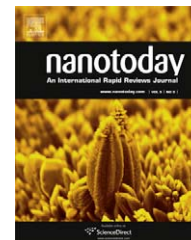


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## REVIEW

# Colloidal heterostructured nanocrystals: Synthesis and growth mechanisms

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**Summary** One frontier approach of colloidal chemistry to nanoscale entities capable to exhibit enhanced or even unconventional physical–chemical properties as well as diversified capabilities for multitask applications envisages fabrication of breed-new hybrid nanocrystals (HNCs) with a spatially controlled distribution of their chemical composition. These are all-inorganic multicomponent nanoheterostructures in which domains of distinct materials are arranged via permanent bonding interfaces in elaborate concentric/eccentric onion-like or oligomer-type architectures. This review covers recent progress achieved in the wet-chemical development of HNCs based on functional associations of semiconductors, metals and magnetic compounds. Within the frame of seeded-growth techniques to heteroepitaxial deposition in solution media, relevant synthetic strategies are illustrated, along with systematic examination of the mechanisms by which heterostructures can be selectively accessed in nonequivalent topological configurations. The peculiar properties and technological perspectives offered by such novel generations of complex nanomaterials are also succinctly highlighted.

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**Introduction**

The recognition of the unique dimensionality dependence of the chemical–physical properties of nanoscale matter has propelled efforts toward controllable fabrication and in-depth characterization of inorganic nanostructures with programmable compositional and geometric features. At the forefront of the current scientific revolution of nanoscience colloidal nanocrystals (NCs), crystalline particles grown in

liquid media, stand out over other classes of inorganic nanomaterials due to the high degree of control with which their crystal structure, size, shape, and surface functionalities can be engineered in the synthesis stage and to the versatility with which they can be processed and implemented into a large spectrum of mesoscopic materials, devices, and processes [1–5]. Valuable technological applications have already been envisaged in disparate fields, including optoelectronics, catalysis, energy conversion and production, sensing, environmental remediation, and biomedicine [4–7].

Wet-chemistry approaches have especially been acknowledged for their capability to produce a variety of semiconductor, metal and oxide NCs systematically tailored

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with sub-nanometer level accuracy over a broad range of dimensional-morphological regimes by careful regulation of thermodynamic parameters and growth kinetics in liquid media under assistance of selected solvents, ligands, surfactants or catalyst additives [1–5,8–10]. While this synthetic expertise is yet susceptible to be refined, new challenges are presently being imposed on nanochemistry research to meet the rising demand for advanced breeds of colloidal nanostructures entities that should not only exhibit reinforced properties, but also demonstrate diversified capabilities to be simultaneously exploitable in multiple applications. In this regard, nanochemistry research has recently made tremendous advances with the solution-phase synthesis of generation-new heterostructured NCs with a topologically defined distribution of their composition, broadly referred to as hybrid nanocrystals (HNCs). HNCs are elaborated multicomponent NCs, consisting of two or more different material sections that are permanently joint through chemical bonding interfaces (i.e., without any molecular bridges), eventually attaining heteroepitaxial junctions. Available examples include elaborate concentric or eccentric core@shell and yolk@shell geometries, as well as intricate phase-segregated hetero-oligomer architectures made of discrete shaped sections fused via small connecting areas at selected locations [2,4,5,11–16].

Development of HNCs represents a new generic paradigm in synthetic nanochemistry, whereby an increased level of structural-architectural sophistication is pursued as a means of boosting the technological potential of conventional nanoparticles beyond the limitations imposed by their inherent compositional and geometric features. Elaboration of multicomponent heterostructured NC-based entities allows enhanced and/or diversified capabilities to be achieved through controlling the size, morphology and crystal-phase of the constituent building units, on one side, and through engineering their relative spatial arrangement and relevant interface structure, on the other side.

The technological scenarios that HNCs promise to open up are extraordinarily wide. Primarily, individually processable HNCs made of coexisting inorganic portions, each characterized by peculiar optical, electric, magnetic, and/or chemical properties, hold potential as key multifunctional nanostructured elements over which new transition pathways to unprecedented applications can be founded. These include, for example, the possibility to assemble “superstructures” made of nanoscale building blocks, to implement cooperative catalytic conversions, to create anisotropic surface distribution of selected molecules, to devise multimodal techniques for biomedical diagnostics/therapeutics [2,4,5,11–16]. Additionally, HNCs represent artificial platforms on which electronic communication establishing across neighbouring material sections can generate synergistically enhanced and/or tunable chemical–physical responses, or even lead to emergence of unusual phenomena, not otherwise accessible by any of the single components alone, or their physical mixture counterparts. For example, the peculiar optical and/or conduction behaviour observable for HNCs based on semiconductors and/or noble metals can result from altered quantum confinement degree, modified charge-carrier recombination or separation dynamics, and/or plasmon-to-exciton coupling effects. In the case of HNCs incorporating magnetic phases

anomalously modified hysteresis parameters can reflect establishment of magnetic exchange-coupling mechanisms and/or induced extra anisotropy [2,4,5,11–13]. These findings have preliminarily suggested that creating effective bonding junctions among dissimilar nanoscale domains may be utilizable as a new tool to engineer the performances of complex HNCs thereof, as well as a source of novel magneto-optical or spintronic phenomena that may originate from interaction of nonhomologous properties across suitably devised nanoheterostructured material platforms [11–13].

Research on HNCs has expanded tremendously in the past five years. Following previous efforts to categorize and explain reaction pathways to heterostructures that had been discovered to date [4], a few review articles have later addressed the field of HNCs, either focusing on particular classes of materials [11,13,16] and selected configurations [16], or addressing specific applications [4,13–15], patents [11], and technology perspectives [4,5]. However, a comprehensive classification and in-depth mechanistic examination of synthetic routes by which structure-tailored HNCs can be created so as to meet specific functional requirements is still lacking.

The synthesis of colloidal HNCs requires developing a higher degree of synthetic ingenuity and creativity. Indeed, the formation of multimaterial architectures occurs at a critical thermodynamic-kinetic crossover, whereby the delicate balance that governs the size and shape evolution of individual component portions is further complicated by the interplay of atomic diffusion and/or exchange, facet-specific reactivity, and/or insurgence of interfacial strain. Control over such a complex dynamics is inherently difficult to achieve, since pathways underlying HNC formation and topology selection are not fully understood and may be broadly varying, depending on the specific material association concerned and the particular reaction conditions adopted.

This review will examine recent progress made in the development of colloidal strategies for the tailored synthesis of breed-new HNCs with a topologically controlled distribution of their chemical composition, spanning from concentric/eccentric core@shell and yolk-shell geometries to more spatially elaborate hetero-oligomer architectures. The mechanisms by which heterostructures can be accessed in nonequivalent configurations will be systematically illustrated and discussed for a rich selection of material associations within the frame of general seeded-growth techniques to heteroepitaxial deposition in solution media. The main properties and technological advantages offered by such generations of complex nanomaterials will also be succinctly highlighted.

## Basic concepts in wet-chemical synthesis of heterostructured nanocrystals

### Synthesis of single-material nanocrystals

Colloidal NCs are generated upon reaction of molecular precursors (that carry the atomic species necessary to build up the targeted material) in a liquid solution that may contain coordinating solvents and some stabilizing agents,

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