CHEMICAL REVIEWS

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Editorial

Introduction: Anisotropic Nanomaterials

Cite This: *Chem. Rev.* 2023, 123, 3325−3328

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Opposite to isotropy that implies "identical properties in all directions", anisotropy means directional dependence. It can be viewed as the difference, when measured along different axes, in a material's properties, including physical dimension, refractive index, emission polarization and directionality, electrical and thermal conductivity, and tensile strength, among others. In principle, true isotropy can only exist in an amorphous or noncrystalline material, like a liquid or a glassy solid. For a crystalline material, anisotropy is always present owing to the inherent disparity in interaction strengths among the constituent atoms along different directions. In the case of a nanomaterial, anisotropy can manifest in its atomic arrangement (i.e., structural anisotropy), elemental distribution (i.e., compositional anisotropy), geometric shape (i.e., morphological anisotropy), and physical properties (i.e., functional anisotropy), as well as its chemical reactivity and formation process.

Anisotropy means materials' diversity and complexity in structure and function. For example, one of the major motivations for studying nanoparticles with anisotropic shapes is the diversity and complexity that can be brought into a nanosystem, for both individual particles and their assembled structures. For individual particles, anisotropy leads to enhanced properties and new opportunities. A classic example can be found in nanorods, a popular nanomaterial characterized by morphological anisotropy. Different from the case of a gold nanosphere, the conduction electrons in a gold nanorod can collectively oscillate along two directions parallel to the short and long axes of the nanorod. As a result, the localized surface plasmon resonance (LSPR) peak splits into two modes: a transverse mode with a spectral position similar to that of a gold nanosphere and a longitudinal mode whose position is highly tunable depending on the aspect ratio (i.e., the ratio of length to diameter) of the nanorod. By simply increasing the aspect ratio, the longitudinal peak can be continuously red-shifted from the visible (around 525 nm) to the infrared region (2 μm and even beyond), making gold nanorods ideal candidates for biomedical applications such as optical contrast enhancement and photothermal treatment. Similarly, the emission characteristics of semiconductor nanorods also manifest anisotropic behaviors. Beyond a relatively small length-to-diameter ratio, the emission becomes polarized preferably along the long axis. Moreover, for both nanorods and nanoplatelets, emission directionality may be achieved. These consequences of anisotropy are of applicative significance as well, for example in the utilization of emission in displays where directionality and polarization may be beneficial or in the selective detection of polarized emission. For self-assembly, anisotropy leads to directional interactions and sometimes non-closely packed structures with novel functions such as negative Poisson ratio, photonic bandgaps, and chiroptical activity.

Anisotropy can also mean simplicity for the synthesis. In many cases, the morphological anisotropy exhibited by nanoparticles would be naturally developed during a synthesis due to the generically anisotropic interaction among the atomic/molecular building blocks. One of the most prominent examples can be found in inorganic minerals such as asbestos and chrysolite, which are well-documented to exhibit a fibrous growth habit owing to their anisotropic crystal structure. In addition, many polymeric and biological systems are also known to preferentially exist in the fibrous form because of anisotropy in bonding, with notable examples including cellulose and collagen. Chalcogens (specifically, selenium and tellurium) represent another interesting system that can naturally grow into highly anisotropic nanostructures with one-dimensional (1D) morphology. While oxygen exists primarily as diatomic molecules, selenium and tellurium tend to form polymeric, helical chains through covalent bonding. In the trigonal phase, the helical chains are further packed into a hexagonal lattice through van der Waals interactions. As a result, these two solid materials have a strong tendency to grow into nanorods or nanowires even when crystallized from an isotropic medium, favoring the stronger covalent bonds within the spiral chains over the relatively weaker van der Waals forces among the chains. A similar argument also applies to metal chalcogenides, which tend to form two-dimensional (2D) structures as a result of their anisotropy in atomic bonding. For metals, although metallic bonding is isotropic, the steric effect only allows each atom to be in contact with a limited number (e.g., 12 for a face-centered cubic metal) of nearest neighbors. Such restriction also leads to anisotropy naturally, including the variation in atomic packing density along different directions and thereby the disparity in free energy among different types of crystallographic facets. However, such anisotropy is often inadequate for inducing the formation of nanoparticles with noticeably anisotropic morphology. Under thermodynamic control, nanoparticles comprised of a face-centered cubic metal are supposed to take a cuboctahedral profile, the so-called Wulff shape, with the surface enclosed by

Special Issue: Anisotropic Nanomaterials

Published: April 12, 2023

a mix of {111} and {100} facets to minimize the total surface free energy. The high order of symmetry makes a cuboctahedron look like an isotropic rather than an anisotropic structure. In this case, one has to break the thermodynamic confinement using various strategies in order to generate highly anisotropic structures such as nanorods.

If there is anything one should complain about regarding anisotropy, it is the complexity! For isotropic nanoparticles, it is comparatively straightforward to characterize and model them using the conventional tools. For example, one can easily measure the size of a spherical particle from dynamic light scattering or its projected area using transmission electron microscopy (TEM). For a particle with anisotropic morphology, however, it is a nontrivial task to even just measure its physical dimensions under TEM, as the results critically depend on its orientation relative to the electron beam. In some cases, one has to rely on electron tomography to resolve the three-dimensional (3D) morphology of anisotropic nanoparticles.

This thematic issue combines articles written by leaders in key areas of fundamental and applicational research as well as emergent opportunities on the anisotropy of nanomaterials.

In the context of structural anisotropy, Jeong and co-workers discussed recent progress in layer-structured metal chalcogenides. The unique electronic and catalytic properties of such anisotropic nanomaterials have gained tremendous interest for various applications. The authors not only reviewed different synthetic methods such as solution-phase synthesis, vapor-phase synthesis, and exfoliation but also discussed various strategies for manipulating their dimension, phase, composition, defect, and heterostructure. Furthermore, they highlighted recent processes in applying these nanomaterials to electronics, optoelectronics, thermoelectrics, catalysis, batteries, supercapacitors, and sensing, among others.

In the context of morphological anisotropy, Yang and co-workers reviewed 2D metal nanostructures, particularly nanosheets, with a focus on mechanistic understanding and experimental control. Since metals often crystallize in a high-symmetry crystal phase, such as the face-centered cubic lattice, the symmetry of the growth pattern must be reduced to generate 2D nanostructures. The authors started with a discussion on the relevant theoretical framework of symmetry reduction, followed by multiple examples to illustrate the chemical driving force responsible for the creation of nanosheets. They then highlighted applications of 2D metal nanostructures in fields such as catalysis, bioimaging, plasmonics, and sensing. Millstone, Liz-Marzán and co-workers reviewed a related system—plate-like metal nanoparticles. Their 2D morphology makes them one of the most anisotropic, mechanistically understood, and tunable nanostructures available. The authors highlighted recent progress in solution-phase synthesis, with an emphasis on mechanistic insights for different synthetic strategies, the crystallographic habits of different metals, and the use of such plates as templates for the synthesis of other derivative structures. They also discussed an array of self-assembly techniques and offered a brief overview of the optical properties associated with the 2D morphology.

Ithurria and co-workers reviewed colloidal II−VI semiconductor nanoplatelets, which manifest narrow emission at room temperature, that is tunable over a broad spectral range via control of platelet thickness and composition, and also exhibit good material stability over time. The article centers on synthetic developments, spectroscopic properties, and optoelectronic integration of such nanoplatelets. It also covers growth mechanisms and explains how a thorough understanding of the growth process has enabled the development of nanoplatelets and heterostructured nanoplatelets with multiple emission colors, spatially localized excitations, narrow emission, and high quantum yields over a broad spectral range. Furthermore, it discusses how the relaxation processes and lifetime of the carriers and excitons are modified in nanoplatelets compared to both spherical quantum dots and epitaxial quantum wells. Finally, it illustrates how nanoplatelets with strong and narrow emissions can be utilized for the fabrication of pure-color light emitting diodes (LEDs), strong gain media for lasers, and luminescent light concentrators. Jia and co-workers reviewed anisotropic nanocrystals of heavy-metal-free semiconductors. These nanocrystals possess not only low toxicity but also unique optical and electrical properties arising from the anisotropy in both morphology and composition. Specifically, the authors started with an overview of the hazards of heavy metals and introduced the typical heavy-metal-containing and heavy-metal-free nanocrystals. They then discussed the anisotropic growth mechanisms, including solution−liquid−solid (SLS), oriented attachment and ripening, and template-assisted growth. They further highlighted the properties of anisotropic heavy-metal-free nanocrystals, including optical polarization, fast electron transfer, and LSPR, among others. Finally, they showcased various applications based on the anisotropic heavy-metal-free nanocrystals, including those related to catalysis, fabrication of solar cells, photodetectors, and LEDs, as well as biological labeling.

On a general and broad basis, Xia and co-workers reviewed the concept of asymmetrical growth and symmetry breaking involved in the colloidal synthesis of metal nanocrystals. They provided an account of recent progress in both mechanistic understanding and experimental control. With a touch on both the nucleation and growth steps, they discussed a number of methods capable of generating crystalline seeds with diverse symmetry while achieving asymmetrical growth for mono-, bi-, and multimetallic systems. They then showcased various examples of symmetry-broken nanocrystals that have been reported, together with insights into their growth mechanisms. Finally, they highlighted the properties and applications of these nanocrystals and concluded with perspectives on future directions in developing symmetry-broken nanomaterials.

In the context of compositional anisotropy, Shim and co-workers discussed the design principles of colloidal nanorod heterostructures. They reviewed the effects of crystal structure, surface faceting/energies, lattice strain, ligand sterics, precursor reactivity, and reaction temperature on the growth of nanorod heterostructures through heteroepitaxy and cation exchange reactions. With a good understanding of the roles played by various thermodynamic and kinetic parameters, it is feasible to synthesize complex nanorod heterostructures with unique properties. The authors also highlighted some application prospects arising from such capabilities. Banin, Ben-Shahar, and co-workers discussed the rich landscape of colloidal semiconductor-metal hybrid nanostructures, including synthesis, synergetic characteristics, and emerging applications. They reviewed recent progress in the field, with a focus on systems involving metal chalcogenides and metals. They started with a discussion on the synthetic methods that had led to a myriad of possible hybrid architectures, including

https://doi.org/10.1021/acs.chemrev.3c00092
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Janus zero-dimensional (0D) quantum dot-based systems, as well as anisotropic quasi-1D nanorods and quasi-2D platelets. They then discussed the unique properties of these hybrid nanostructures, with a focus on emergent synergetic characteristics. As for application, the authors showcased their functionality as photocatalysts for a variety of uses, including solar-to-fuel conversion, as a new type of photoinitiators for photopolymerization and 3D printing, and in novel chemical and biomedical uses. Dukovic and co-workers reviewed the electronic structure and excited state dynamics of cadmium chalcogenide nanorods. In addition to the bandgap tunability inherent to nanocrystals, nanorods have polarized light absorption and emission, as well as high molar absorptivities. Nanorod-shaped heterostructures feature control of electron and hole locations, in addition to light emission energy and efficiency. Specifically, the authors started with methods for synthesizing the colloidal nanorods. They then discussed the electronic structure of single-component and heterostructure nanorods, followed by light absorption and emission in these anisotropic nanomaterials. Next, they described the excited state dynamics of these nanorods, including carrier cooling, carrier and exciton migration, radiative and nonradiative recombination, multiexciton generation and dynamics, and processes that involve trapped carriers. Finally, they accounted for the charge transfer from photoexcited nanorods and connected the dynamics of these processes with light-driven chemistry.

In terms of functional anisotropy, Sun and co-workers reviewed the synthesis, anisotropy, and applications of magnetic nanoparticles. In this specific case, the introduction of anisotropy to magnetic nanoparticles has emerged as an effective method to obtain new characteristics and functions critical for many applications. They first discussed the anisotropy-dependent ferromagnetic properties, from intrinsic magnetocrystalline anisotropy to extrinsic shape and surface anisotropy. They then reviewed the syntheses of magnetic nanoparticles with desired controls over the dimension, shape, composition, and structure. Such controlled syntheses of magnetic nanoparticles allow their magnetism to be finely tailored for various applications, including biomedicine, magnetic recording, magneto transport, permanent magnet, and catalysis. In another example, Mou, Guan, and co-workers discussed new strategies for lighting up micro-/nanorobots (MNRs) with fluorescence. MNRs can be autonomously propelled on demand in complex biological environments and thus may bring revolutionary changes to biomedicine. The inclusion of fluorescence offers MNRs immediate advantages such as optical trackability, on-the-fly environmental sensitivity, and targeted chemo-/photon-induced cytotoxicity. After the introduction of MNRs with various propulsion mechanisms and fluorescent materials, the authors systematically illustrate the design and preparation strategies to integrate MNRs with fluorescent substances and their biomedical applications in imaging-guided drug delivery, intelligent on-the-fly sensing and photo(chemo-) therapy. In a third example, Ding, Lin, Ke, Liu, and co-workers discussed recent advances in DNA origami-engineered nanomaterials and related applications. Specifically, the authors highlighted the progress in DNA origami-engineered nanomaterials over the past five years, including both the exciting achievements and unexplored research avenues.

In the context of tool development, Chen and co-workers discussed the use of advanced electron microscopy (EM) for the investigation of soft (including biological) nanomaterials that are often anisotropic and heterogeneous. They highlighted how developments of both the hardware and software of EM had enabled new insights into the formation, (electro)chemical reaction, assembly, and functioning of nanoparticles, biomolecules, polymers, and other carbonaceous materials by providing shape, size, phase, structural, and chemical information at the nanometer or higher spatial resolution. Specifically, they first discussed real-space 2D imaging and analytical techniques that are offered conveniently by microscopes without special holders or beam technology. The discussion was then extended to include recent advancements, including visualizing the 3D morphology of soft nanomaterials using electron tomography and its variations, identifying local structure and strain by electron diffraction, and recording motions and transformation by in situ EM. Recent integration of machine learning and its impacts on various aspects of EM imaging from smart acquisition to data-mining was also discussed in detail, with a concluding discussion on future research opportunities.

Last but not least, Fichthorn reviewed the theory of anisotropic metal nanostructures. A major challenge in the development of anisotropic nanomaterials is elucidating the mechanistic details involved in their growth and transformations. To this end, theory and simulations can provide insightful guidance. The author discussed how results from first-principles calculations and classical techniques, such as Monte Carlo and molecular dynamics simulations, had been integrated into multiscale theoretical predictions useful in understanding the colloidal synthesis of metal nanocrystals with various shapes. Also discussed are examples in which machine learning has started to make a positive contribution.

In organizing this thematic issue, we aim to bring snapshots of exciting, representative, and timely research on different aspects of anisotropic nanomaterials to the readers. Because of its fast-evolving and highly dynamic nature, in addition to the enormous breadth of the field, it is impossible to cover all aspects. Due to the interruption caused by COVID-19, the submission of some manuscripts was delayed. These manuscripts will still be published in this journal in the future and virtually linked to this thematic issue. It is hoped that the readers will enjoy the mix of topics presented in this thematic issue and find inspiration to push this exciting field toward greater success in terms of fundamental knowledge development and application.

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Notes

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https://doi.org/10.1021/acs.chemrev.3c00092
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Biographies

Younan Xia received his B.S. degree in Chemical Physics from the University of Science and Technology of China in 1987, his M.S. degree in Inorganic Chemistry from University of Pennsylvania (with Alan G. MacDiarmid) in 1993, and his Ph.D. degree in Physical Chemistry from Harvard University (with George M. Whitesides) in 1996. He started as an Assistant Professor of Chemistry at the University of Washington, Seattle in 1997 and then joined the Department of Biomedical Engineering at Washington University in St. Louis in 2007 as the James M. McKelvey Professor. Since 2012, he has held the position of Brock Family Chair and Georgia Research Alliance Eminent Scholar at the Georgia Institute of Technology. His group invented a myriad of nanomaterials with controlled properties for applications related to plasmonics, electronics, photonics, photovoltaics, display, catalysis, fuel cells, nanomedicine, and regenerative medicine.

Qian Chen received her B.S. degree in Chemistry from Peking University of China in 2007 and her Ph.D. degree in Materials Science and Engineering from the University of Illinois, Urbana−Champaign (with Steve Granick) in 2012. She continued under a three-year Miller fellowship with A. Paul Alivisatos at the University of California, Berkeley (2012−2015). From 2015, she started as an Assistant Professor of Materials Science and Engineering at the University of Illinois, Urbana−Champaign and was promoted to Associate Professor with a Racheff Faculty Scholarship in 2021. Her group focuses on the broad scheme of imaging, understanding, and engineering soft, biology, and energy materials at the nanoscale, including systems such as colloidal self-assembly, protein transformation, advanced battery devices, and energy-efficient separation strategies.

Uri Banin received his B.Sc. (1989) and Ph.D. in Physical Chemistry (1994) from the Hebrew University of Jerusalem, Israel. After postdoctoral research at the University of California, Berkeley (1994−97), he joined the Hebrew University, where he has been a Full Professor since 2004, holding the Alfred and Erica Larisch Memorial Chair. He was the founding director of the Hebrew University Center for Nanoscience and Nanotechnology (2001−2010), served on the scientific advisory board of Nanosys Inc. (2002−2007), was the founder of Qlight Nanotech (2009−15) that developed the use of nanocrystals in displays, and served as an Associate Editor of the ACS journal *Nano Letters* (2013−2021). Banin is studying the chemistry and physics of nanocrystals and is best known for inventing new types of semiconductor and hybrid semiconductor-metal nanocrystals and for his studies on their unique chemical and physical properties with relevance for applications in nanotechnology in the fields of displays, alternative energy especially photocatalysis, materials science, optoelectronics and quantum technologies.

https://doi.org/10.1021/acs.chemrev.3c00092
Chem. Rev. 2023, 123, 3325−3328