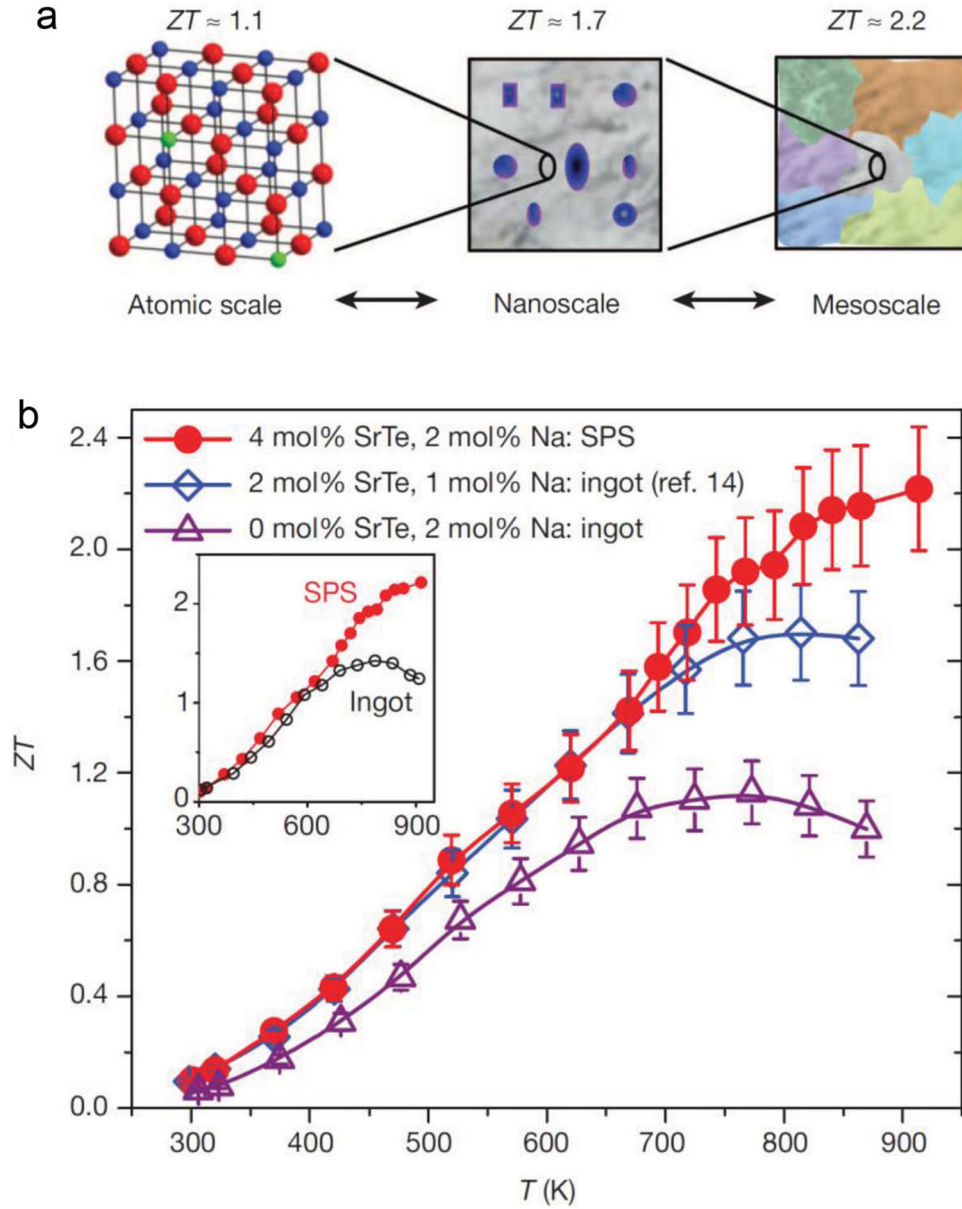


Figure 7. Thermoelectric performance of all-length-scale heterostructured materials. (a) Maximum achievable ZT values for the respective length scales: the atomic scale (alloy scattering: red, Te; blue, Pb; green, dopant), the nanoscale (PbTe matrix, gray; SrTe nanocrystals, blue) to the mesoscale (grain-boundary scattering). (b) Temperature dependence of ZT value for an ingot of PbTe doped with 2 mol% Na (atomic scale), PbTe–SrTe(2 mol%) doped with 1 mol% Na (atomic + nanoscale) and spark-plasma-sintered PbTe–SrTe(4 mol%) doped with 2% Na (atomic + nano + mesoscale). Inset, comparison of ZT in SPS and ingot samples with the same composition.

of the system is derived as

$$\Delta G = \frac{4}{3}\pi r^3(\Delta G_v + \Delta G_s + W) + 4\pi r^2\gamma \quad (3)$$

where the ΔG_v is the free energy difference between the new phase and the matrix per unit volume, the ΔG_s is the elastic strain energy per unit volume of the nucleus that results from the volume changes attendant to its formation, the W is the elastic strain energy per unit volume induced by HPTC on the nucleus, and the γ is the nucleus/matrix interfacial energy.

From Equation (3), the critical free energy change (ΔG^*) and the critical nucleus radius (r^*) for the formation of the new phase are derived:

$$\Delta G^* = \frac{16\pi\gamma^3}{3(\Delta G_v + \Delta G_s + W)^2} \quad (4)$$

$$r^* = -\frac{2\gamma}{\Delta G_v + \Delta G_s + W} \quad (5)$$

Although both the ΔG_s and γ are associated with crystallographic orientations of a new phase in solid-state phase

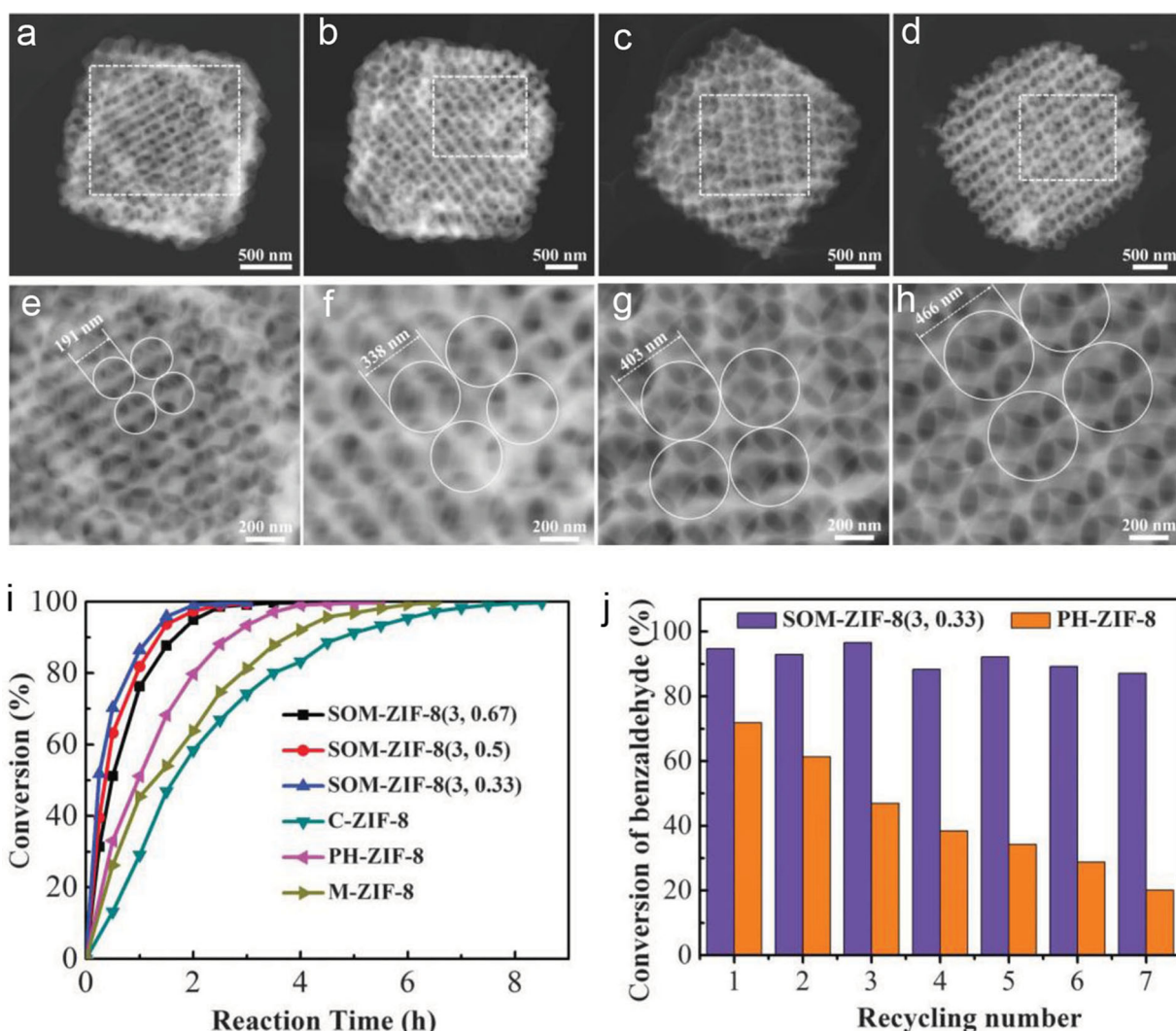


Figure 8. Heterostructured porous materials containing meso- and nanopores. (a to h) Scanning transmission electron microscopy images of various metal-organic framework crystals containing meso- and nanopores, denoted as SOM-ZIF-8. The SOM-ZIF-8 crystals have mesopore sizes from 190 to 470 nm: (a and e) 190 nm, (b and f) 340 nm, (c and g) 400 nm, and (d and h) 470 nm. Comparison of catalytic performance (i) and recyclability (j) of SOM-ZIF-8 crystals.

transformations, the anisotropy originating from them is usually not enough to align the new phase. To solve this issue, an anisotropic parameter—crystal strain energy W is designedly introduced in Equation (3). According to Equations (4) and (5), both the ΔG^* and the r^* are related to the W . A small W along a specific crystallographic direction will lead to small ΔG^* and small r^* (Figure 9), facilitating crystal oriented nucleation. This intentionally introduced strain-energy anisotropy W term can therefore be used to align the new phase. In principle, this strategy enables a simultaneous control over crystal orientation and grain size at the nanoscale [28].

Controlling multiple structural properties simultaneously: Ideally, for heterostructured functional materials, multiple structural properties such as grain size and crystal orientation need to be controlled simultaneously.

However, such control becomes increasingly difficult with increasing the number of constituent components and even impossible when some of structural properties conflict.

To overcome this challenge, a combined strategy might be promising that enables a separating control over the conflicting constituents. A successful example is to fabricate hybrid nanostructured magnets [19], where the size (~ 10 nm), volume fraction and distribution of soft-magnetic grains can be effectively controlled by distributing them within an amorphous matrix via ball milling, while hard-magnetic nanograins can be aligned by the HPTC method, yielding a simultaneous control of the soft- and hard-magnetic structures. This combined strategy could be readily applied to other heterostructured functional materials.

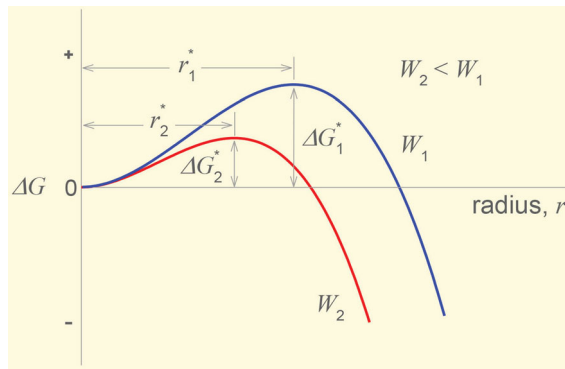


Figure 9. Schematic curves of free energy change versus embryo/nucleus radius in a solid-state phase transition under high-pressure thermal compression (HPTC). The curve varies with the elastic strain energy W introduced on crystal nucleus by the HPTC, $W = (1/2)E_{hkl}\epsilon^2$, where E_{hkl} is the elastic modulus along the $[hkl]$ direction and ϵ is the strain. A small W will lead to a small critical free energy change (ΔG^*) and a small critical nucleus radius (r^*), facilitating crystal oriented nucleation.

Structure–property relationships

Quantitative understanding of structure–property relationships is vital for rational design of heterostructured functional materials with desired performance, and is also critical for optimizing their overall properties. To meet this challenge, creating ordered or periodic heterostructures is particularly required, such as gradient and layered structures. With these structures, the effect of heterostructures on properties can be studied easily. Such heterostructures also enable theoretical simulations of the structure–property relationships. New results from these studies will renew the traditional processing–structure–property relationships in materials science that lack the variant of heterostructure.

Outlook

Exciting material performance and novel functionalities normally stem from a delicate concert among trade-offs between conflicting properties, such as strength and ductility, magnetization and coercivity, electrical conductivity and Seebeck coefficient, reactant mobility and catalytic active site, polarization and breakdown strength [29], ferromagnetism and ferroelectricity [30], transparency and conductivity [31] (Figure 10). How to break these trade-offs has been the key scientific problems and frontier fields in materials science and condensed matter physics. Any success in this respect would be a breakthrough, which generally depends on composition designs [32,33], e.g. creating hybrid materials. But now the heterostructure emerges as a new approach to overcoming the trade-offs, providing a new dimension to tune material performance. Certainly, the combination of heterostructures and hybrid materials will provide us an even larger space to achieve the competing properties, with unparalleled freedom that could not be realized previously. Therefore, engineering hybrid and heterostructured functional materials will open up new opportunities for yielding unprecedentedly high performance or entirely new functionalities beyond the reach of existing materials.

Heterostructured functional materials synthesized so far are mainly limited to the structures with bimodal grains, other types of heterostructures that are prevailing in structural materials remain unexplored, although they could exhibit unusual properties. For example, a gradient hybrid structured magnet might hold potential to break the trade-off between magnetization and coercivity by enhancing the resistance to magnetization reversal with

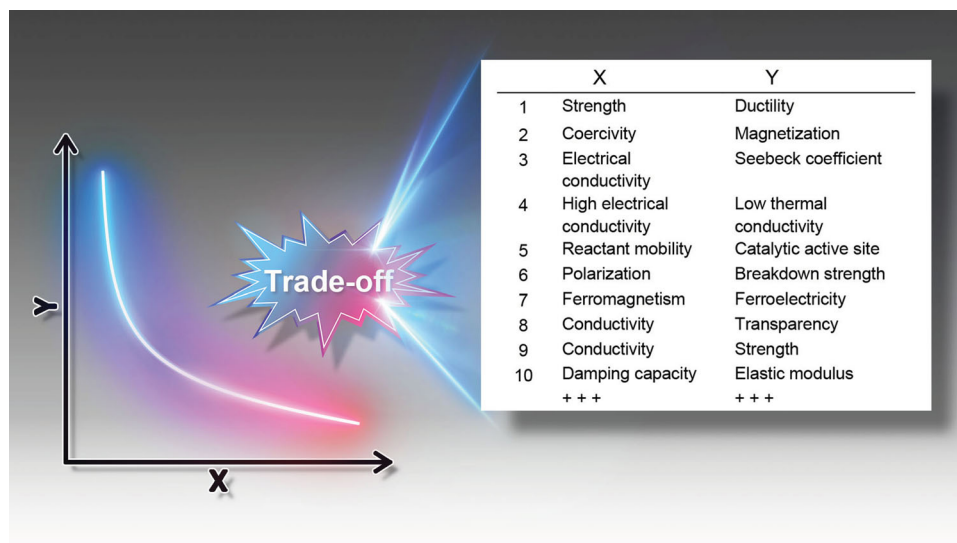


Figure 10. Schematics of trade-offs between conflicting properties.

gradient variations of coercivity. Moreover, a gradient nanotwinned or hierarchical layered-structured thermoelectrics, with favorable crystal orientations, could have promise to achieve the conflicting properties—high electrical conductivity and low thermal conductivity—via strong phonon scattering but minimal electron scattering. Undoubtedly, the exciting functional properties in gradient and hierarchical layered materials need to be explored promptly.

Despite their excellent performance and extraordinary potential, heterostructured functional materials are only in the infancy. Disruptive breakthroughs in processing techniques, microstructural control and understanding structure–property relationships will provide the ability to create heterostructured functional materials with unprecedented properties and functionalities. A hybrid method may show promise in particularly, with the combined application of external fields such as temperature, pressure and strain fields [19].

The exciting prospects and new challenges call for more experimental and theoretical studies on the topic of heterostructured functional materials. Progress in such functional materials, in turn, will inspire the research of structural materials and accelerate the development of heterostructured materials as an important member in material family. I hope that this Perspective can timely turn the attention of scientific community to the emerging research field, opening up new opportunities for functional materials.

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Disclosure statement

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