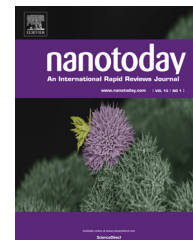




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REVIEW

Self-assembly and applications of anisotropic nanomaterials: A review



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Summary Anisotropic nanoparticles are ideal building blocks for a variety of functional materials due to their unique and anisotropic optical, electronic, magnetic and mechanical properties. Precise control over the orientation and spatial arrangement of these nanomaterials is often requisite to achieve coupling between nanoparticles and thereby translate the properties of individual nanoparticles to macroscopic material properties. The physics and thermodynamics involved in the self-assembly are inherently more complex than isotropic nanoparticles due to the anisotropy within the system. However, the anisotropy also introduces anisotropic nanoparticle surface chemistry and stronger interparticle interactions which could be leveraged to achieve self-assembly. To address these challenges and opportunities, a plethora of strategies have been conceived and developed to induce the self-assembly of anisotropic nanoparticles into desired nanostructures over macroscopic areas and volumes. These strategies involve manipulation of interparticle physical interactions, modification of nanoparticle surface chemistry, application of external fields, and utilization of physically or chemically patterned templates to achieve the required level of spatial and orientational control over the assembly of anisotropic nanoparticles. The resulting ordered anisotropic nanoparticle assemblies display strong plasmonic, electronic, and excitonic coupling, which render these assemblies as ideal materials for chemical and biological sensing, energy harvesting, and many other technological applications. Considering the rapid advancement in this field of research, this review aims to provide an overview of the assembly, applications, and opportunities of anisotropic nanomaterials.

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Introduction

Nanoscale materials possess many unique electrical, mechanical, and optical properties not found in bulk materials. However, precise control over the spatial distribution and orientation of these nanomaterials is often requisite to tune their ensemble properties and fully realize their use in practical applications. Macroscopic assemblies of nanoscale materials have the potential to revolutionize a wide variety of technologies, including photovoltaics, plasmonics, magnetic storage, and sensing [1–5]. The unique properties of these assembled materials may lead to significant improvements in device size and efficiency. Anisotropic nanomaterials, in particular, are increasingly important materials, as their nanoscale anisotropy in structure and composition gives rise to similarly anisotropic properties [4,6]. However, the assembly of anisotropic nanomaterials faces additional challenges beyond those inherent in assembling isotropic particles. For some applications, such as plasmonically active materials, it is important to control the orientation of the particles relative to their neighbors or the underlying substrate [7]. In other applications, such as mechanically strengthened composites, the nanomaterial used must form an interconnected network to be effective [6,8]. In general, the orientation and/or connectivity of the nanoparticles relative to their neighbors must be controlled simultaneously with their spatial arrangement to harness their unique anisotropic properties.

In addition to requiring a high level of structural and orientational control, the use of ordered nanomaterials in device fabrication also necessitates a method of imposing order that is rapid, scalable, and compatible with existing processes. The “bottom-up” fabrication involves employing and manipulating particle–particle or particle–scaffold interactions to induce the assembly of the nanoscale building blocks into ordered structures, and has shown significant promise in assembling particles in a reliable and scalable manner. This class of methods is quite broad, incorporating approaches involving a variety of materials and techniques, including DNA [1,9–11], functional polymers [12,13], surface modification [14–16], external fields [17–20], and prefabricated and co-assembling templates [8,21–24]. A recent review by Xu et al. highlights the application of these aforementioned techniques on the assembly of spherical nanoparticles [25], while a recent review by Composto et al. offers detailed discussion of anisotropic nanorod assembly within polymeric matrices [26]. This review aims to extend the discussion of these topics and provide a survey of the methodologies, applications, and outlook of self-assembled anisotropic nanomaterials, with an emphasis on nanorod self-assembly.

Self-assembly

The first class of self-assembly techniques encompasses those that require neither modification of the nanomaterials nor an external field or template to drive assembly. Instead, assembly is accomplished through depletion attraction, capillary forces, dipole–dipole attractions, or some combination of the above. Typically, assembly is performed

in a solvent, or during solvent evaporation, to ensure the particles have enough mobility to assemble.

The depletion attraction ($4–12kT$ [27]), a fundamentally entropic force, originates from particles in a solvent moving close enough to each other that their excluded volumes overlap, increasing the available volume for smaller molecules or additives dissolved in the solvent [28,29]. This results in an osmotic pressure that forces the particles together. Since the depletion attraction scales with the excluded volume overlap of the particles, particles with relatively low curvature, such as nanorods and nanocubes, experience this attraction strongly and thus assemble into well-defined structures in solution.

Capillary forces ($\sim 10^2 kT$ [30]), in contrast, come into effect as a solution containing particles is dried, exerting a strong force drawing parallel surfaces together as the solvent molecules between the neighboring particles evaporate [31]. Thus, as a solvent front moves through a collection of particles, it exerts forces that when carefully controlled can be used to align and pack particles.

Finally, interparticle dipole–dipole interactions ($1–2kT$), i.e. the forces arising from the interaction of dipoles in two neighboring particles, can be harnessed for assembly [32]. Some materials, such as cadmium chalcogenides, possess intrinsic dipole moments (in this case an electric dipole) that can facilitate particle assembly through interaction with the dipoles on nearby particles. These dipole moments come from anisotropy in the atomic lattice of cadmium chalcogenides, the same anisotropy that makes cadmium chalcogenides useful materials for nanorod and nanotetrapod synthesis.

As far back as 1997, computational studies by Lekkerkerker et al. on the phase behavior of rod-like colloids due to the depletion attraction and other pairwise attractions predicted the presence of a liquid-crystalline phase for nanorods [33], i.e. nematic assemblies forming spontaneously in concentrated nanorod solutions. This prediction was later experimentally confirmed by Alivisatos et al. for CdSe nanorods [34] and Murphy et al. for Au nanorods [35], and it was later shown that CdS nanorods exhibit self-assembly into bundles at far lower concentrations than previously observed [36]. The depletion forces between nanoparticles leading to this assembly can be precisely controlled through the amount of hydrocarbon additives to the nanoparticle solution, allowing assembly of not only nanorods [28], but also tetrapods and octapods [37] (Fig. 1). In this way, micrometer-sized sheets of aligned anisotropic nanoparticles could be constructed.

Capillary forces have also been effective in inducing nanorod assembly. Specifically, capillary forces between adjacent nanorods become significant as solvent within a nanorod solution evaporates. Earlier approaches found success in allowing the solvent edge to move from one side of the film to another by suspending a substrate at the surface of a solution and allowing the surface of the solution to move over the substrate as the solvent evaporated. In this manner, gold nanorods were assembled on TEM grids [38] by Alivisatos et al., and CdSe nanorods were assembled on a mica substrate [39] by El-Sayed et al. Although crystalline structures were formed in both cases, this approach also demonstrated the formation of phases with little positional order. For example, the CdSe nanorod assemblies

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