



Flexible One-Dimensional Nanostructures: A Review



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This review discusses the recent reports on one-dimensional (1D) nanostructures with unusual flexibility. We discuss the importance that flexibility could have in future applications of nanowires and other nanostructures, and detail the two main approaches that have been followed to this day to synthesize highly flexible 1D nanostructures. One approach is based on making crystals in which one or two dimensions of the structure are comparable in size with the unit cell. Such thinness has been shown to provide unusual flexibility. The other approach conjoins hard nanostructures with flexible joints.

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1. Introduction

The interest in nanowires has been largely associated with their integration in electronic circuits, due to their one-dimensional (1D) morphology and nanoscale diameter. Intel and other companies are now working out industrial scale processes for the fabrication by top-down lithography of integrated circuits with 7 nm features: the margin of improvement that bottom-up free-standing nanowires can bring to traditional electronic application is rapidly decreasing. Niche applications that involve non-planar geometries and soft substrates (e.g., integration of electronic devices with living tissues) that are currently incompatible with traditional nanofabrication are promising. Similarly to electronics, applications of nanowires in optics, photonics, and plasmonics are sometimes difficult to justify, given the increasing capabilities of top-down approaches. The relatively low error-tolerance of such applications also limits the potential of bottom-up self-assembly approaches.

Other applications for 1D nanostructures (i) take full advantage of their 1D morphology, (ii) are more defect-tolerant than traditional applications in electronics or optics, (iii) do not require the exact positioning of nanowires on surfaces or in volumes, and (iv) require scalability that is currently incompatible with costly top-down fabrication approaches. Some of the samples here are

nanowire meshes for separation, nanowire arrays for battery and solar cell applications, nanowire fillers for composites, and highly flexible nanowires with polymer-like behavior. This review discusses the potential application of highly flexible nanowires.

Nanowires and linear polymer molecules share a fundamental characteristic: a 1D morphology. The 1D morphology of polymers is one of the three factors (chemical tunability and the flexibility of their backbone being the other two) that contribute to the pervasiveness of polymers in technological applications. The reason why the morphology and flexibility of polymer backbones are so important to their properties can be understood from a thermodynamic standpoint. The backbone of a typical linear polymer consists of C–C single bonds which spontaneously rotate around their axis due to thermal fluctuations (i.e., Brownian motion). This constant, spontaneous motion implies that the backbone samples a large number of conformations (i.e., microstates) over time, while being in thermal equilibrium with its solvent. The number of microstates that are sampled connects to the entropy of the backbone and is specifically called conformational entropy. A zeroth order approximation shows this entropy (i) to scale linearly with the number of rigid segments of the polymer backbone, and (ii) to be much larger than Boltzmann constant (k_B) for relatively small numbers of rigid segments^[1,2]. In summary, entropy determines polymer behavior and is responsible for much, if not most, of the unique properties of polymers that make them irreplaceable in technology.

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Inorganic crystals and their behaviors as ensembles can instead be largely described through the influence of their reciprocal interactions at a distance, i.e., the enthalpy of the ensemble. Entropic effects in the assembly of colloids are gaining remarkable and justified attention^[3–6] but are different from the effects observed in polymer solutions or melts. The structure of crystals is such that their spontaneous flexing due to thermal fluctuations is minimal and therefore their conformational entropy is negligible. However, recent results suggest that certain nanowires are capable of spontaneously changing conformation in solution, thereby suggesting the possibility they could be analogues to polymer molecules.

The technological opportunities offered by the development of inorganic crystals with polymer-like behaviors can be estimated by considering polymer-based composites. Polymer-based composites and their applications largely stem from the need of combining the viscoelastic properties of polymers with the physical properties (e.g., conductivity, dielectric constant, refractive index, magnetic susceptibilities) of inorganics. Major challenges exist in that class of materials: (i) the homogeneous dispersal of an inorganic phase is typically thermodynamically unfavorable and must be therefore kinetically trapped (this kinetically trapped state often tends to phase segregate over time under the influence of mechanical solicitations or thermal fluctuations), (ii) the increased volume fraction of inorganic filler leads to the progressive loss in the viscoelastic properties of the matrix (e.g., brittleness), which therefore limits the range of properties that can be achieved with polymer-based composites, (iii) the nature of the interface between the filler and the matrix is extraordinarily important and yet exceedingly difficult to control, especially on an industrial scale, and (iv) the intrinsic weaknesses of the matrix (e.g., thermal sensitivity) are shared by the composite. The above problems become increasingly severe as the characteristic dimensions of the filler decrease into the nanoscale. As the filler becomes smaller, it diffuses faster, has a higher surface energy, and creates more interfaces with the matrix. Remarkable and creative work has been done to circumvent these obstacles and composites are, of course, amply used in technological applications, but the underlying fundamental limitations persist and could be significantly alleviated by the discovery of a class of single phase materials displaying both the properties of polymers and crystals.

One-dimensional nanomaterials with polymer-like flexibility can potentially expand the scope of application of 1D nanostructures significantly as in (i) crack free, solution processed, inorganic coatings (differently from spherical nanoparticles, flexible nanowires can form self-assembled coatings that do not crack as a result of shrinkage), or (ii) materials for soft robots and responsive matter (most polymers used for soft robotic and stimuli-responsive applications lack the mechanical and electrical properties that would be necessary for reliable field-based applications).

Polymer-like nanostructures are typically obtained by either making very long and thin nanowires or by connecting in a 1D-manner some isotropic nanostructures. Previous reviews by distinguished colleagues and us have outlined the synthetic strategies to produce ultrathin nanostructures^[1,2,7,8]. This review focuses squarely on the aspect of flexibility and therefore addresses the general strategies of producing nanoscale, colloidally stable objects that could spontaneously flex at room temperature, therefore giving rise to polymer-like behavior.

Flexibility is sometimes a poorly defined quantity: it implies that something can flex but without specifying clearly the amount of stress that is required. In the case of inorganic materials science and solid state chemistry, a material is considered flexible if it is capable of significant elastic (i.e., fully reversible) deformation, whereby “significant” is some relative measure of deformation (e.g., $\Delta l/l$). In the case of polymer science the concept of flexibility is

underpinned by thermal fluctuations. The flexibility of a polymer backbone is typically quantified by how much the polymer flexes under the stimulus of thermal fluctuations. Since the flexing is spontaneous, the degree of flexibility of a polymer chain is quantified by characterizing its conformation in solution, and extracting the value of the so-called persistence length, p . The persistence length indicates the minimum distance between two points along the backbone whose tangents are uncorrelated in their orientation. In other words, the tangents to the backbone taken at two points separated by p will have uncorrelated directions. The smaller p is, the more flexible the polymer is. In most cases, the persistence length is not directly measured since the knowledge of the molecular structure of the polymer allows one to make an estimate of the length of the rigid segment.

So far there are no direct demonstrations and thorough characterizations of dynamic flexibility of inorganic crystalline nanowires. There exists one example of such study demonstrating spontaneous flexing of a barcoded nanorod in which two rigid segments are separated by a flexible hinge^[9]. The understanding of the strategies that reliably lead to polymer-like nanostructures is unclear at this point. We discuss here those approaches that appear more likely to give the combination of large aspect ratios and high flexibility that underlies polymer-like behavior.

2. Strategies to Produce Flexible One-Dimensional Nanostructures

Two synthetic strategies have been used to produce flexible colloidal 1D nanomaterials: reducing their diameter or introducing flexible joints along a rigid backbone (Fig. 1).

2.1. Reducing diameter in nanowires

The flexibility of a 1D object can be quantified by the ratio L_n/p between the length of the object's backbone (contour length L_n) and its persistence length p . The larger the ratio (larger L_n and/or smaller p), the more the object will behave as a polymer molecule. In fact, the ratio L_n/p can be shown to be proportional to the number of “rigid segments” (i.e., Kuhn segments) in a polymer molecule and, therefore, determining the conformational entropy of the molecule^[1,2]. An object with $L_n \gg p$ will behave like a random coil (Gaussian coil). The two strategies mentioned above could serve to address the issue of how to obtain small p . One of them is reducing the diameter of the 1D nanostructures.

A variety of synthetic methodologies have been examined and developed for the preparation of 1D nanostructures^[2,7,10,11], such as using templates (hard and soft) and capping agents, vapor–liquid–solid (VLS) methods, anisotropic assembly of isotropic nanoparticles, and size reduction (e.g., etching) by physical and chemical methods. However, some of them are not scalable to the large-scale synthesis of ultrathin colloidal 1D nanostructures. For example, the yield of nanomaterials synthesized using hard templates with ultrathin pores or diameters (e.g. Al_2O_3 membranes, carbon nanotubes) is usually low due to imperfect infiltration of precursors, difficulties in liberating the nanostructures, and the overall cost of the templates in case these are to be sacrificed^[7]. Nanomaterials with ultrathin lateral diameters can rarely be produced by top-down size reduction strategies^[10]. Soft templates^[12–16], ligand control^[17–20], and anisotropic aggregation/attachment (including oriented attachment)^[21–23] have demonstrated to be suitable for the large-scale synthesis of ultrathin colloidal 1D nanostructures with increased flexibility.

Of these strategies, the spontaneous aggregation (also called attachment or coupling) of preformed nanostructures in a 1D fashion to form longer nanostructures (e.g., oriented attachment) is

Flexible Colloidal 1D Nanostructures

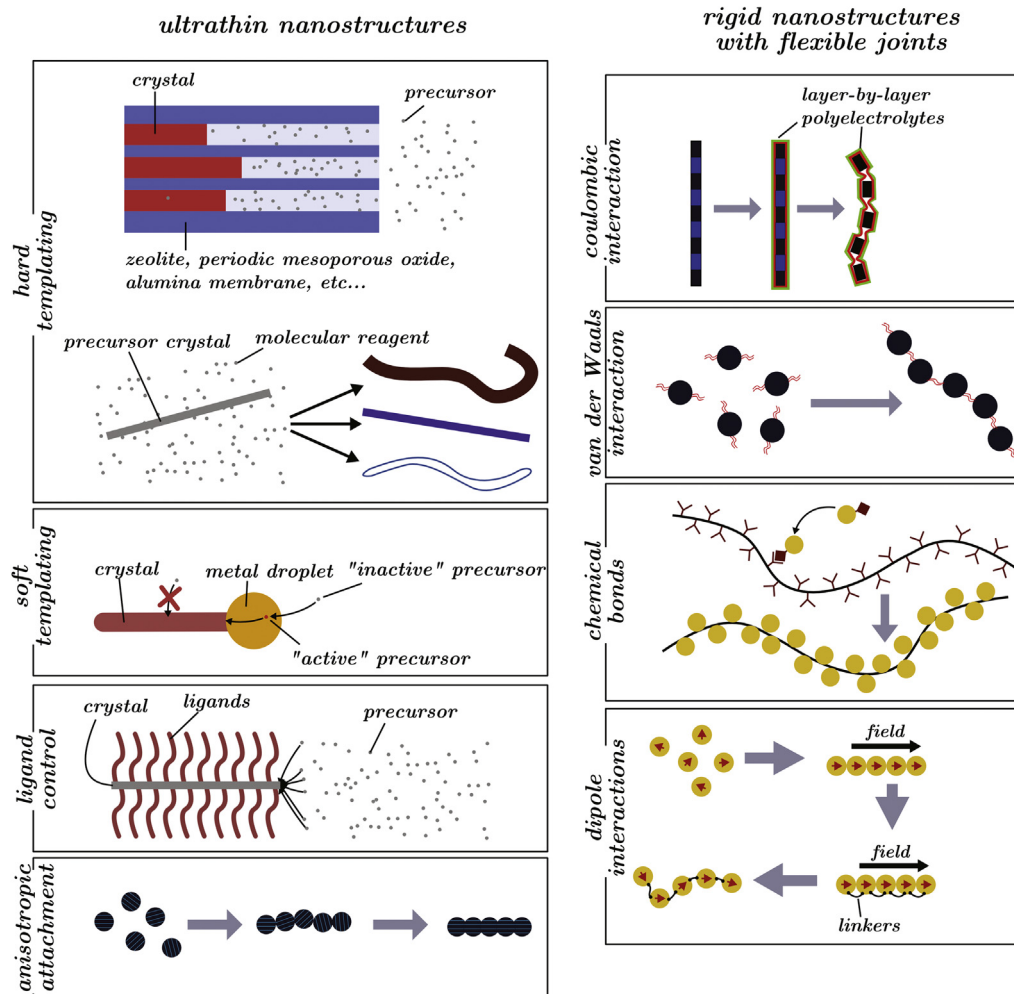


Fig. 1. General methodologies for the synthesis of flexible and colloidal 1D nanostructures^[1,2].

especially worth noting for three reasons^[1]. (i) The diameter of the 1D nanostructures can be predetermined by the diameter of the building blocks from which they are assembled^[7]. (ii) These processes can produce extremely high L/p ratios (i.e., growth happens only in one direction), because of their high selectivity towards 1D aggregation (especially in oriented attachment). (iii) The purely one-dimensional growth, along with the ability of any nanostructure to attach to any other nanostructure, makes this process describable by the same kinetic equations of step-growth polymerization.

Recent reviews by us^[2,7] and others^[24] provide detailed accounts of the strategies for the synthesis of ultrathin nanostructures. Here we review some of the most recent advances that have been reported since those reviews were published.

A number of synthesis of colloidal inorganic nanowires have been ascribed to oriented attachment processes^[25–28]. Tian and co-workers recently demonstrated the formation of ultrathin (~2 nm diameter) GdF_3 nanowires through a solvothermal reaction (Fig. 2(a))^[23]. Gadolinium nitrate and hydrofluoric acid were used as precursors, and two capping agents, i.e. *n*-octylamine and oleic acid, were used in concert to control the morphology and diameter of the final product. These ultrathin nanowires appeared to be flexible as they could conform to the flat surface of a TEM grid and to each other without fracturing. It is worth noting that the ability of a nanowire to conform to a flat surface or to another nanowire

(bundling) upon drying only demonstrates that the forces — capillary, gravitational, electrostatic, van der Waals — involved in the drying process are capable of bending the structures. Per se, this observation does not demonstrate the ability of the nanowires to spontaneously change conformation in solution in the manner of a polymer molecule since the forces exerted by Brownian motion are different in timescales and intensities.

Apparently flexible indium sulfide nanoribbons were reported recently by Wang's group^[29]. They were synthesized by a solvothermal reaction (between 180 and 220 °C) between sulfur and indium acetate in an ethanol/octylamine mixture. These nanoribbons were mechanically flexible (because they were extraordinarily thin (~0.9 nm) with high aspect ratios) and exhibited toroidal conformations (Fig. 2(b)). At extended reaction time and lower amounts of ethanol, the ~13 nm toruses self-organized into remarkable 2D or 3D superlattices with hexagonal symmetry (Fig. 2(c)). The reaction mechanism for the formation of the nanoribbons was not investigated in the report.

In another remarkable report from Wang's group, ultrathin $GdOOH$ nanowires with diameters smaller than 1 nm and lengths greater than 1 μm were synthesized using $GdCl_3$ as the precursors through solvothermal reaction in a mixture of water, ethanol, oleic acid and oleylamine at 170 °C for 4 h (Fig. 2(d))^[30]. The diameter and length of the nanowires could be controlled by the reaction

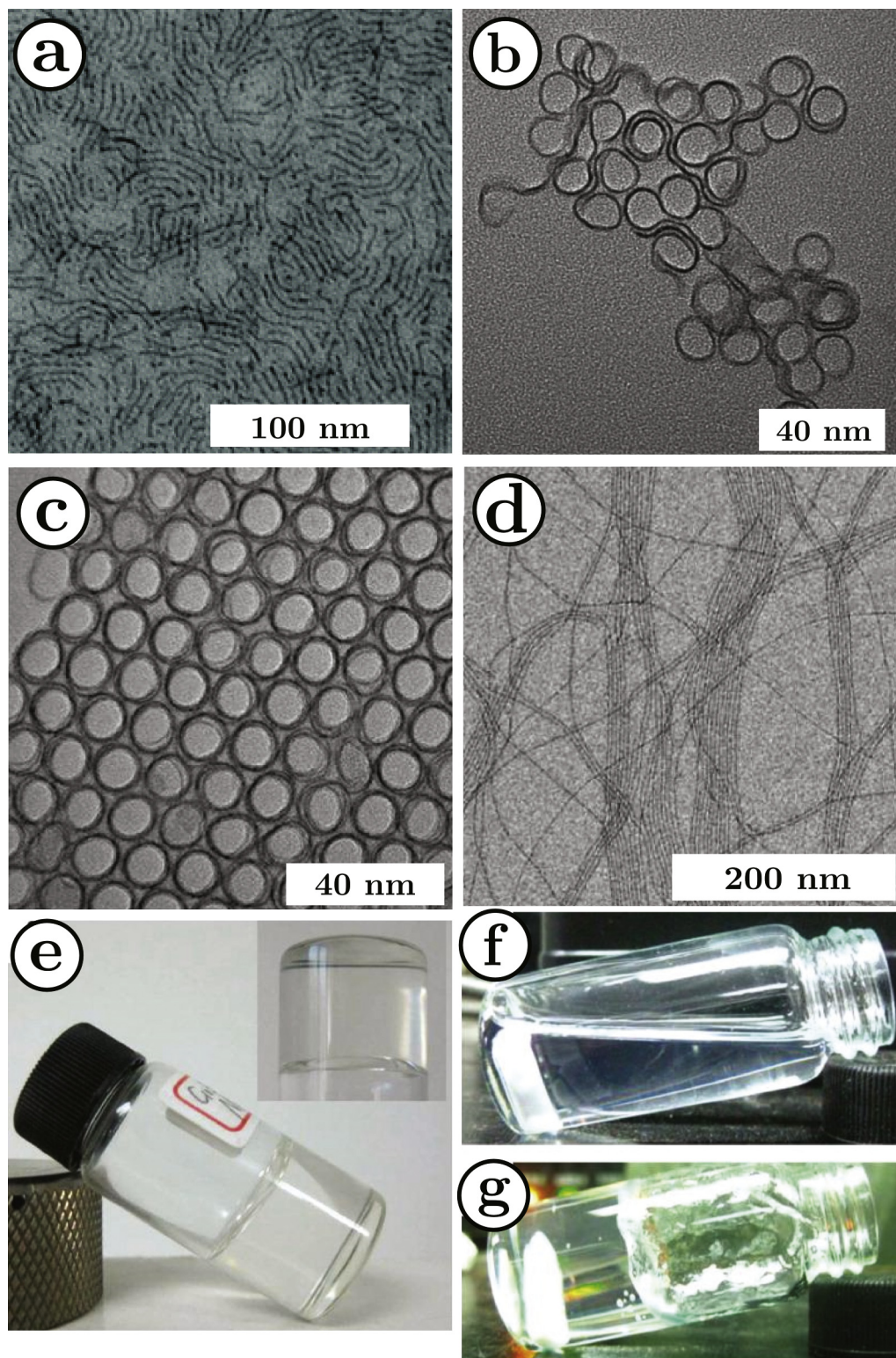


Fig. 2. Recent reports of ultrathin nanowires with apparent flexibility. (a) TEM image of the ultrathin GdF_3 nanowires^[23]. Reproduced with permission of The Royal Society of Chemistry. (b) and (c) TEM image of ultrathin indium sulfide nanoribbons with toroidal conformations^[29]. Reprinted with permission from Ref. [29]. Copyright (2013) American Chemical Society. (d) TEM image of ultrathin GdOOH nanowires^[30]. (e) Gel formation of the GdOOH ultrathin nanowires with high concentration after 2-day aging^[30]. (f) and (g) before and after acid-induced gel formation of the ultrathin nanowires with low concentration, respectively^[30]. Reprinted with permission from Ref. [30]. Copyright (2013) American Chemical Society.

conditions. The growth mechanism was proposed to be oriented attachment: TEM images from samples taken at early stages of the reaction showed 1 nm nanoclusters. Some viscoelastic properties were characterized in colloidal dispersions of these nanowires.

Shear thinning, chain-length-dependent viscosity, and gelation (Fig. 2(e)–(g)) were also demonstrated by the nanowires. Ultrathin $\text{Y}(\text{OH})_3$ nanoribbons were also synthesized via a similar procedure in the same report.

2.2. Introducing flexible joints

The strategies displayed above require (i) the ability to grow crystals anisotropically (which typically requires either an anisotropic template, i.e., Al_2O_3 membranes, or an anisotropic crystal structure, i.e., Bi_2S_3), and/or (ii) diameters that are comparable to the atomic lattice's unit cell ($\sim 1\text{--}2\text{ nm}$). The existing results suggest that the majority of crystalline nanostructures with at least one dimension in this “ultrathin” range will display some unusual flexibility. On the other hand, most inorganic crystalline nanostructures are thicker and thereby rigid.

The strategy alternative to thinning is to create flexible joints (typically organic in composition) that connect otherwise rigid components. (Nanostructures can be also joined by inorganic material but the result is typically rigid^[31–37]). The disadvantages of this approach mostly lies in the added complexity of the material and in the fact that the functional inorganic fraction is not contiguous: charge transport along the backbone of such structures would be, for example, typically limited by the joints. Mechanical properties would also probably be affected by the large number of interfaces along the heterogeneous backbone. The advantages, on the other hand, lie in the fact that (i) rigid segments of different compositions could be combined, (ii) flexibility could be more easily controlled since it would not be as rigidly tied to the diameter of the nanostructure, and (iii) multiple approaches could be devised to control the formation of the joints.

We review here some of the most interesting approaches that have been used to form 1D assemblies of rigid nanostructures joined through chemical bonds or longer range physical interactions.

2.2.1. Flexible joints based on Coulombic interactions

Syntheses of heterostructured nanomaterials — nanostructures featuring different phases in different, controlled locations — such as heterostructured nanowires and Janus nanoparticles have been extensively explored^[10,35,38–41]. Strategies to produce flexible joints often modified existing strategies to fabricate heterostructured nanomaterials. For example, Ozin and co-workers demonstrated that the strategy developed at Penn State University to produce barcoded nanorods^[42] could be used to prepare 1D nanochains with flexible polymer hinges^[9]. In this approach, barcoded Pt/Au nanorods were first prepared by alternating electrodeposition of Pt and Au metals into the pores of alumina template. After the removal of the template, a polymer coating on the surfaces of the barcodes was achieved by layer-by-layer assembly (LbL). The selective removal of Au segments in the barcodes by wet-chemical etching led to 1D rods composed of alternating rigid Pt segments and flexible polymer hinges (Fig. 3(a)). When suspended in water, the rigid Pt segments in the flexible rods spontaneously bent around the flexible polymer hinges under the stimulus of Brownian motion (Fig. 3(b)). One fascinating advantage of this approach is that the contour length, the sequence of compositions, and the persistence length of the rods are all independently controllable: the contour length is determined by the number of segments deposited, the sequence of compositions is dictated by the sequence of metals that are electrodeposited, and the persistence length can be controlled by the number of polyelectrolyte layers deposited by LbL.

2.2.2. Flexible joints based on van der Waals interactions

The anisotropic assembly of isotropic nanoparticles (i.e., isotropic shape and highly symmetric atomic lattice) seems impossible without a template that would allow the existing symmetry in the system to be broken. The elegant work of Chen's group at Nanyang Technological University (NTU) demonstrated

one such template. Recently, they demonstrated how individual spherical polymer micelles could be turned into cylindrical micelles to govern the anisotropic assembly of otherwise isotropic building blocks^[43–45]. Amphiphilic polystyrene-block-poly(acrylic acid) (PSPAA) was used to encapsulate spherical Au nanoparticles, yielding core-shell-structured polymer micelles with Au nanoparticles in their core (Fig. 3(c))^[46]. Upon supplying acid and heat, the micelles underwent 1D fusion and rearrangement, “bringing along” the encapsulated Au nanoparticles and thereby forming 1D Au nanoparticle chains (up to 300 particles in a chain) with uniform diameter (Fig. 3(d)–(e)). This process was characterized to be similar to chain growth polymerization. Single-stranded and double-stranded chains were also controllably obtained.

Nie et al. took advantage of the anisotropy of gold nanorods coated with a bilayer of cetyl trimethylammonium bromide (CTAB) by selectively decorating both ends with thiol-terminated polystyrene (PS) molecules ($M_n = 12,000$), leading to a nanostructure superficially analogous to amphiphilic triblock copolymers^[47,48]: these anisotropic structures possess flexible hydrophobic end blocks and a rigid hydrophilic middle block. Dimethylformamide (DMF) was a good solvent for both polystyrene and the CTAB-capped nanorods. Adding water solely decreased the “quality” of the solvent for the hydrophobic tails blocks and led to the formation of various aggregates, including flexible chains of nanorods (Fig. 3(f)). The contour length was tunable by the amount of water added: more water led to increasingly unfavorable PS-solvent interactions and therefore more stable bonds between nanorods. The influence of the molecular weight of the thiol-terminated polystyrene and solvent quality on the assembly of the nanorods were also revealed in detail^[49,50].

2.2.3. Flexible joints based on chemical bonds

Jackson et al. reported that a binary mixture of “immiscible” ligands with different chain lengths on the surface of a nanoparticle with an appropriate diameter and surface curvature will spontaneously phase-separate into domains^[51–55]. A later report by de Vries et al. used the resulting arrangement of ligands to yield “divalent” gold nanoparticles that assembled in short chains due to the reaction of ligands placed preferentially at opposite sides of the nanoparticle (Fig. 3(g))^[56]. A remarkable report by Mokari et al. showed that CdSe nanorods with gold tips could be self-assembled into chains by connecting the gold tips with dithiol crosslinkers^[57].

Assembly of preformed nanoparticles onto 1D soft or flexible templates, such as polymers and biomolecules, provides another pathway for the generation of 1D flexible nanostructures^[58–60]. In this case, the flexibility of the resulting chains is largely determined by the flexibility of the templates and the loading of nanoparticles on the templates. Although electrostatic interaction is commonly implemented as the mechanism for the assembly^[61–64], Watson–Crick base pairing interaction between complementary deoxyribonucleic acid (DNA) strands enables programmable, and reversible assembly of building blocks into high level nanoarchitectures^[65–70]. For example, nanoparticles grafted with DNA on their surfaces can assemble into superlattices whose structure can be encoded in the nucleic acid sequence^[71,72]. Here we only describe one example of guided assembly of nanoparticles into 1D nanostructures by DNA^[73–76]. Telomers that consisted of many repeating segments (up to $3.5\text{ }\mu\text{m}$) were used as templates. Au nanoparticles functionalized with oligonucleotides with a nucleotide sequence complementary to the repeating segments in the telomers bound onto the telomer templates and yielded 1D Au nanoparticles chains^[75]. Similarly, micrometer-long DNA templates with many repeating units were first synthesized by rolling-circle DNA polymerization and long Au nanoparticle chains were obtained by the hybridization between the templates and the

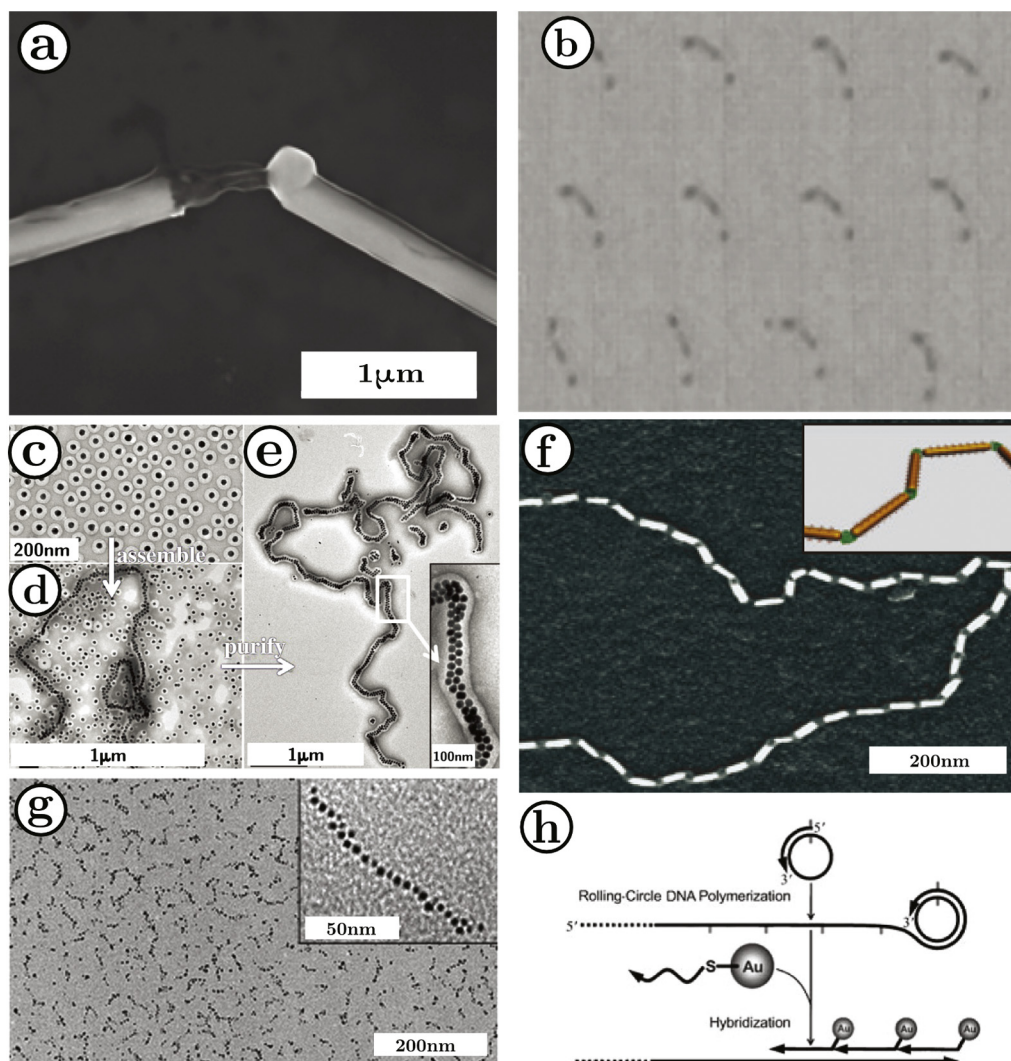


Fig. 3. (a) SEM image of Pt segments connected by flexible polymer sheath^[9]. (b) Timelapse images of hinged nanorods in water displaying spontaneous conformational changes. Reprinted by permission from Macmillan Publishers Ltd: [Nature Nanotechnology] (Ref. [9]), copyright (2007). (c) TEM image of Au nanoparticles encapsulated in the center of polymer micelles^[43]. (d) and (e) TEM images of double-stranded Au nanoparticle chains before and after purification, respectively^[43]. Copyright (c) [2012] [WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim]. (f) SEM image of chain formation from Au nanorods by changing the quality of the solvent. The inset illustrates the end-to-end assembly of Au nanorods. Reprinted by permission from Macmillan Publishers Ltd: [Nature Materials] (Ref. [47]), copyright (2007). (g) TEM image of Au nanoparticles chains formed by connecting "divalent" Au nanoparticles with linkers via a chemical reaction. From Ref. [56]. Reprinted with permission from AAAS. (h) Diagram describing the formation of a 1D colloidal array by DNA-encoded self-assembly^[77]. Copyright (c) [2005] [WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim].

complementary oligonucleotides grafted on the surface of the nanoparticles (Fig. 3(h))^[77].

2.2.4. Flexible joints based on dipole interactions

Dipole–dipole interactions are another fascinating tools to govern the formation of flexible joints in 1D assemblies^[78–85].

Ferromagnetic nanoparticles with high inherent dipole moments can self-organize into chain nanostructures. Similarly, the induced net dipoles in superparamagnetic nanoparticles by external fields can orient the nanoparticles into 1D nanostructures. External magnetic fields are also commonly applied to ferromagnetic nanoparticles to improve their assembly.

Among the many parameters, the size and magnetic moment of the nanoparticles, the inter-particle distance, and the strength of the external magnetic fields are most responsible for controlling the strength of the magnetic dipole interactions, determining the strength of the "bonds" between the adjacent nanoparticles in the assembled nanochains and further controlling the flexibility of the resulting nanostructures. Lalatonne and Pileni have shown that the

occurrence of the nanochains from 10 nm γ -Fe₂O₃ nanoparticles under a magnetic field is tunable by controlling the inter-particle distance via surface coating^[86]. Wen et al. demonstrated that the flexibility and conformation of chains of paramagnetic bead can be tailored by adjusting the strength of the external fields^[87]. Semi-flexible chain assembled from paramagnetic iron oxide nanoparticles exhibited S and U shape structures under rotating magnetic fields^[88].

Ferromagnetic cobalt nanoparticles can self-assemble into well-aligned/randomly-oriented 1D chains with/without an external magnetic fields^[85,89–92]. Similarly, superparamagnetic Fe₃O₄ spheres can be aligned into chains with the aid of external fields^[93,94]. This strategy has also been exploited to assemble nanowires into longer chains such as the nickel chains assembled from shorter wires reported by Tanase and co-workers (Fig. 4(a))^[95]. Pyun and co-workers synthesized polymer-coated ferromagnetic cobalt nanoparticles with diameters of ~20 nm^[96]; these nanoparticles can self-assemble into flexible chains with relatively high aspect ratio (Fig. 4(b)). The authors investigated also

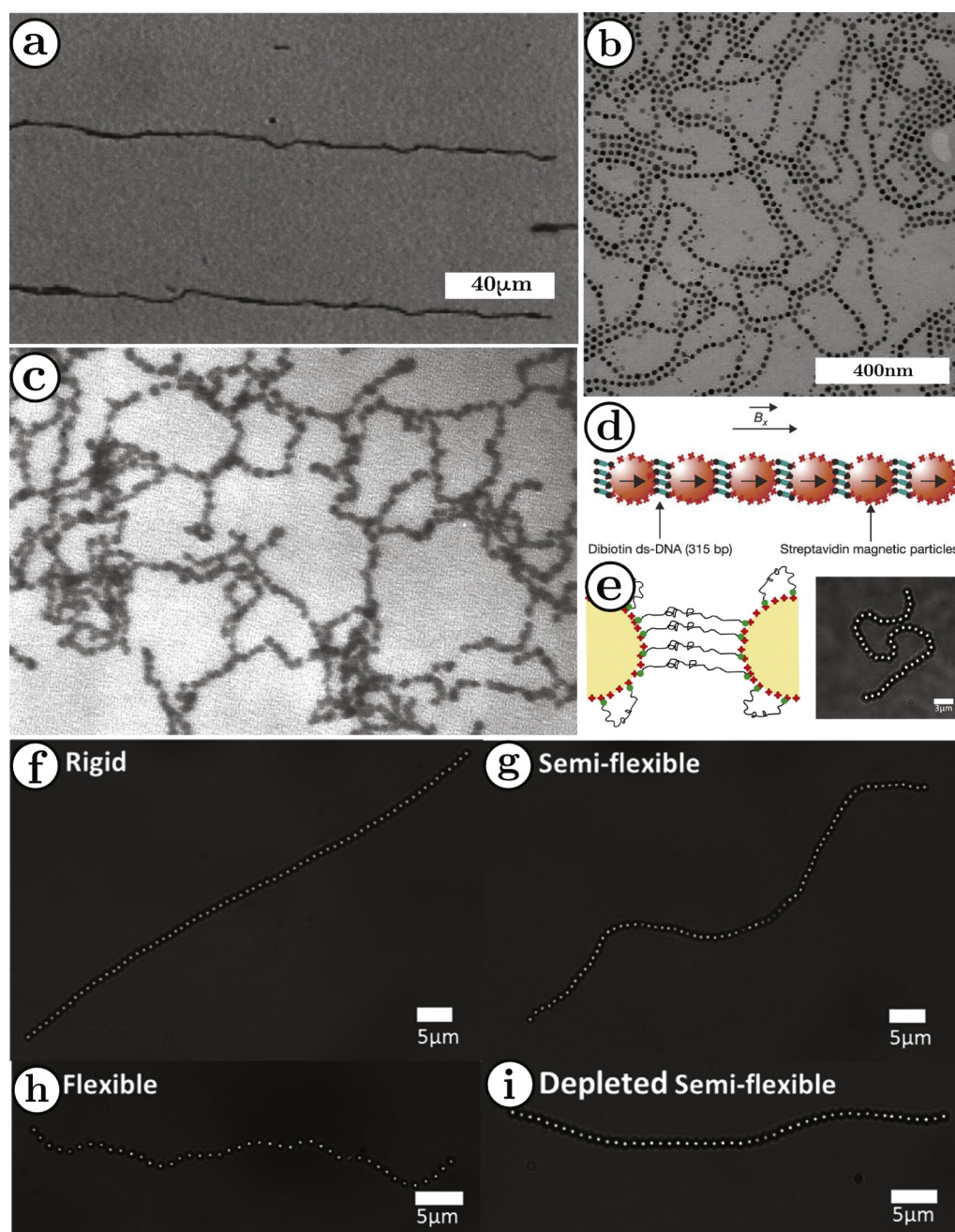


Fig. 4. (a) Chain formation from short Ni nanowires in an external magnetic field. Reprinted with permission from Ref. [95]. Copyright (2001) American Chemical Society. (b) TEM image of self-assembled ferromagnetic cobalt nanoparticles surface-coated with polystyrene. Reprinted with permission from Ref. [96]. Copyright (2007) American Chemical Society. (c) TEM image of self-assembled CdTe nanoparticles via dipole–dipole interaction, showing the nanoparticle–nanowire transition. From Ref. [97]. Reprinted with permission from AAAS. (d) Schematic diagram of the structure of flexible 1D chains. Streptavidin grafted superparamagnetic particles were assembled into chains by an external magnetic field and bound by biotinylated double-stranded DNAs (315 base pairs). Reprinted by permission from Macmillan Publishers Ltd: [Nature] (Ref. [115]), copyright (2005). (e)–(h) Schematics and images of rigid, semi-flexible, and flexible chains with increasing DNA linker lengths. (i) Image of semi-flexible chain due to the depletion of long DNA linkers at high magnetic field strength. (e)–(i) Reprinted with permission from (Ref. [116]). Copyright (2014) American Chemical Society.

the influence of the thickness of polymer coating, the external fields, and the solvent on the morphology of the assembled structures.

The anisotropic electric dipole–dipole interaction has also been widely used for 1D assembly of nanostructures. Semiconductor nanoparticles (or quantum dots) with noncentrosymmetric crystal lattice structure (e.g. CdSe, CdS), asymmetric surface charging^[97,98], surface defects^[11], or other characteristics^[22,99,100], can display an electric dipole moment, which can be used to assemble

nanostructures^[101–104]. In a classic example, Kotov and co-workers demonstrated that strong dipole–dipole interaction between the CdTe nanoparticles, increased by partial removal of stabilizers on their surfaces, led to the 1D assembly of the particles and eventual attachment into single crystalline nanowires^[97,105], as shown in Fig. 4(c). In another classic demonstration, PbSe nanocrystals were shown to have a very high probability (89%) of losing their centrosymmetric crystal structure due to asymmetric distribution of surface charge which then leads to a nonzero dipole moment,

which subsequently induced the oriented attachment into nanowires^[22]. While these two examples led to rigid nanostructures (they were purely crystalline structures with diameters of several nanometers and no flexible joints), they demonstrate the efficiency of dipole moments in leading to 1D assembly. The formation of CdS stripes from nanorods with the aid of electric dipolar interaction between the rods under nonequilibrium assembly condition is another example^[106].

The “bonding” strength between adjacent particles/rods in an assembled chain stemming from dipolar interactions could be too weak to maintain the assemblies organized against perturbations^[11,106,107]. For example, the assembled 1D nanostructures may degrade, collapse, or form nanorings after the removal of the external fields^[108–110]. Forming stronger joints — based, for example, on covalent bonds — after the directed assembly is a possible solution to combine the efficiency of directed assembly with the resilience of chemical bonds. Generally, bifunctional molecules and specific biomolecular interactions have been frequently used as linkers^[111–114]. For example, Dreyfus and co-workers produced resilient and flexible 1D chains via first constructing a chain of superparamagnetic particles by an external magnetic field and then connecting adjacent particles in the chain via DNA hybridization (Fig. 4(d)). Remarkably, the flexible chains could be actuated by varying externally applied magnetic fields and mimic flagellas, moving cells attached to one end of the chains^[115]. More recently, Byrom et al. reported that microchains with aspect ratio of more than 100 can be prepared through this strategy. The flexibility of the chains were easily tuned by the strength of magnetic field and the length of the DNA spacer (Fig. 4(e)–(i))^[116].

3. Conclusions

Flexibility is a trait of matter that gains remarkable scientific importance when it allows for structures to reconfigure spontaneously due to thermal fluctuations at room temperature. Matter then gains two formidable capabilities: (i) a large conformational entropy which drives unconventional and useful behaviors (e.g., rubber elasticity, large responsiveness to stimuli), and (ii) the ability to fold into stable conformations whose structure can be encoded by interactions and constraints. The first capability, when first introduced in the realm of materials science by the discovery of polymers, transformed our society by providing solutions to intractable problems. The second capability is currently beyond much of our reach (i.e., we can synthesize only relatively small proteins and we have a really hard time predicting what structure will be produced by a certain type of amino acid sequence), but it enables life.

As a goal for synthetic materials science and nanotechnology we believe there is little that is more stimulating and challenging than pursuing materials that could fundamentally mimic the molecular building blocks of life, and transform society by combining the unique properties of polymers with the extraordinary physical properties of inorganic crystalline matter.

At this early stage of this emerging field, plenty of questions remain to be solved, such as (i) to what degree can we integrate the quantum size effects of nanomaterials, the physical and chemical properties of inorganic crystals, and the topological properties of polymers in a single phase material? (ii) to what extent can flexible 1D nanostructures capture the essential topological properties of polymers, (iii) can information be encoded into the polymer-like flexible 1D nanomaterials in a similar way as in biopolymers (e.g., DNA)?, (iv) what technological opportunities will flexible 1D nanomaterials bring as a result of their integration of properties? (v) can we directly borrow the existing knowledge in polymer chemistry to develop the polymer-like inorganic nanomaterials with controlled architecture and composition?

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