

Nanoparticle Brushes: Macromolecular Ligands for Materials Synthesis

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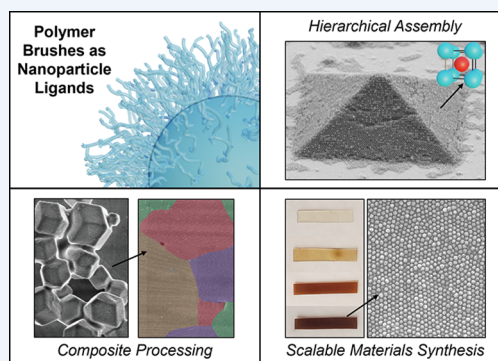
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CONSPECTUS: Colloidal nanoparticles have unique attributes that can be used to synthesize materials with exotic properties, but leveraging these properties requires fine control over the particles' interactions with one another and their surrounding environment. Small molecules adsorbed on a nanoparticle's surface have traditionally served as ligands to govern these interactions, providing a means of ensuring colloidal stability and dictating the particles' assembly behavior. Alternatively, nanoscience is increasingly interested in instead using macromolecular ligands that form well-defined polymer brushes, as these brushes provide a much more tailorable surface ligand with significantly greater versatility in both composition and ligand size. While initial research in this area is promising, synthesizing macromolecules that can appropriately form brush architectures remains a barrier to their more widespread use and limits understanding of the fundamental chemical and physical principles that influence brush-grafted particles' ability to form functional materials. Therefore, enhancing the capabilities of polymer-grafted nanoparticles as tools for materials synthesis requires a multidisciplinary effort, with specific focus on both developing new synthetic routes to polymer-brush-coated nanoparticles and investigating the structure–property relationships the brush enables.

In this Account, we describe our recent work in developing polymer brush coatings for nanoparticles, which we use to modulate particle behavior on demand, select specific nanoscopic architectures to form, and bolster traditional bulk polymers to form stronger materials by design. Distinguished by the polymer type and capabilities, three classes of nanoparticles are discussed here: nanocomposite tectons (NCTs), which use synthetic polymers end-functionalized with supramolecular recognition groups capable of directing their assembly; programmable atom equivalents (PAEs) containing brushes of synthetic DNA that employ Watson–Crick base pairing to encode particle binding interactions; and cross-linkable nanoparticles (XNPs) that can both stabilize nanoparticles in solution and polymer matrices and subsequently form multivalent cross-links to strengthen polymer composites. We describe the formation of these brushes through “grafting-from” and “grafting-to” strategies and illustrate aspects that are important for future advancement. We also examine the new capabilities brushes provide, looking closely at dynamic polymer processes that provide control over the assembly state of particles. Finally, we provide a brief overview of the technological applications of nanoparticles with polymer brushes, focusing on the integration of nanoparticles into traditional materials and the processing of nanoparticles into bulk solids.



KEY REFERENCES

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Lewis, D. J.; Zornberg, L. Z.; Carter, D. J. D.; Macfarlane, R. J. Single-Crystal Winterbottom Constructions of Nanoparticle Superlattices. *Nat. Mater.* **2020**, 19 (7), 719–724.² DNA brushes assemble nanoparticles on DNA-functionalized substrates to form superlattices with specific orientations and shapes.

Kubiak, J. M.; Macfarlane, R. J. Polymer-Grafted Nanoparticles as Single-Component, High Filler Content Composites via Simple Transformative Aging. *Adv. Funct. Mater.* **2022**, 32 (6), 2107139.³ Polymer brushes facilitate the synthesis of

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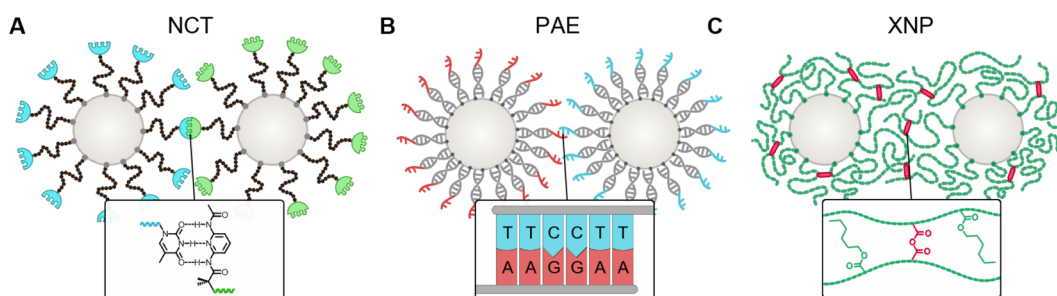


Figure 1. Species of polymer brush nanoparticles. Polymer-brush-coated particles described in this work can be classified by their compositions and the different types of chemical interactions they use to drive materials synthesis. (A) Nanocomposite tectons (NCTs) employ synthetic polymers end-functionalized with supramolecular recognition groups that dictate particle binding and assembly. (B) Programmable atom equivalents (PAEs) are coated in synthetic oligonucleotides, with interparticle interactions governed by sequence-dependent nucleobase pairing. (C) Cross-linkable nanoparticles (XNPs) have functional groups throughout their polymer brushes that permit cross-linking with other particles or a surrounding polymer matrix. For each classification, nanoparticle cores have diameters ranging from 5 to 250 nm. The sizes of the polymer brushes can vary but are generally between $\sim$ 5 and 100 kDa, giving brush heights comparable to the radii of the nanoparticle cores.

composites whose majority component is inorganic but can still be macroscopically molded at room temperature and then cross-linked to provide mechanical resilience.

INTRODUCTION

Nanomaterials are of interest in multiple technological applications and scientific fields, as sub-100 nm features can enable unique properties or behaviors not observed in a macroscopic material.^{4–7} These beneficial properties require control over multiple aspects of nanomaterial design—composition, feature size and shape, and the local chemical environment. Colloidal synthesis and assembly of nanoparticles is therefore an attractive means of materials development,⁸ as judicious ligand selection can both control the particle synthetic protocol and the final particles' interactions with the surrounding environment and each other.^{9–12}

Most colloiddally synthesized nanoparticles are stabilized in liquid suspension via small-molecule surface ligands like oleic acid or trioctylphosphine oxide.¹³ While such ligands are readily available and commonly used, colloidal nanoparticles can alternatively be stabilized with macromolecular ligands (*i.e.*, polymer “brushes”) that offer a wider range of ligand lengths and greater compositional versatility.¹⁴ Despite this potential advantage, macromolecular ligands are far less commonly used than their small-molecule counterparts, indicating the need for more investigation in this area in the fields of chemistry, materials science, and nanotechnology.

Here we present examples that demonstrate the utility of macromolecular ligand brushes in nanomaterials development and thus warrant further investigation and adoption by the nanotechnology research community. We specifically note three categories of polymer-brush-coated nanoparticles that enable different types of materials and properties: nanocomposite tectons (NCTs), programmable atom equivalents (PAEs), and cross-linkable nanoparticles (XNPs) (Figure 1).^{2,3,15–17} We also outline the current state and potential of the technique for advancement in materials synthesis, highlighting critical challenges that need to be addressed. Finally, we present a set of opportunities for collaboration between the colloid, nanotechnology, and polymer communities and aim to inspire these communities to work together to make macromolecular ligands more accessible for the fields of chemistry, materials science, and nanoengineering.

DEFINITION OF A NANOPARTICLE “BRUSH” COATING

It is important to first provide a practical definition of what types of ligand coatings constitute a “polymer brush” (Figure 2A). While small-molecule ligand coatings (*e.g.*, oleic acid) are obviously excluded from this category of ligand, oligomeric species of lengths between these small molecules and full polymers will also be excluded in this discussion, as their molecular weights are far lower than what is necessary to impart many of the properties unique to a polymer brush coating (*vide infra*). While the cutoff length for defining which ligands can constitute a “brush” is somewhat flexible,¹⁸ the brushes discussed here use polymer synthesis protocols that typically have a practical lower limit of $\sim$ 2 kDa due to challenges in both synthesis and purification.

Additionally, macromolecular coatings that allow polymers to lay flat against a particle surface via multiple points of attachment along the polymer backbone are also not discussed. While such “polymer coatings” can also stabilize colloidal nanoparticles,¹⁹ the brush topology (where one end of each polymer chain extends outward from the particle surface) affords several opportunities to tailor nanoparticle and polymer behavior that would not be observed in a “polymer coating” and introduces synthetic challenges that must be addressed for the brush to be useful and well-controlled.

Finally, to constitute a “brush”, sufficient grafting density must be achieved to force the polymer chains to push off of the particle surface in an oriented manner. By crowding polymer chains via dense grafting, their configurations and interactions with one another and nearby solvent molecules are significantly different than sparse grafts where the polymer ligands adopt what have been dubbed “pancake”- or “mushroom”-like configurations (Figure 2B).^{20,21} Most of the properties and behaviors discussed here are a direct result of the brush architecture's influence on chain behavior, and thus, properly controlling graft density is a crucial component of their synthesis.

Synthesizing polymer brushes that meet all of these criteria is nontrivial due to challenges arising both from aspects of polymer grafting that are inherent to the brush architecture and thus inescapable and from aspects that are addressable but represent a technical barrier to a researcher inexperienced in polymer synthesis. For example, high graft densities are entropically disfavored for macromolecules due to steric

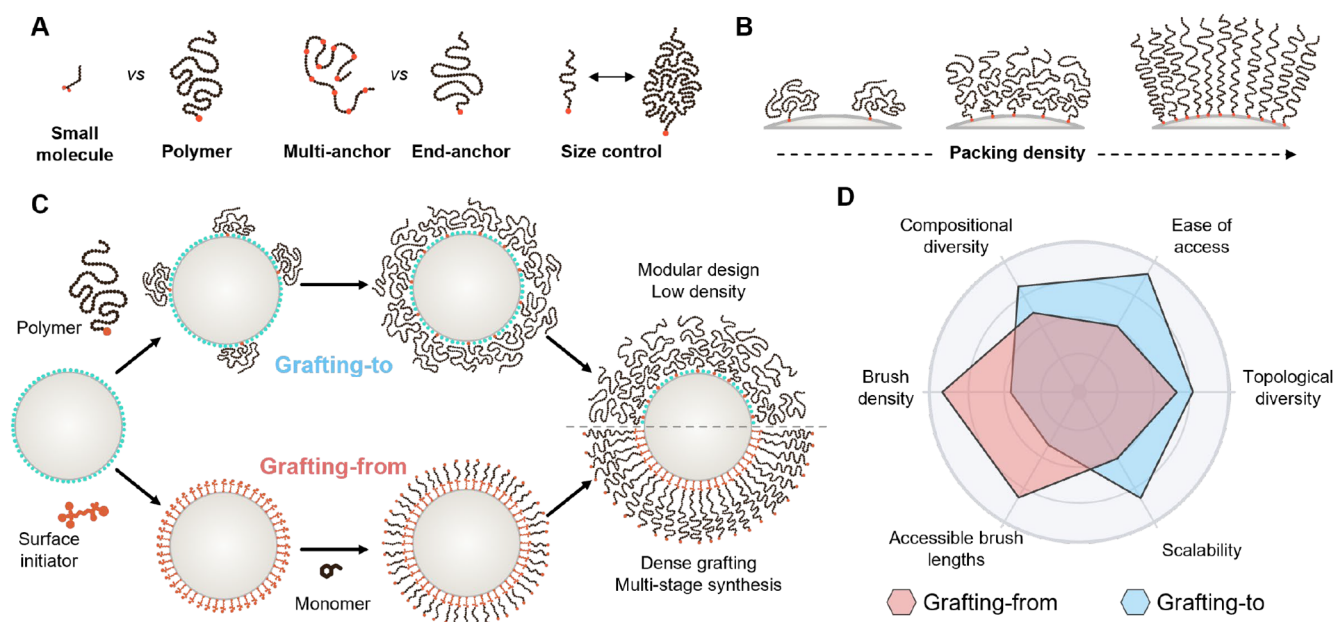


Figure 2. Polymer brush design features. (A) Polymer brushes require macromolecular ligands with tailorable lengths, functionalized only at chain ends with particle anchoring groups. (B) At increasing packing densities, steric crowding forces polymer chains to extend radially outward, altering their configuration. (C) Synthetic methods to form polymer brushes on nanoparticles include “grafting-from” and “grafting-to” approaches. “Grafting-from” requires nanoparticle functionalization with a surface initiator, followed by polymerization from the surface. “Grafting-to” requires a polymer whose chain-end functionalization can bond to the nanoparticle surface. (D) Qualitative spider-web plot of the attributes of “grafting-from” versus “grafting-to” synthesis methods.

crowding effects,¹⁸ often preventing formation of a fully formed brush coating. A more practical consideration is that ready-made polymers with chain ends modified to permit nanoparticle grafting are significantly less available commercially than small-molecule ligands (meaning researchers interested in using a specific macromolecule ligand may need to synthesize it themselves).^{15,22}

A major area of investigation for advancing this field must therefore be developing brush synthesis strategies that are accessible to the broader nanochemistry community. Such strategies can be broadly grouped into two categories: “grafting-from” and “grafting-to” approaches. Our group and others have employed both strategies, and thus, we will provide a simple discussion of the differences and advantages of each (and direct interested readers to recent reviews^{23,24} for more thorough information) (Figure 2C).

“Grafting-from” strategies first functionalize nanoparticle surfaces with a polymer initiator and then form the brush directly via surface-initiated polymerization. Such approaches can be used for any nanoparticle to which an initiator can be attached and readily achieve uniform brushes with dense surface coverage. For example, we have recently demonstrated silica particle brushes with chain densities up to ~ 0.5 chains/nm².³ However, new protocols must be developed for each particle type to be coated, and most existing protocols are for solution-phase, radical-based vinyl polymerizations (e.g., acrylates, styrenes)¹⁸ and thus preclude brushes of many polymer types that would be of interest (e.g., poly(ethylene glycol), polyethylene, polysiloxanes).^{13,21,23} Finally, maintaining colloidal stability while also managing polymerization kinetics and reaction yield limits the amount of nanoparticle brushes that can be grown in a single reaction, making grafting-from options difficult to scale.

In “grafting-to” strategies, polymers are synthesized in solution such that their termini possess anchoring groups to later permit particle attachment—these approaches are similar to simple ligand exchanges commonly used for small molecules.^{9,13,23} Provided that the polymer synthesis method permits chain-end modification with appropriate nanoparticle anchoring chemistry, grafting-to approaches can, in principle, be used for any combination of polymer and nanoparticle composition. The nanoparticle chemist interested in making the brush would not even need to synthesize the polymer themselves if a commercial source were available. Nevertheless, although some polymer compositions with appropriate end group functionalities can indeed be purchased, commercial sources of these ligands are still scarce, typically limited to a narrow range of polymer compositions or lengths. Even if such sources were available, “grafting-to” approaches are generally regarded as inferior to “grafting-from” because the steric bulk of the large macromolecular ligands prevents efficient adsorption and thus limits brush density.^{13,18}

It is worth stating, however, that there are some examples of dense brushes via “grafting-to”, most notably those that use thiols to attach polymers to gold nanoparticles.^{13,15,16} The simplicity of gold–thiol attachment methods and the high grafting density they achieve is a promising sign that “grafting-to” chemistries could expand the utility of polymer brushes if similar attachment chemistries were found for other nanoparticle compositions. For example, we recently demonstrated that phosphonic acid-terminated macromolecules can readily be grafted to oxide particles with densities comparable to (or higher than) those obtained with gold–thiol chemistry.^{15,22}

■ SYNTHETIC POLYMER BRUSHES: CROSS-LINKABLE NANOPARTICLES AND NANOCOMPOSITE TECTONS

The effort required to develop new chemistries to produce macromolecular brushes can be justified by the potential they have in enabling new composite materials that would not be possible with small-molecule ligands. For instance, polymer brushes provide colloidal stability via steric repulsion arising from entropic penalties and confinement of polymer chain configurations that can be readily tuned by brush design (Figure 3A).^{25,26} Brush coatings therefore also permit nanoparticles to be embedded within a polymer matrix without aggregating (as is often observed for small-molecule-coated particles),²⁷ provided that the brush polymers can either entangle or form favorable bonds with the surrounding matrix polymer.

While most brush particle materials have used polymer entanglement to provide mechanical robustness, entanglement between brush chains typically only occurs when the polymers are so long that they limit the accessible inorganic volume fractions to <15%.^{11,21,26} Such materials have significant benefit in mechanically strengthening polymer composites, but we have recently pioneered the development of cross-linkable nanoparticles (XNPs), which use functional handles dispersed throughout short polymer brushes to form covalent bonds between XNPs.^{3,17,26} The introduction of covalent cross-links allows XNPs to possess as much as 85 wt % inorganic content (~60 vol %) but still be easily processed under ambient conditions and subsequently cross-linked into mechanically robust solids. These high-inorganic-content composites that maintain the mechanical properties and processability of the polymer components broaden the scope of applications for such materials.

While XNPs and covalent cross-links between brushes provide a versatile platform for embedding nanoparticles within a polymer matrix, additional control can be gained by incorporating reversible supramolecular interactions between brushes. Tailoring the energetics of these dynamic bonds between particles allows for the formation of organized particle arrays where the particle lattice symmetry and interparticle distances can be influenced by the design of the polymer brush. The specific chemistries used to induce cross-linking and the properties they enable are discussed below (*vide infra*). As an example of this control, our group has established nanocomposite tectons (NCTs) (Figure 3B),^{1,15,28} which comprise inorganic particle cores coated with polymer ligands that express molecular recognition units at the NCT periphery. Through a variety of complementary supramolecular interactions,²⁹ NCTs can be programmed to bind to one another in a predetermined manner, forming composites consisting of 3D nanoparticle arrays embedded within a polymer matrix. Initial work has demonstrated the formation of body-centered-cubic, CsCl, and face-centered-cubic lattices with lattice parameters that can be tuned as a function of polymer brush height.

The initial and most commonly employed NCT design uses polystyrene (PS) brushes with two different end group functionalizations that form a complementary hydrogen-bonding pair, namely, diaminopyridine (DAP) and thymine (Thy).¹⁵ Individual DAP–Thy bonds are relatively weak, but the dense brush coating and flexibility of individual polymer chains permit highly multivalent supramolecular interactions between particles. Altering NCT brush design (e.g., polymer

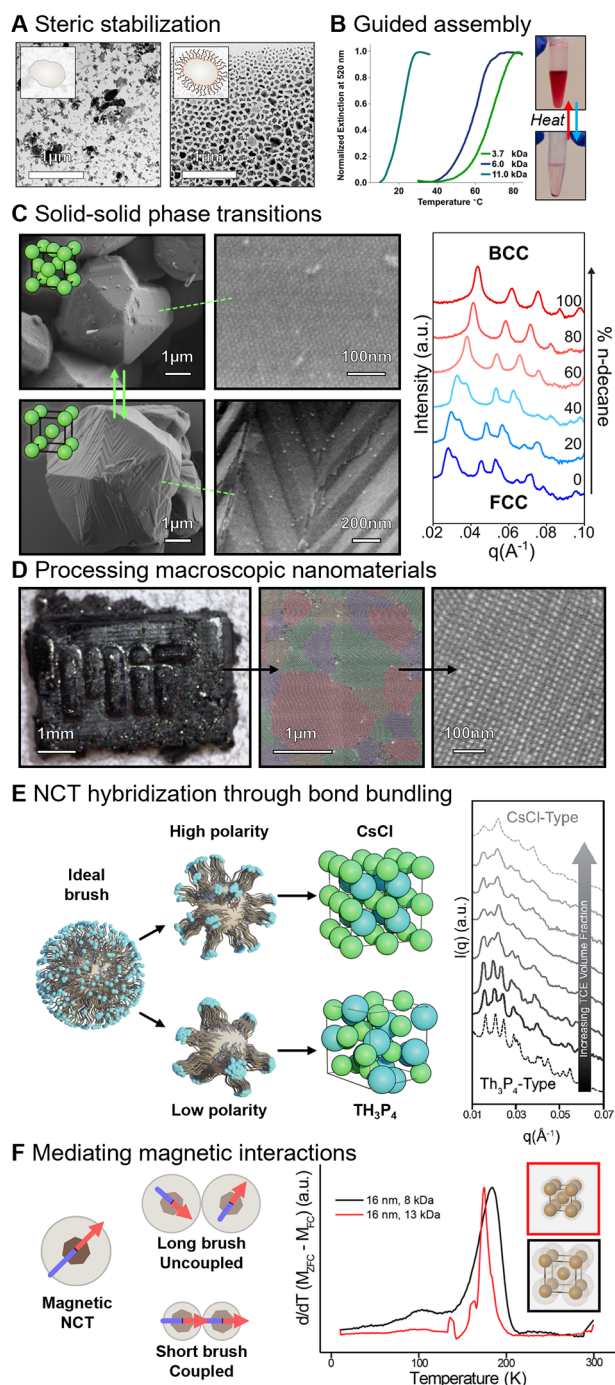


Figure 3. Capabilities of polymer brush particles. (A) Polymer brushes provide steric stabilization: while precipitated suspensions without stabilization flocculate (left), brush-coated particles remain physically separated (right). Adapted from ref 26. Copyright 2022 American Chemical Society. (B) Due to the presence of supramolecular groups at the brush periphery, NCT assemblies can be thermally transitioned from bound to unbound states. The thermal profile of this transition can be engineered by controlling the brush length. Adapted from ref 15. Copyright 2016 American Chemical Society. (C) Collapsing the NCT brush can induce a martensitic phase transition that induces unique microstructural features; these structural changes arise due to differences in polymer chain packing upon brush collapse. Adapted from ref 31. Copyright 2023 American Chemical Society. (D) Discrete single crystals of NCTs can be pressed into macroscopic solids that have specific macroscopic shapes

Figure 3. continued

and microstructures while retaining the nanoscale ordering of the particles. Adapted with permission from ref 1. Copyright 2021 the authors of ref 1, under exclusive license to Springer Nature. (E) NCT chain ends undergo solvent-dependent phase separation into discrete bundles, and this bundling affects the NCTs' preferred crystallographic arrangement. Adapted from ref 33. Copyright 2019 American Chemical Society. (F) The magnetic dipoles of adjacent NCT cores can couple, but the brush length determines the proximity of the magnetic core and the strength of the interaction. Adapted from ref 22. Copyright 2020 American Chemical Society.

length or grafting density) therefore modifies the thermodynamics of multivalent NCT–NCT bonding, since the initial conformation of individual chains constituting the brush affects how much configurational freedom is lost upon supramolecular bond formation. This effect can be accounted for *ab initio* by appropriately designing the polymer brush composition. It can also be modified *in situ* by adding a nonsolvent to induce brush contraction or free polymers to induce osmotically driven collapse.³⁰ We have even demonstrated that reversible collapse of the polymer brush can induce superlattice order-to-order phase changes and novel microstructural features like twinning (Figure 3C).³¹ Importantly, these effects are inherently due to the way the polymer chain behaviors are affected by alterations to brush topology. Given the microstructure's well-documented importance in dictating the properties of bulk materials (and near complete lack of examination in nanoparticle assemblies), the design handles provided by brush architectures make NCTs uniquely poised for major advances in colloidal materials development.

The transition from microcrystal to functional device is not straightforward, though, even with exquisite control over nanoscale structure. To utilize these crystals in functional devices, techniques to process them into macroscopic materials will need to be further developed. Inspired by metallurgic processing, we showed that NCTs can undergo sintering with moderate pressure generated via centrifugation, transforming discrete crystals into bulk polycrystalline solids.¹ The sintered material can be subsequently pressed into a mold to form a specific macroscopic shape (Figure 3D). Notably, the nanoscopic order of the crystals is retained through all processing steps, and thus, NCTs can control material hierarchical structure across 7 orders of magnitude in length scale simultaneously.

While the direct correlation of polymer brush thickness and interparticle spacing is straightforward, the polymer brush topology also induces more subtle effects on supramolecular-driven assembly. For example, since PS chains modified at their end groups with DAP or Thy functionalities are amphiphilic, there is a natural phase separation that occurs in the functional groups when NCTs are suspended in solvents of different polarities. Specifically, in nonpolar solvents, the DAP and Thy headgroups can “bundle” together to minimize contact with the nonpolar solvent. Interestingly, however, computational modeling indicates that the entropic penalty of this bundling behavior only occurs in the assembled systems, as the enthalpic benefit of forming a DAP–Thy supramolecular bond must be present to make this alteration to the brush topology thermodynamically favorable.³² As a result, the bundling behavior can be employed as a design handle to alter NCT superlattice formation, as different lattice configurations

require different amounts of polymer brush bundling. NCT lattices can even be reversibly driven between CsCl-type and Th₃P₄-type phases by changing the solvent polarity, as these lattices have different coordination environments for the particles and thus require different brush configurations to maximize multivalent bonds (Figure 3E).³³

The use of modified polymer brushes to drive particle assembly also provides a means of tailoring interparticle coupling as a function of polymer length. As an example, the inherent superparamagnetism of iron oxide NCTs leads to increased thermal stability of assembled particles compared with gold NCTs of equivalent size and brush coating. This observed increase in stability is due to the coupling of nearby particle magnetic moments (Figure 3F). While a pairwise coupling of magnetic moments between individual particles would be too weak to induce assembly, lattices of particles have collective magnetic interactions that provide a small additional stabilizing force that is distance-dependent and thus can be manipulated as a function of polymer brush height.²²

While the polymer brushes utilized by NCTs have been demonstrated as a robust platform for self-assembly and a useful tool to generate scalable complex materials by design, there are many ways to further expand their capabilities in materials synthesis. For instance, polystyrene has been extensively explored, but NCTs utilizing brushes of mixed polymers, block polymers, and other more complex polymer architectures have yet to be synthesized. Additionally, thermally controlled assembly via hydrogen bonding is the most explored supramolecular bonding, but other possibilities have been demonstrated that enable light, pH, or chemical stimuli to control assembly;³⁴ these additional designs permit further manipulation of material properties. Finally, a better understanding of how the brush architecture affects supramolecular multivalency enables enhanced control over bonding geometry and potentially allows for soft NCT building blocks to generate highly open lattices with advanced mechanical, electronic, magnetic, and optical properties.

■ SYNTHETIC DNA STRANDS AS PARTICLE BRUSHES

One of the most successful examples of a macromolecular ligand coating is the formation of “spherical nucleic acids” (SNAs).³⁵ Although the moniker SNA specifically denotes a spherical shape, the term more broadly refers to nanoparticle brushes composed of synthetic DNA strands modified to enable chain-end attachment and high grafting density. Thus, SNAs are not always “spherical”, but they do constitute a unique form of DNA, since the 3D arrangement of a dense DNA brush around a finite-sized colloidal core imparts different properties and behaviors compared to an individual DNA strand.

DNA brushes on nanoparticles are primarily synthesized via a “grafting-to” strategy, most commonly the chemisorption of thiolated DNA onto gold nanoparticles, though DNA brushes have also been grafted onto multiple other nanoparticle core types.³⁶ SNAs with dense DNA brushes exhibit long-term stability in solution over a wide range of pH, solvent, and ionic strength conditions due to the high density of charge around the brush. The dense DNA brushes also possess unique biophysical properties that make SNAs useful for biomedical applications in diagnostics and therapeutics; we direct the reader to recent reviews highlighting advancements in this area.^{35,37}

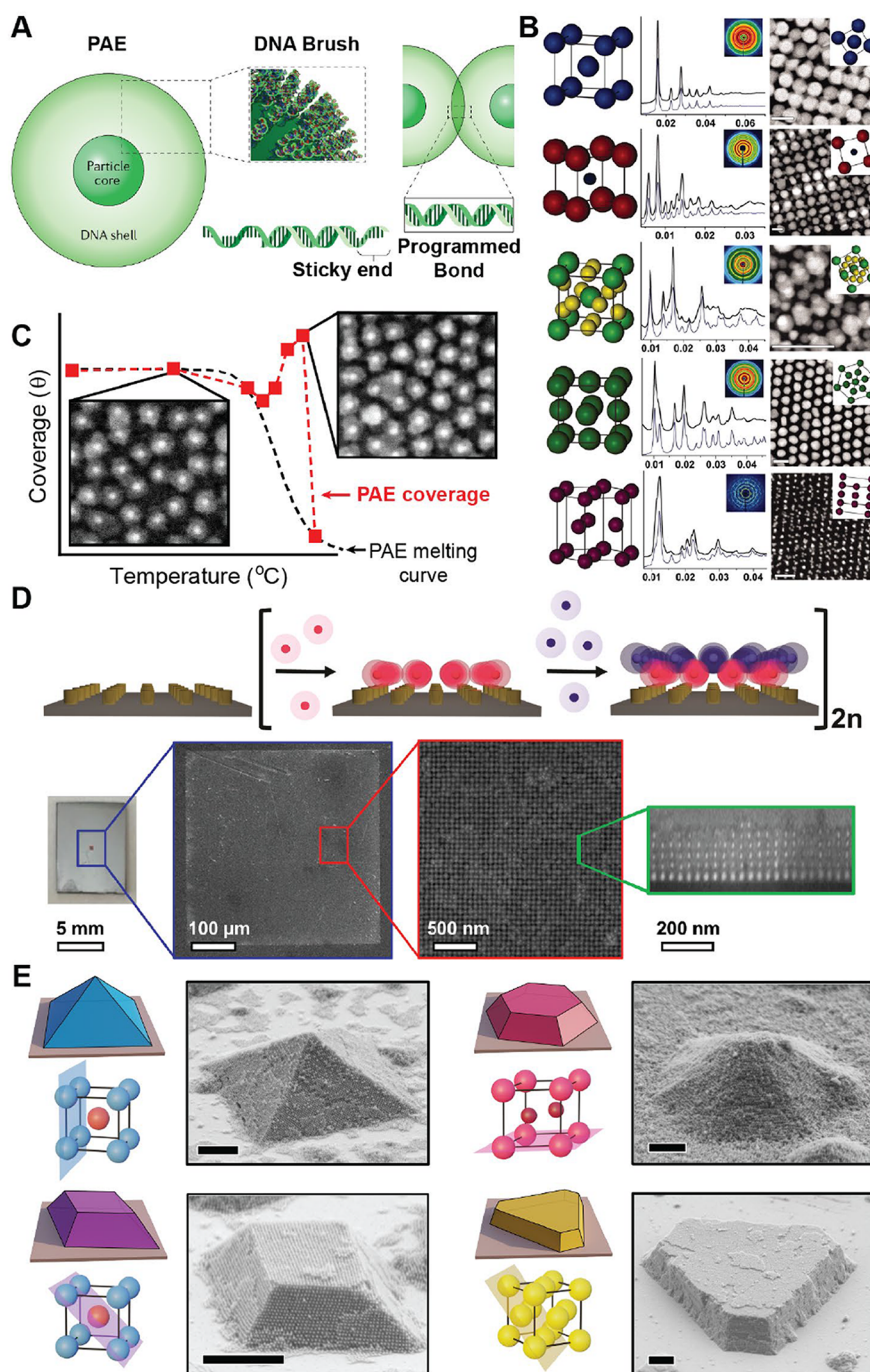


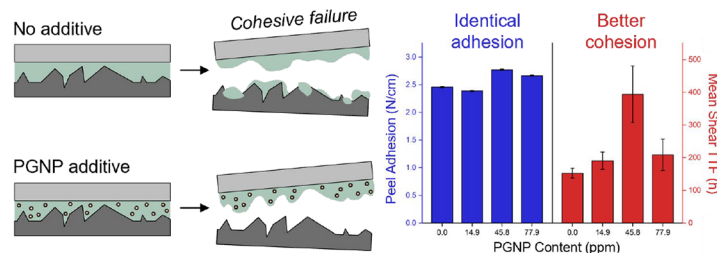
Figure 4. DNA-brush-coated nanoparticles for materials engineering. (A) Schematic of nanoparticles coated with DNA brush as programmable atom equivalents (PAEs). Adapted with permission from ref 40. Copyright 2022 Wiley-VCH. (B) Examples of nanoparticle superlattices engineered with PAEs. Scale bars: 50 nm. Adapted with permission from ref 16. Copyright 2011 AAAS. (C) DNA-brush-enabled non-Langmuir PAE deposition profiles. Adapted from ref 41. Copyright 2018 American Chemical Society. (D) Epitaxial growth of macroscale single-crystal PAE films on a lithographically patterned substrate. Adapted from ref 43. Copyright 2016 American Chemical Society. (E) Winterbottom crystal structures programmed by equilibrium PAE assembly on brush-coated substrates. Scale bars: 1 μm . Adapted with permission from ref 2. Copyright 2020 the author(s) of ref 2, under exclusive license to Springer Nature.

In the context of materials development, the sequence-dependent specificity of DNA hybridization enables the synthesis of nanoparticle superlattices with controllable composition and nanoscale crystal symmetries.^{38,39} In this context, SNAs are often termed “programmable atom equivalents” (PAEs), where the “atom equivalent” component refers to the nanoparticle cores of various sizes, shapes, and

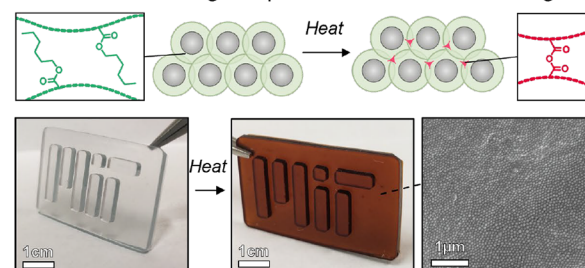
compositions that can be coated with DNA; the DNA brush provides “programmable” bonding interactions analogous to ionic or covalent bonding in atomic lattices (Figure 4A).³⁶

In typical PAE designs, the PAE brush is primarily double-stranded DNA; the brush height and rigidity imposed by DNA hybridization are critical in programming PAE crystal symmetry.¹⁶ The termini of each DNA strand possess short,

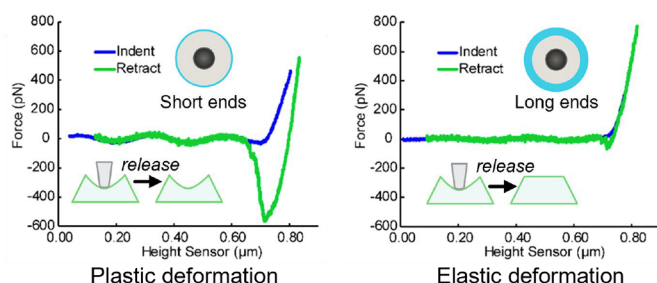
A Improving PSA cohesion with nanoparticle brush additives



B Moldable but strong composites via brush crosslinking



C Brush controlled deformation behavior



D Assembly of functional microdevice components

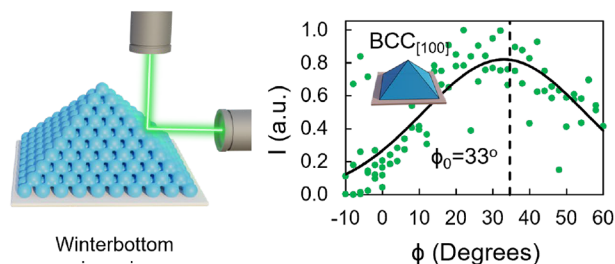


Figure 5. Applications of polymer-brush-coated nanoparticles. (A) In pressure-sensitive adhesives, cohesive failure modes are undesirable, as they leave polymer residue on the substrate. With nanoparticle brush additives, the cohesion of the PSA increases while retaining identical adhesive strength. Adapted from ref 46. Copyright 2022 American Chemical Society. (B) XNPs can be molded into various shapes with minimal thermal energy, even at ≥ 60 wt % inorganic content. Upon cross-linking, the inorganic particle cores remain discrete, but the materials exhibit a significant increase in mechanical performance. Adapted with permission from ref 3. Copyright 2021 Wiley-VCH. (C) PAE deformation can be dictated by tailoring the strength of PAE–PAE sticky-end interactions. Two PAE lattices with identical superlattice structures can be made to deform either plastically or viscoelastically without any change in material modulus. Adapted from ref 47. Copyright 2020 American Chemical Society. (D) The regular shape of PAE Winterbottom crystals can be utilized as micromirrors in optical devices, where the lattices have specific angular reflection profiles based on the shape of the crystallite. Adapted from ref 49. Copyright 2023 American Chemical Society.

single-stranded regions (“sticky ends”), and PAE–PAE bonding occurs via the hybridization of complementary sticky ends (Figure 4A). The guiding principle for generating different PAE crystal symmetries is thus tailoring the sizes and shapes of the nanoparticles and the density of their DNA brushes such that only a specific crystal unit cell maximizes the number of sticky-end hybridizations (Figure 4B). To date, over 70 crystal symmetries have been reported using this approach.^{39,40}

DNA brushes can further be used to control higher-order structural features beyond just PAE crystal unit cell symmetries. For example, macroscopic surfaces can also be functionalized with DNA brushes, permitting layer-by-layer growth of large-scale (though nominally 2D) superlattices. Importantly, the multivalent and dynamic DNA interactions between PAE brushes and surface-grafted brushes allow PAEs to attach and readily diffuse across macroscopic brush-coated surfaces without ever fully desorbing. As a result, PAEs deposit with non-Langmuir deposition profiles, where the gradual reorganization of PAEs across the brush-grafted surface permits denser packing near the PAEs’ melting temperature (Figure 4C).⁴¹ Once multilayer films are formed, this brush-enabled reorganization process can also dominate the crystallization pathway, thereby permitting a means of controlling mesoscale crystalline texture (*i.e.*, the orientation of crystal grains).⁴²

In a more complex example, PAE assembly on patterned substrates coated with DNA brushes enables the growth of arbitrarily shaped single-crystal lattices with millimeter-scale dimensions (Figure 4D).⁴³ These single crystals are synthesized by using electron beam lithography to pattern arrays of

gold nanodots that mimic the chosen crystal plane of the PAE lattice. By grafting these nanodots with DNA brushes, subsequent layer-by-layer deposition of PAEs allows the superlattices to grow epitaxially. Interestingly, the DNA brushes can be compressed or rearranged during assembly to enable heteroepitaxial growth on nanodot arrays with intentionally mismatched lattice parameters, resulting in unique microstructural defects.⁴⁴

When slowly assembled at near-equilibrium conditions, the dynamic DNA interactions between PAE brushes permit superlattice reorganization into shapes that not only maximize DNA interactions between PAEs but also minimize the number of unpaired DNA sticky ends at the surface of a crystal. This principle was first used to create micrometer-sized Wulff polyhedra via homogeneous nucleation of PAE crystals in solution.⁴⁵ While these single-crystal PAEs presented a unique opportunity to examine and tailor structure–property relationships, practical applications require controlled placement and alignment of the lattices on a device surface. To this end, our lab first reported the on-substrate fabrication of such single-crystal superlattice structures of PAEs with defined sizes, shapes, and orientations via heterogeneous nucleation on a DNA-brush-grafted surface (Figure 4E).² These structures, termed Winterbottom constructions, are essentially thermodynamically favored Wulff polyhedra truncated at a plane that maximizes binding between PAEs and the substrate. By altering the DNA brush design to favor different unit cell geometries and different orientations on the substrate brush, multiple distinct crystallite geometries can be obtained.⁴¹

■ MATERIAL APPLICATIONS OF NANOPARTICLE BRUSHES

Macromolecular ligand brushes are interesting tools for colloidal materials development, as the polymer and nanoparticle components can each be used as design handles to tune the other's behavior—*i.e.*, the nanoparticle scaffold can alter polymer chain configurations and packing, and conversely, the polymer brushes can dictate nanoparticle interactions with their surroundings.

Both of these effects were recently shown to improve the performance of pressure-sensitive adhesives (PSAs).⁴⁶ Specifically, they enable a means to circumvent the (generally undesirable) cohesive failure of a PSA, where bonds within the PSA's elastomeric component break during adhesive removal and leave residue on the substrate (Figure 5A). While most commercial PSAs address this issue by cross-linking PSA elastomer chains, the extent of cross-linking needed to prevent cohesive failure also decreases the ability of the PSA to flow and thus significantly impairs its adhesive strength. The need for a large number of cross-linking points can be mitigated via the addition of a small weight percent of elastomer-brush-grafted nanoparticles. A dense polymer brush allows the particle cores to act as “nodes”, where each cross-linking point between the brush and polymer matrix provides significantly greater cohesion to the bulk material compared to individual polymer chains cross-linked to each other. The net effect is a tripling in the cohesive strength of the PSA, even at cross-link densities low enough to have no observable effect on adhesion.

As noted previously, we have also demonstrated that nanoparticle brushes on XNPs provide a new means of generating polymer nanocomposites with ultralarge quantities of inorganic content (up to 85 wt %) without sacrificing the mechanical properties or processability of the polymer components (Figure 5B). The first iteration of XNPs used polymer brushes containing epoxy groups that could be cross-linked with difunctional amines.¹⁷ XNPs consisting of silica particles (50–250 nm in diameter) with ~15–150 kDa polymer brushes were cast from solvent into films that were up to ~60% silica by mass. Despite these high loadings, the XNPs did not aggregate due to the steric stabilization of the polymer brush. Moreover, the cross-linking of these brushes significantly improved both the hardness and modulus of the composites over films consisting of just the cross-linked epoxy-containing polymer (increases of ~100% and ~60%, respectively).

Subsequent iterations of XNPs used silica particles grafted with methacrylate polymers, which undergo a self-cross-linking reaction at 200 °C in the presence of oxygen via the formation of anhydrides.³ This new composition enabled XNPs to be used as single-component materials that could be easily extruded, molded, vacuum-formed, or otherwise processed into complex, macroscopic, three-dimensional solids. Once cross-linked, these materials retained their shape but exhibited a nearly 1000× increase in modulus. Thus, methacrylate XNPs possess a highly desirable combination of properties: the low-temperature processability of thermoplastics and the mechanical strength of thermosets while still possessing large quantities of inorganic material.

Importantly, because the polymer brush coating and its cross-linkability are not inherently tied to the composition of the nanoparticle core, XNPs potentially enable a wide range of composites with beneficial combinations of properties. As an

initial example, we applied the methacrylate cross-linking strategy to alumina nanoparticles, as alumina has significantly higher thermal conductivity than polymers,²⁶ potentially permitting XNP-based materials for heat-dissipating adhesion layers or protective coatings. Highly loaded alumina XNP solids exhibited up to 4 times higher thermal conductivity than a comparable cross-linked polymer while maintaining the polymer's processability and mechanical strength. Future applications of XNPs are therefore promising in technologies where the properties of inorganic materials greatly surpass those of polymers but their costly and energy-intensive processing methods or brittle mechanical properties make them unsuitable.

DNA brush coatings have also become increasingly useful in applications that exploit the unique properties enabled by the scaffolding of oligonucleotides to a nanoparticle core. Indeed, early work on SNAs showed their ability to create both diagnostic and therapeutic tools for a wide range of applications in biomedical devices.⁴⁰ While PAE assemblies have not yet had as significant an impact in commercial applications, their ability to tailor crystal symmetry and microstructure can potentially benefit the fabrication of microdevices and the investigation and tailoring of structure–property relationships.

In this regard, our lab has shown that the DNA brush offers a unique handle to program the mechanical behaviors of PAE crystals.^{47,48} Specifically, the indentation modulus of a PAE superlattice can be tuned over an order of magnitude by altering the particle core size or DNA brush length. More interestingly, by tuning the strength of the DNA sticky-end hybridization, the deformation pathway of a superlattice can be programmed independently of its mechanical modulus. More simply, two lattices that are structurally and mechanically indistinguishable can be made to either readily dissipate energy and deform or completely elastically recover when mechanical force is applied (Figure 5C).

We have also shown that Winterbottom constructions can form key components of optical devices, specifically micro-mirrors used to couple extraplanar elements of a device (Figure 5D).⁴⁹ Because PAE Winterbottom constructions are thermodynamic products, their microscale shapes (and thus the dihedral angle between the crystal and substrate) are predetermined by the PAE design. To exploit this deterministic shape control, we first embedded the crystallites in silica to stabilize them and then coated them with a thin layer of silver. These silver-decorated PAE Winterbottom structures functioned as micrometer-sized mirrors with known reflection angles, permitting ~90% coupling efficiency between an out-of-plane light source and an in-plane detector positioned at a known angular offset. Future efforts will need to further control the size, orientation, and position of the crystallites to fully exploit their use in planar optical devices, and the work regarding PAE assembly on patterned substrates (Figure 4D) offers a promising method toward this goal. Additionally, direct optical processing of substrate-bound crystals may potentially enable such achievements in a direct-write manner.⁵⁰

■ CONCLUSION AND OUTLOOK

Macromolecular ligands have significant utility in altering the properties and behaviors of colloidal nanomaterials, enabling them to be assembled into complex hierarchical structures or used as additives in polymer composites. Moreover, the inherent properties of the polymer chains themselves can be

tuned as a function of composition or length, providing further means to synthesize interesting materials. The combination of nanoparticles and brush coatings can therefore provide access to materials with a wide range of mechanical, optical, electrical, or chemical properties. Compared with the significantly more examined small-molecule ligand coatings, polymer brushes provide a rich but still largely untapped design space for nanoparticle-based materials.

However, multiple barriers still prevent macromolecular ligand coatings from being fully explored or used broadly across the nanoscience community. For macromolecular brush coatings to have a larger impact on nanoparticle materials development, significantly greater effort needs to be expended in the development of user-friendly or commercially scalable approaches to synthesizing a wider range of macromolecular ligands with versatile monomer and chain end chemistries. Better functionalization methods (especially those using a “grafting-to” ligand-exchange-style strategy) must also be established and presented in the literature with accessible and reliable protocols. Finally, investigations must continue to develop structure–property relationships for these unique nanocomposite building blocks. Specifically, technological advancement requires a better understanding of how both polymer brush configurations and nanoparticle properties are affected via alterations to brush composition, nanoparticle scaffold size and shape, or the hierarchical organization of the brush particles in three-dimensional solids.

Multiple potential directions for the advancement of basic scientific investigation and industrial applications become immediately obvious when considering the breadth and versatility provided by intentionally varying both the inorganic and organic components of these composites. Key examples include energy storage materials via tailored electrical or ionic transport (e.g., brushes of ion-conducting polymers on nanoparticles that can take up ions like Li^+ or Na^+),^{26,51} enhanced mechanical properties (e.g., directional mechanical force dissipation as a function of nanoparticle ordering within a solid or composites that use multivalent interactions between particles to drive self-healing),^{3,47,52,53} controlled light–matter interactions (e.g., distance-dependent plasmonic or luminescent coupling tuned via brush deformation),^{1,49,54–56} or exotic electromagnetic phenomena (e.g., giant magnetoresistance by tailoring the three-dimensional organization of magnetically responsive particles).⁵⁷

The significant potential of brush-based ligands heralds an immense impact on fundamental chemistry and materials science research alongside applications in a variety of industrial technologies. As we continue to understand the chemistry of making, assembling, processing, and applying these materials to different scientific questions or technological applications, we encourage the nanoscience and nanochemistry communities to further experiment with macromolecular ligand coatings as a vital area of investigation.

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Notes

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