

REVIEW SUMMARY

COMPOSITES

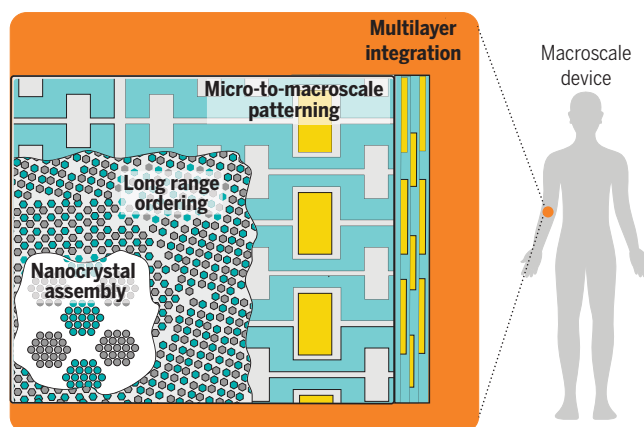
Bridging functional nanocomposites to robust macroscale devices

Matthew R. Begley, Daniel S. Gianola*, Tyler R. Ray

BACKGROUND: Composites comprising nanoscale particles embedded in a second phase (or matrix) create exciting opportunities to design functional materials with strong coupling between optical, electromagnetic, mechanical, and transport phenomena. Such coupling is strongly enhanced by deterministic control of multiple length scales in a hierarchical structure: for example, the ordering of crystalline nanoscale particles with prescribed shape to form “superlattices,” with controlled particle spacing spanning from tens of nanometers to tens of micrometers and exhibiting emergent collective behavior not hosted in the individual particles. Substantial advances in particle synthesis—encompassing a broad range of compositions, sizes, and shapes—have been combined with equally impressive advances in assembly, creating a virtual “materials design palette” for the generation of materials with targeted responses. The resulting functionalities can advance a broad range of transformative technologies, such as wearable sensors that respond to physiological stimuli, flexible displays, batteries and catalysts with enhanced control over ion and electron transport, etc. However, the use of ordered nanocomposites in such applications has historically been hampered by several related factors: (i) limited pathways to synthesize and pattern such materials over length scales required for devices, (ii) fabrication techniques amenable to the integration of nanocomposites with other materials required to connect or protect functional components, and (iii) limited understanding of the thermomechanical stability of nanocomposites, both as isolated materials and as embedded components.

ADVANCES: In addition to the rigorous control of particle shape and size, new techniques to control surface chemistry have advanced the ability to fabricate nanocomposites from the “bottom up” and span large distances. These advances expand the scope of surface capping

ligands that can be used during self-assembly of colloidal crystals and provide pathways to tailor particle spacing and binding (controlling optical and electronic properties), as well as the mechanical properties of the nanocomposite “matrix.” New inorganic surface chemistries also show tremendous promise for solid-state device integration as a result of added control over particle interactions and the opportunity to broaden the range of solvents and their polarity



Depiction of a hierarchically structured functional device (embodied as a wearable device for human health). Deterministically ordered nanoparticle assemblies serve as a bridge between nanoscale and microscale features. Subsequent assemblies reflect multimaterial integration enabled by directed mesoscale assembly methods.

during synthesis. Therefore, new micro- and macroscale fabrication methods are emerging, many of which exploit established solution processing and lithographic patterning techniques that enable facile integration with other device materials and features. Notable recent examples of bottom-up fabrication routes profit from capillary-driven and other liquid-mediated assembly methods that harness evaporation and wetting behavior. Pairing these approaches with new surface functionalization schemes shows promise for maintaining the deterministic ordering of nanoscale building blocks, which underpins much of their emergent phenomena. At the

same time, “top-down” assembly approaches that exploit advances in three-dimensional (3D) printing technology have established bridges from the macroscale down to the nanoscale; direct deposition of nanocomposites has been demonstrated and provides clear pathways for patterning and integration

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of functional nanocomposites. Similarly, advances in direct writing of nanoparticle-based colloidal inks stand to benefit from parallel successes in the implementation of field-directed assembly during 3D printing. The diversity of material systems that can be targeted using acoustophoretic, electrophoretic, and magnetically directed assembly promises a wide canvas of nanocomposite properties and behavior. Advances in composition and fabrication have enabled the development of more robust nanocomposites, which are amenable to thermomechanical characterization critical to device integration.

OUTLOOK: Hierarchical fabrication methods to produced patterned features of nanocomposites continue to emerge and set the stage for more rapid and sophisticated integration in devices. This represents a critical step not only in the development of transformative sensors, displays, and batteries, etc., but also in the science and development of the functional materials themselves. The reasons are twofold: First, the ability to pattern nanocomposites and integrate them with other materials takes the nanocomposites “out of the beaker” and enables critical pathways to characterize structure–property relationships and understand the role of particle binding, defects, “grain” boundaries, etc. Second, the integration of nanocomposites into specific device contexts will identify

important trade-offs—e.g., functional performance, chemical compatibility, and thermomechanical robustness—that will define essential scientific questions regarding the underlying mechanisms controlling performance. Addressing these questions will lead to new understanding that can be used to identify effective nanocomposite compositions, synthesis techniques, and fabrication pathways. ■

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Bridging functional nanocomposites to robust macroscale devices

Matthew R. Begley¹, Daniel S. Gianola^{1*}, Tyler R. Ray²

At the intersection of the outwardly disparate fields of nanoparticle science and three-dimensional printing lies the promise of revolutionary new “nanocomposite” materials. Emergent phenomena deriving from the nanoscale constituents pave the way for a new class of transformative materials with encoded functionality amplified by new couplings between electrical, optical, transport, and mechanical properties. We provide an overview of key scientific advances that empower the development of such materials: nanoparticle synthesis and assembly, multiscale assembly and patterning, and mechanical characterization to assess stability. The focus is on recent illustrations of approaches that bridge these fields, facilitate the design of ordered nanocomposites, and offer clear pathways to device integration. We conclude by highlighting the remaining scientific challenges, including the critical need for assembly-compatible particle–fluid systems that ultimately yield mechanically robust materials. The role of domain boundaries and/or defects emerges as an important open question to address, with recent advances in fabrication setting the stage for future work in this area.

Advanced functional materials with custom-tailored properties are critical to transformative technologies, such as biointegrated wearable systems, ultrathin electronic devices, high-capacity energy storage, and water purification. Composite materials with emergent behavior stemming from nanoscale constituents represent a powerful pathway to meet this need by introducing potentially unprecedented couplings between electromagnetic, optical, transport, and mechanical phenomena. Such coupling enables new devices such as smart windows (1–3) (Fig. 1A), flexible sensors (4), displays and electronics (5, 6) (Fig. 1B), and highly efficient batteries or catalysts (7) (Fig. 1C).

Over the past decade, the pursuit of multifunctional “nanocomposites” has expanded far beyond the random mixing of functionalized nanoparticles with polymers to encompass colloidal “crystals” generated by self-assembly (8), whose long-range ordering between nanoparticles can impart new and enhanced multifunctionality (9). The key enabling concept is the deterministic, multiscale control of the composite structure; this includes both synthesis of nanoparticles with tightly controlled size, shape, and crystallinity (9) and self-assembly of the nanoparticles into ordered superlattices over much larger length scales. These superlattices can take the form of two-dimensional (2D) monolayers or thin films or form 3D supercrystals (8). To generate a successful ordered nanocomposite, the structure–size–property relationships of the

nanoscaled constituents and ordering must be preserved (or even enhanced owing to superlattice effects) in the host (matrix) material, and not be screened by either the matrix material or deleterious interactions at the plentiful interfaces between the matrix and the nanostructures. Further, many transformative devices require that structure–property relationships be retained through multiple processing steps and device-level integration of additional materials and features. As such, these properties emerge as a universally critical requirement due to the demands of numerous thermal, chemical, and mechanical stimuli, in addition to the functionality driving the nanocomposite composition and structure.

The development of effective pathways to ordered, functional nanocomposites and subsequent implementation has accelerated considerably over the last decade, owing to the confluence of targeted synthesis of nanoparticles, nano- and microscale colloidal assembly over large areas, and 3D printing (Fig. 2). The nexus of these fields is creating unprecedented opportunities to bridge the wide range of length scales present in actual devices. For example, successes in synthesizing microscale colloidal crystals from nanoparticles can be combined with the development of 3D printing processes to deposit ordered nanocomposites with patterning at the micro-to-macroscales.

This review illustrates the potential convergence of the successes shown in Fig. 2 by highlighting advances in each area that are accelerating nanocomposite development and building bridges between various length scales. Several other in-depth reviews are available for specific areas such as nanoparticle synthesis and assembly

(9–13), macroscale assembly of microparticles (14), 3D printing (15), composites from sustainable resources (16), biological composites (17), and carbon nanotube and graphene composites (18). In this review, thermomechanical stability and the influence of defects are unifying themes that transcend particle synthesis, ordering, and patterning, and ultimately serve as a gateway to device implementation. However, several key scientific challenges and research opportunities remain for achieving “nanocomposites by design.”

Nanoscale building blocks and nano-to-micro assembly

The deterministic control of nanoparticle type and shape, and their ordering in assemblies, are the inspiration behind new paradigms in multifunctional nanocomposites. Successful outcomes in materials design hinge on the nanoscale building block, where the state of the art in targeted synthesis of colloidal nanocrystals (NCs)—otherwise known as crystalline nanoparticles—in solution has reached a near zenith. Advances in this regard over the last decade have evolved the field to a state where a diverse library of nanoscaled building blocks can be readily synthesized and implemented (8, 9). The exquisite and multipronged control made possible through these synthesis advances includes: (i) ultranarrow size distributions with only a few percent polydispersity; (ii) an extensive shape library beyond spheres, rods, and polyhedra to now include complex branched structures such as octapods; (iii) compositional constitution with multicomponent control that transcends all bonding types; (iv) electronic doping; and (v) tailored surface chemistries. The compositional spectrum of the constituent NCs now nearly spans the spectrum achievable in bulk materials and includes technologically relevant oxides, semiconductors such as group IV elements (Si, Ge) and III-V compounds, metals, chalcogenides, carbon nanostructures, and organic compounds (9, 19, 20).

The rapidly expanding control of surface chemistry demonstrated of late has paved the way for encoding nanocomposites with the properties of the NC building blocks, provided that the resulting structures and functionality could be preserved during the scale-up to macroscale architectures. Not only does the surface molecular cladding on the NCs mediate the synthesis pathways and, ultimately, colloidal stability, but it is also responsible for many of the attractive properties of nanocrystals and their assemblies. In particular, the surface-capping ligands play a decisive role in optical properties and electronic transport (21). Organic ligands prevail in the vast majority of colloidal NCs, but new inorganic surface chemistries show tremendous promise for solid-state device integration owing to the elimination between insulating bridges between adjacent NCs (21, 22). This new library of inorganic surface chemistries is a key enabler for facile integration in macroscale devices, owing to the ability to stabilize NC colloids in a broader range of solvent polarity, which is a

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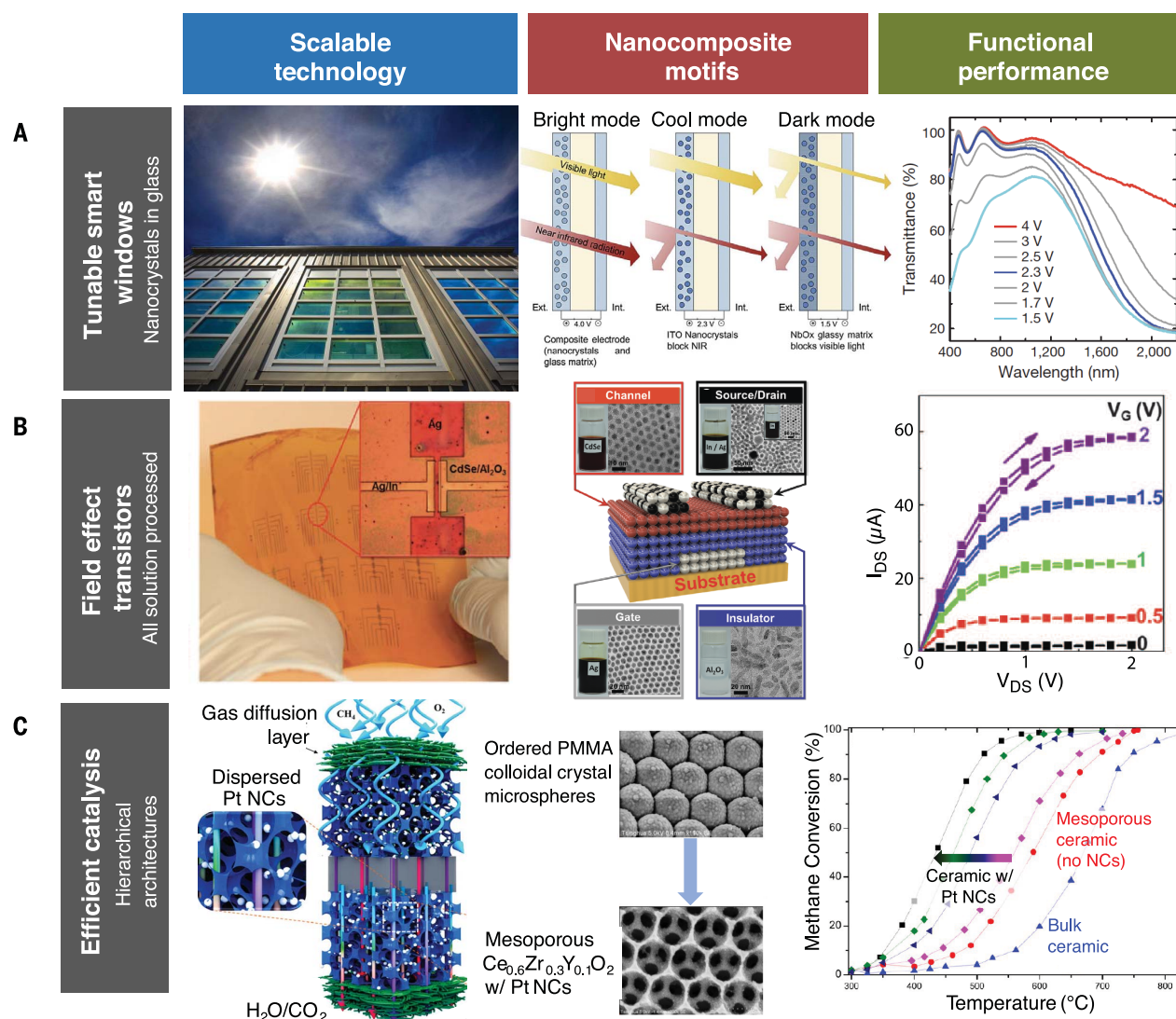


Fig. 1. Applications of functional nanocomposites. Examples of applications that utilize the unique multifunctional properties enabled by nanoscale building blocks in nanocomposites. Nanocomposites enable novel coupling of electrical, optical, mechanical, and transport properties to enable (A) smart windows, (B) electronics and displays, flexible energy storage devices, wearable sensors, skin-like barrier layers, and (C) more efficient catalysis. Adapted from (1–3, 5, 7) with permission.

central ingredient for micro- and meso-scale fabrication using solution-based assembly methods. Inorganic surface functionalization provides electronic links throughout a device irrespective of the hierarchy and enables incorporation of the NC building blocks into nanocomposites formed using inorganic hosts, such as amorphous matrices (3). Two additional strategies for surface functionalization of NCs worth noting are patchy particles (23, 24) and DNA-based attachments (25). Patchy particles encode spatially heterogeneous binding sites that offer new phase selection during assembly, whereas DNA-mediated NC assemblies show a pronounced selectivity in binding (26, 27). Entropic considerations can also direct packing and assembly of NCs to mediate, or even compete with, the enthalpic interactions in unique ways (28–30). These new synthetic strategies represent an exciting opportunity

for bridging length scales with encoded nanoscale functionalities.

The profound size confinement present in NCs is the origin for the attractive properties not found in their bulk counterparts. Central to these new properties are the matching of NC length scales with fundamental physical ones. Examples include quantum confinement for optoelectronic response and plasmonic control, phonon scattering for high-efficiency thermoelectrics and thermal management, and short diffusion lengths and fracture resistance in rechargeable battery electrodes (9). Although demonstrations of attractive device performance (that in some cases is competitive with legacy technologies) in laboratory-scale implementations are numerous (8, 9), harnessing the true power of such NC building blocks in nanocomposite form comprising bulk solids, devices,

and ultimately architectures represents the desired objective.

Indeed, random (stochastic) dispersions of nanostructures, including NCs, in composite form largely result in an ensemble performance that is far removed from those of the constituent building blocks. This points to the challenges of assembly of NCs across many lengths in a manner that preserves the original ordering and collective response of small NC aggregates, which in some cases even give rise to additional or amplified properties not found in the individual NCs. Micrometer-scaled solids of NCs with long-range ordering in superlattices represents one exciting and encouraging avenue (8, 31). The efficacy of the self-assembly processes (32) that drive superlattice formation is another natural consequence of the advances in the synthesis of monodisperse NC building blocks. The vast

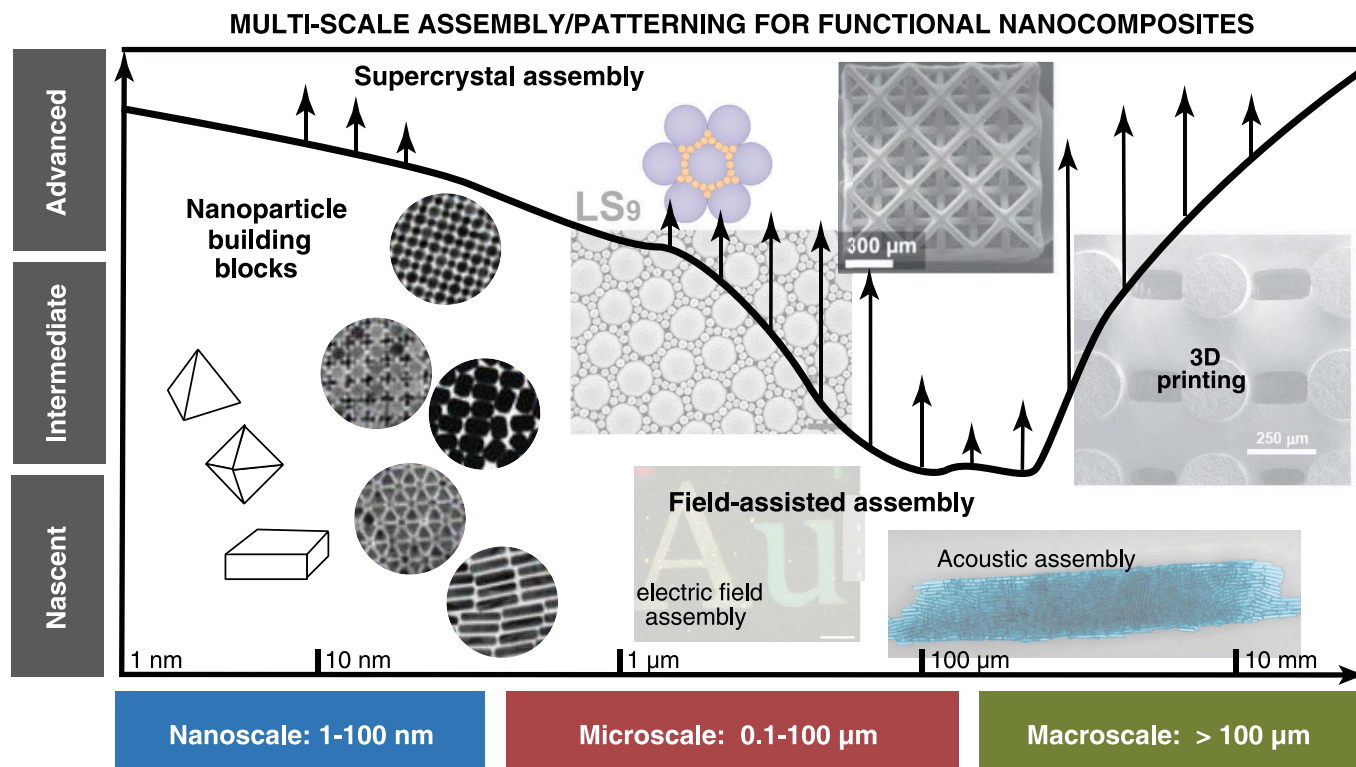


Fig. 2. Convergence of nanoparticle synthesis, multiscale self-assembly, and 3D printing. Well-established pathways to a wide diversity of nanocrystals and advances in assembly and patterning provide clear opportunities for transformative devices; hierarchical assembly techniques that exploit microscale assembly create new opportunities to pattern supercrystals at the device level. Adapted from (8, 14, 52, 77, 78) with permission.

structural diversity of these “artificial atoms” comprising superlattices is truly staggering, as highlighted in (33). Another exciting synergy between the library of NC building blocks, surface chemistries, and superlattice assemblies is the advent of ligand-exchange chemistry, wherein ligands can be exchanged after self-assembly of superlattices of a particular ordering (11, 34, 35). This modality, in addition to galvanic reactions and Kirkendall effects, opens the door to a large tunability in the properties of superlattices given the control of the “bond” length and physical attributes. Ligand exchange can additionally provide pathways to structural transformations that would be thermodynamically or kinetically hindered during the initial self-assembly process, although one persistent challenge is maintaining mechanical robustness of the assemblies and avoiding crack formation (36).

Fabrication of nanocomposites from NCs: Scaling up and patterning

The pace of nanocomposite development depends critically on effective pathways to embed NC building blocks within patterned features needed for device integration (Fig. 3). Bridges are needed between nanocomposite synthesis, the controlled ordering and spacing of nanoparticles, and patterning at large length scales. Broadly speaking, “bottom-up” and “top-down” strategies exist for fabrication and patterning of high-volume fraction, ordered nanocomposites

over large areas. Compelling examples of bottom-up approaches use solution-based assembly of nanoparticles in thin films that cover large areas (8, 37–39) (Fig. 3, A and B). Promising top-down approaches use direct deposition (i.e., direct-write 3D printing) (14, 15, 40) (Fig. 3, C and D). Hierarchical approaches that target rapid assembly of microscale features (e.g., colloidal crystals) may enable bridges between these approaches, with subsequent patterning either by directed film growth (Fig. 3C) or direct writing (Fig. 3D) (41, 42). Ultimately, the seamless marriage of bottom-up and top-down approaches is most likely to pay dividends in the final nanocomposite.

Bottom-up solution-based assembly approaches exploit surface functionalization, controlled evaporation of a solvent, and/or substrate templating to order nanostructures over large areas (8, 9, 39, 43). Currently, liquid-mediated assembly processes (Fig. 3A) (37), including those that combine transfer printing approaches (44), are making substantial progress toward device-scale nanostructured features. Liquid patterning typically exploits directed capillary interactions to control the assembly process of nanoparticle (and microparticle) suspensions, which, when integrated with specific geometries, enables the long-range 2D patterning of ordered colloidal structures (Fig. 3A) (37). These liquid-based approaches enable the integration of multiple materials while retaining the patterning abilities and are amenable to a variety of surface chem-

istries and sizes (39). However, the stochastic nature of packing and evaporation frequently lead to the presence of cracking or imperfect ordering. Additionally, bottom-up methods require preexisting templates, such as those fabricated in a cleanroom, and thus they are not extensible to “on-the-fly” patterning of arbitrary long-range shapes and out-of-plane patterning is limited. Several compelling examples of robust approaches overcome many of these limitations (38) (Fig. 3B), such as by exploiting silk fibroin as an infiltration material. The resulting film is robust and capable of substantial mechanical deformation, and also harnesses the unique water and photo-responsive nature of silk to enable top-down patterning of the structural features (in this case, interpore spacing). This allows manipulation of the resulting optical properties in two dimensions, the pore size itself and the long-range design, in an arbitrary manner (in contrast to cleanroom-fabricated templates). Other promising strategies to overcome the need for templating profit from hierarchical self-assembly and include patterned deposition by controlled evaporation (45, 46) and control of wetting phenomena (47, 48).

Top-down patterning by direct-write deposition provides a direct pathway for generating multiscale 3D features, and it is well suited to the integration of multiple materials. Early successes in direct printing of highly ordered nanoparticles across millimeter-scale features has been demonstrated for thin films (49, 50).

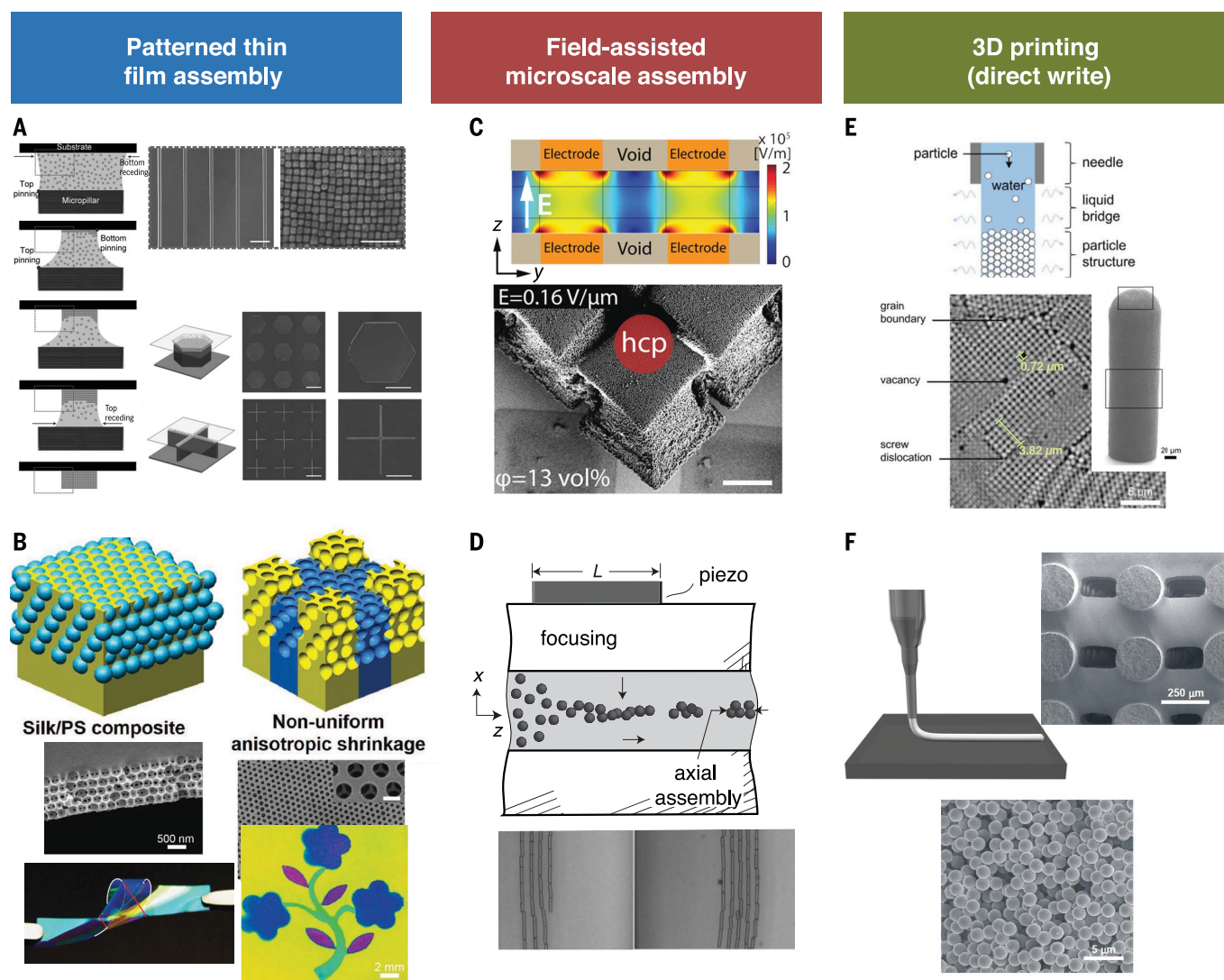


Fig. 3. Emerging multiscale assembly techniques for fabrication and patterning of nanocomposites. (A) Evaporative assembly of ordered nanoparticles in patterned features. (B) Colloidal assembly of nanoparticles followed by infiltration with silk to produce patterned, robust devices that modulate color based on particle spacing. (C) Microscale assembly and patterning of 3D ordered nanostructures

using dielectrophoretic confinement. (D) Microassembly and patterning of particles using acoustics, which can be performed in curable matrices. (E) 3D printing of ordered nanostructures across multiple length scales using an evaporative process. (F) 3D printing with nanoparticle inks that spans multiple length scales. Adapted from (14, 37, 38, 40, 41, 52) with permission.

However, the method has not yet been extended to include matrices for tailored, robust inter-particle bonding or out-of-plane fabrication, which is likely because truly 3D printing by direct-write deposition requires specific ink rheology (14). More recently, direct writing that exploits evaporation-driven assembly has been shown to produce fully 3D features at micrometer to millimeter scales, with fully ordered nanostructures (Fig. 3E) (40). New paradigms for 3D nanocomposite synthesis and patterning would emerge by identifying particle functionalization that produces matrices with thermo-mechanical robustness. Finally, colloidal inks using nanoparticles in solution to fabricate compelling 3D structures (with disordered nanostructure) are well established, with features

spanning from $100 \mu\text{m}$ upward (Fig. 3F) (14). Here again, the development of inks that allow for self-assembly while meeting known shear-thinning requirements would provide unparalleled opportunities for patterning of ordered nanocomposites across multiple length scales and facile integration with other materials.

Beyond thin films comprising superlattices of NCs or 3D assemblies with weak interactions, well-bonded superlattices with sophisticated 3D ordering may be amenable to additional fabrication pathways. The ordered structure of these NC aggregates is often defined by surface functionalization and coordinated through diffusion-controlled assembly (8, 51). As such, the assembly of microscale superlattice particles is relatively fast, but continued growth to larger scales is often

prohibitive. Hierarchical assembly techniques that use microscale assembly in an intermediate step may provide a powerful bridge between NC assembly and microscale-to-macroscale patterning.

The key concept is to exploit assembly mechanisms that are insensitive to solution chemistry to avoid assembly-driven modifications that interfere with surface functionalization, evaporation conditions, or ink rheology. Field-assisted assembly provides highly rapid assembly pathways for microscale particles; the forces generated by externally imposed electric, magnetic, and acoustic fields typically scale with particle volumes, implying that manipulation of micro-particles is three orders of magnitude faster than that of nanoparticles. Two recent examples of

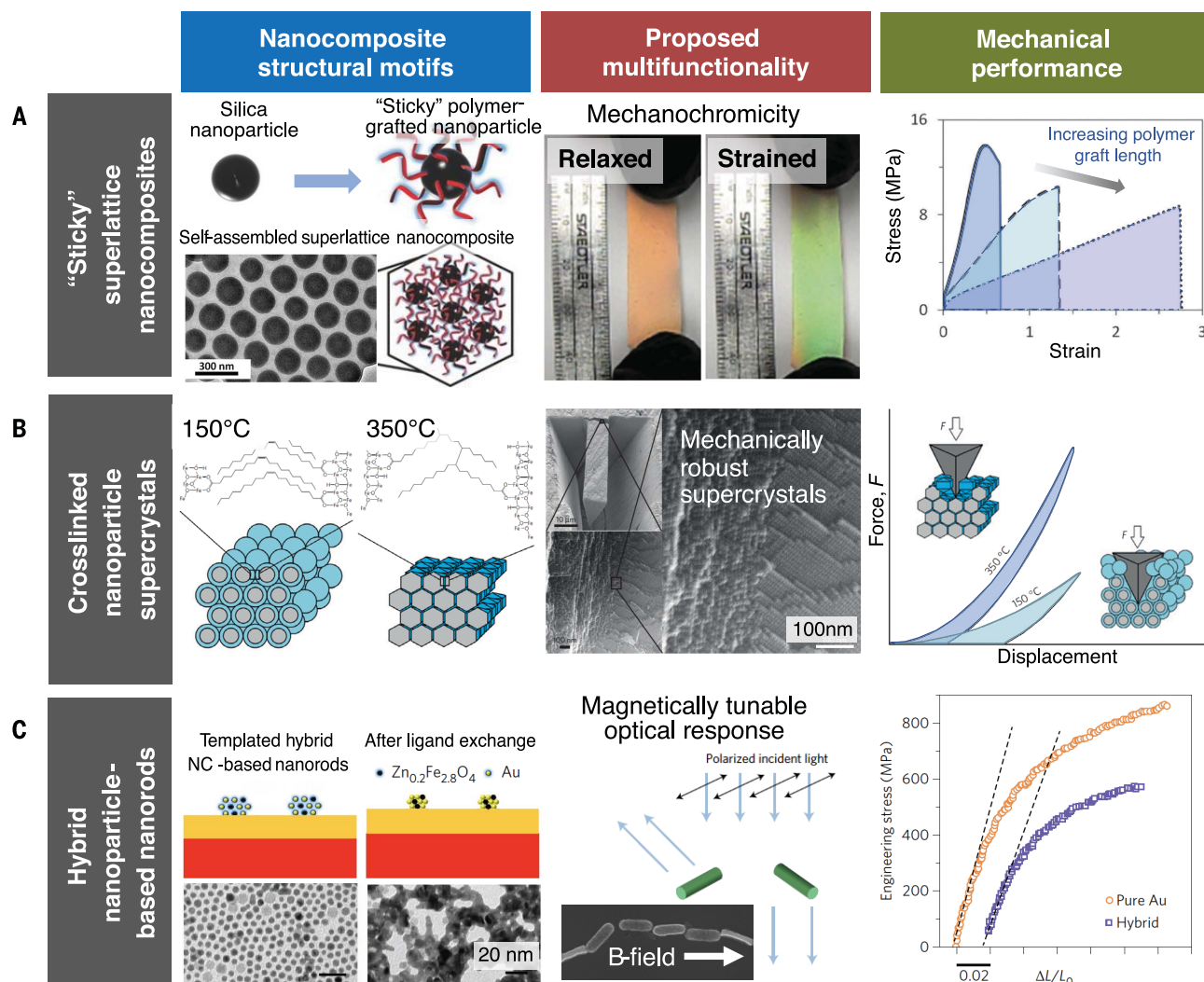


Fig. 4. Strategies for endowing functional nanocomposites with mechanical robustness. A key challenge in nanocomposite development is to identify strategies to produce robust structures that can survive multiple processing steps and device operating conditions. Recent advances in fabrication and patterning create new opportunities to conduct the thermomechanical characterization needed to establish viability, including: (A) the use of “sticky” polymer-grafted nanoparticles, (B) controlled cross-linking of nanoparticle supercrystals, and (C) hybrid nanoparticle-based structures using a combination of bottom-up and top-down approaches. Adapted from (34, 69, 70) with permission.

field-assisted microparticle assembly are electrophoretic confinement and acoustic wavefields. Electrophoretic confinement enables 3D construction of colloidal solids with impressive patterning defined by microfabricated electrodes (Fig. 3C) (41). This approach provides an interesting opportunity to rapidly form patterned structures of 3D superlattice particles, provided the dielectric properties of the 3D superlattices and suspension fluid are properly balanced. Similarly, forces generated by standing acoustic waves produce rapid microscale assembly, both of standing micro- to milliscale patterns (Fig. 3D) (52, 53) and on the fly during direct-write deposition (42, 54). A key advantage of this approach is that it is fairly materials agnostic because the chemistry of the fluid and particles is inconsequential, making it highly amenable to integration with solution-based assembly approaches. A wide variety of particle–fluid systems pro-

vide effective impedance mismatch, and the irrelevance of electromagnetic properties implies that it is applicable to any NC superlattice. Such approaches, when applied to emerging 3D supercrystal-based building blocks, promise to pair the attractive features of deterministic NC assemblies brought together by self-assembly (13, 29, 55) or sequential capillary deposition (56) with larger orders of structural hierarchy.

Incorporating mechanical robustness: A necessary ingredient

The successful bridging of length scales from nanoscale building blocks to macroscopic devices with arbitrary 3D geometries hinges on the intrinsic thermomechanical robustness of the nanocomposites. This is true of many of the facets of synthesis, assembly, and printing, as well as the demands of the multifunctional applications in which thermomechanical duress during opera-

tion is a common feature. Here, the emphasis is on purely mechanical characterization as knowledge of the influence of temperature on mechanical response is still in its infancy (57).

In the case of inorganic NCs, although the particles themselves may have excellent mechanical properties (58), the utilization of organic ligands introduces a relatively weak interaction between neighboring particles in a self-assembled aggregate, ultimately mediating properties such as stiffness, strength, and fracture toughness (59). Recent advancements in the mechanical testing of micrometer- and submicrometer-sized materials enabled the determination of the mechanical properties of a host of nanoparticle assemblies (60). Other characteristics of the nanoscaled assemblies, such as the dimensionality of the assembly (monolayer films assembled at liquid–air interfaces versus 3D supercrystals), the structural ordering or

disordering of the building blocks, and the ligand conformations (60, 61) illustrate some degree of tailoring of the mechanical properties of the nanocomposites.

However, these results show a surprisingly limited range of elastic moduli (of the order ~1 to 10 GPa) despite a large diversity in the inorganic NC material and the synthesis chemistry and procedures (60), suggesting that the mechanics of the ligands govern that of the assembly. The hardness and strength of nano-assemblies appear to be most sensitive to the specific conformation of the ligands, and thereby the spacing between adjacent NCs. Typical hardness measurements range between 50 and 500 MPa (61). However, accurately assessing the fracture toughness of nanoscaled assemblies is challenging. Recent measurements of both PbS NC assemblies with oleic acid ligands and SiO₂ NCs linked with polymethyl methacrylate (PMMA) exhibited values of ~50 kPa m^{1/2} (62, 63), reflecting the brittle nature of these nanocomposites with toughnesses comparable to those of polymeric foams. The new surface functionalization of NCs with inorganic chemistries is emerging (11, 21, 64) and represents a potentially promising path to enhancing the thermomechanical robustness of NC superlattices.

The influence of these relatively low fracture strengths and toughnesses of inorganic NC packings linked by organic ligands manifests at larger length scales during processing and scale-up. In the case of solution processing of nanoparticle assemblies, the interfacial tension imposed by the drying solvent front can lead to tensile stresses that exceed the strength of the particle ensembles, ultimately leading to microscopic cracking (65, 66). With the possible exception of engineered porosity for the purposes of controlling transport, the presence of cracks is deleterious to one or more of the functions of a device, such as electrical conductivity and optical quality. Approaches such as altering the suspension chemistry (66) and using anisotropic NC shapes (67) and layer-by-layer assembly (65) have been shown to mitigate the formation of cracks, but these methods may disrupt the intended structure and ultimately the performance of the material. On the other hand, modifying the drying mechanism using supercritical drying (68) may be precluded by the constraints of the multiscale synthesis and assembly pathway. Further mechanical degradation may occur during chemical processes to modify the nanoparticle functionalization through steps such as ligand exchange, which can lead to pronounced volumetric changes and even phase transformations of NC superlattices, leading to cracking (36).

These challenges and the inherently low fracture strengths and toughnesses of inorganic and organic nanocomposites point to the decisive role of mechanics as a hurdle in realizing macroscale functional nanocomposites. As Fig. 4 highlights, several recently reported approaches appear to impart dramatic improvements to the mechanical robustness of assemblies of nanoscale building blocks and show promise

in paving the way toward hierarchical assembly. In one example, “sticky” silica nanoparticles, synthesized by introducing hydrogen-bonding sites on polymer grafts, exhibit a strong, attractive interaction amenable to both self-assembly into superlattices and relatively strong and tough nanocomposites (Fig. 4A) (69). The ensuing sticky nanoparticle solutions could subsequently be dried and pressed to form macroscopic tensile specimens. The bulk nanocomposites show large strains to failure and intriguing multifunctionality including mechanochromaticity and self-healing characteristics. In a different approach, spherical iron oxide nanoparticles with oleic acid, a widespread organic ligand, were produced, self-assembled into superlattices, and subsequently thermally treated to promote cross-linking of the oleic acid molecules (Fig. 4B) (70). At the highest reported heat treatment of 350°C, faceting of the iron oxide particles occurred, reminiscent of the locking inorganic “bricks” found in mechanically robust natural materials such as nacre. Given the short linkages between particles, the role of the covalent backbone is assumed to dominate over entropic elastic effects. These new structural motifs result in impressive mechanical properties of the ordered nanocomposites, with bending moduli of 114 GPa and hardnesses of 4 GPa.

An orthogonal approach to imparting mechanical robustness is the use of sacrificial colloidal templates, which are then infiltrated to create a continuous and functional matrix material that does not suffer from the weaker NC interactions. The resulting structure is interconnected, and thus mechanically strong and stiff, while also introducing tunable nanoscale porosity. The porosity itself can be viewed as an emergent property arising from the hierarchical structure of pore channels and ligament networks, providing intriguing opportunities for ion transport, high catalytic activity, and photonics (71–73). The use of core-shell particles for melt-shear processing extends the tunability of opal composite materials (74).

In a final example in which mechanical integrity is paired with synergistic multifunctionality enabled by nanoscale phenomena, hybrid nanorods composed of a mixture of plasmonic Au and superparamagnetic Zn_{0.2}Fe_{2.8}O₄ NCs are produced by combining bottom-up self-assembly and top-down templating (Fig. 4C) (34). Chemical ligand exchange is then performed, resulting in a compact ligand, driving cold sintering of Au particles to ultimately produce a nanoporous structure that encapsulates the iron oxide nanoparticles. Whereas the Au nanoparticles and rod dimensions encode the plasmonic response in the infrared, the iron oxide particles (which are sufficiently small to exhibit superparamagnetism and thereby preclude spontaneous aggregation) facilitate magnetic tunability of the optical response. This tunable behavior, showing promise for applications such as smart windows, is accompanied by the excellent mechanical behavior of the nanorods, which exhibit an elastoplastic response with ~350 MPa yield strength,

~700 MPa ultimate tensile strength, and an elastic modulus of ~35 GPa. Such a dynamic restructuring that occurs during ligand exchange affords an additional pathway for robustness in multifunctional nanocomposites.

Much like atomic crystals, NC assemblies are often imperfect and can host a hierarchy of packing defects with the full range of dimensionalities: point defects, line defects, planar defects, and bulk volumetric defects (8, 75, 76). At the superlattice (or supercrystal) level, point defects, dislocations, and planar faults are commonly observed and elucidating their role in functional and mechanical response is a rich area of inquiry. At larger assembly scales, the ordered supercrystal building blocks rarely compact in an epitaxial fashion where the long-range ordering is extended to larger sizes. Instead, domain (grain) boundaries prevail and introduce an additional length scale that could influence the emergent functional response through confinement and scattering effects. Directed assembly approaches that provide alignment (or intentional misalignment) of supercrystals would enable new hierarchical structural, and concomitant property, control. In analogy to defect–property relationships supplanting structure–property ones in atomic crystals, a detailed understanding of defects along an order–disorder spectrum would greatly advance the field of functional nanocomposites and potentially pave the way to strategies for defect- and damage-tolerant response.

Outlook and the path forward

The advances highlighted above enable a new era in ordered nanocomposites in which transformative devices drive a more holistic approach to materials development. The convergence of nanoparticle synthesis, multiscale assembly, patterning, and 3D printing enables more advanced and more specific device concepts, which, in turn, will identify definitive performance and processing targets. However, meeting those targets requires scientific advances in understanding relationships among processing, structure, and properties. The development of “multifunctional” particle–solution combinations emerges as a critical need. Ideally, a single colloidal solution can be used to self-assemble colloidal crystals, pattern features (e.g., through photolithography or 3D printing), and provide a clear pathway to generate robust matrices. This requires a deeper scientific understanding of ligand–particle and particle–fluid interactions at multiple scales (e.g., both within and between supercrystals), subject to a variety of conditions (e.g., evaporation, shearing during printing, field-assisted assembly). Scalability of the sequence of processes needed to realize these goals remains as a major challenge for the future of nanocomposites. Compellingly, advances in assembly and patterning provide a strong foundation upon which to develop new multiscale thermomechanical tests by enabling the fabrication of sample geometries that facilitate subsequent characterization. Simply put, whereas individual advances have put nanocomposites solidly on the path to device implementation,

the convergence of several fields has enabled new avenues to directly probe the nature of particle binding, structural defects, and the influence of domain boundaries (i.e., “grain boundaries” between assembled supercrystals). These scientific studies will undoubtedly unlock new understanding critical to the development of successful holistic approaches that parallel traditional and highly successful alloy development addressing processing, structure, and properties simultaneously.

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Bridging functional nanocomposites to robust macroscale devices

Matthew R. Begley, Daniel S. Gianola and Tyler R. Ray

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Hierarchical functional nanocomposites

Composite materials are constructed from materials that vary in size. Nanoscale materials have unique properties that may be very useful for developing new types of devices. Begley *et al.* review synthesis and assembly methods for functional nanocomposites with a focus on potential applications. Some challenges include scaling and ensuring mechanical stability. Combining new developments from a range of disciplines will be key for enabling advanced device concepts.

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