Current Opinion in Solid State and Materials Science 14 (2010) 83–94

Contents lists available at ScienceDirect

Current Opinion in Solid State and Materials Science

journal homepage: www.elsevier.com/locate/cossms

Anisotropic nanocrystal heterostructures: Synthesis and lattice strain

Moonsub Shim *, Hunter McDaniel

Department of Materials Science and Engineering and Frederick Seitz Materials Research Laboratory, University of Illinois at Urbana-Champaign, 1304 W. Green St., Urbana, IL 61801, United States

ARTICLE INFO

Article history:
Received 4 February 2010
Accepted 21 April 2010

Keywords:
Nanocrystals
Nanorods
Heterostructures
Anisotropy
Expitaxy
Lattice strain

ABSTRACT

Emerging multi-component hybrid nanocrystalline materials are prompting new approaches to engineering materials' properties with nanoscale precision and providing complex systems with multiple functionalities. In particular, chemical synthesis of nanocrystal heterostructures where two or more distinct phases are brought together epitaxially in an anisotropic manner is providing novel materials with unique combinations of optical, electronic, magnetic, and chemical properties. However, in order to develop high quality materials with property combinations that can be precisely tailored, a better understanding of growth/formation mechanism(s) that will allow versatile and scalable synthetic approaches to be developed is necessary. Here, we review recent advances in anisotropic nanocrystal heterostructures with a special focus on how lattice strain arising from the heterointerfaces affects materials synthesis.

1. Introduction

Improvements in synthetic precision over the size, size distribution, shape, and composition of nanoscale materials are leading to ever increasing number of technological breakthroughs being envisioned [1–5]. In particular, colloidal nanocrystals (NCs) exhibit much promise in multiple areas including lasers [6], electrochromic displays [7], solar energy conversion [8], catalysis [9], and biomedical imaging [10]. For example, high photoluminescence (PL) quantum yields and size-tunable band gaps make quantum dots particularly attractive in lasers [6]. Electrically (or electrochemically) variable optical absorption and emission may enable novel NC-based display technologies [7,11,12]. Although debates continue, the possibility of efficient carrier multiplication is prompting new solar cell concepts [13,14]. Inherently large surface areas make metal and metal oxide NCs ubiquitous in catalyst technologies [9]. Both magnetic and fluorescent NCs are facilitating advances in biomedical diagnostics [15,16].

Unique tunable properties of nanoscale materials allow us to envision capabilities well beyond the current state-of-the-art. However, there are many obstacles in transitioning from interesting properties being observed to functional devices and systems. Highly efficient, size-tunable PL makes semiconductor NC solids attractive as lasing media but the problem of fast Auger recombination rates necessitate femtosecond pumping [6]. High PL efficiencies along with resistance to photobleaching also place semiconductor NCs at the forefront of bioimaging research but uncontrolled blinking is a hindrance for pushing the limits especially at the single-particle level [17,18]. Large surface-to-volume ratio provides an advantage for photocatalytic production of hydrogen as well as a variety of other catalytic processes with TiO_2 NCs but UV band gap of TiO_2 renders solar energy driven photocatalysis inefficient [19]. As diverse as the potential applications of nanoscale materials may be, there are as many, if not more, challenges still to be tackled en route to manufacturing advanced nanomaterial-based products.

Utilizing nanocrystal heterostructures (NCHs), possible solutions for many of these challenges are now starting to emerge. For example, core/shell NCHs with type II band offset are allowing optical gain at the single exciton level avoiding the problem of fast Auger relaxation [20]. Core/shell NCHs with graded alloy structure of CdZnSe/ZnSe are exhibiting PL without blinking [21]. NCHs that incorporate both magnetic and fluorescent NCs are opening new directions in biomedical applications with dual imaging capabilities [22,23]. As these examples demonstrate, the ability to coherently bring together different types of materials with nanoscale precision provides versatile and innovative approaches to alleviate many difficulties lying ahead. Much like advantages gained in engineering composite materials for tailored properties, advances in NC-based technologies will undoubtedly benefit from NCHs where each component's composition, location, shape, reactivity, etc. can be varied precisely and independently. Hence, developing NCHs with anisotropic shapes and independently tunable properties may provide the necessary means for engineering NCs and related materials to meet current and future technological challenges. Anisotropic structures will be especially important for processes that require directionality (e.g. spatial control over where

* Corresponding author. Tel.: +1 217 333 7361; fax: +1 217 333 2736.
E-mail address: mshim@illinois.edu (M. Shim).

1359-0286/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cossms.2010.04.001

photogenerated carriers end up) and exposure of all components to the outside environment (e.g. for catalysis). They also provide multi-functional building blocks for developing complex hierarchical systems beyond the close-packed structures achievable with spherical nanoparticles.

Initial methods of achieving multi-component NCs of non-core/shell geometry have mainly consisted of "linking" pre-synthesized NCs with bi-, tri-, or multi-dentate molecules [24]. Main control over the number of NCs linked together relies on stoichiometry between the NCs and the molecules. More sophisticated approaches including DNA have also been shown [25]. However, difficulties in controlling the number of binding sites on each NC limit the usefulness of molecularly linked NC systems. Molecular linkers are often electronically insulating and can hinder synergistic effects between properties of different NCs. NCHs where the second component nucleates and grows from or directly attaches to the first component with coherent crystallographic interfaces are now being reported [26–28] and may be one of the best approaches to achieving single-particle precision in structure and composition of "designer" multi-NC systems.

Using the direct seeded growth method, there have now been several different materials incorporated into non-core/shell heterostructures [26–37]. Many topologies are possible with the potential to extend to multi-dimensional/hierarchical systems as schematically illustrated in Fig. 1 for spherical seed based binary NCHs. The TEM images shown are selected examples of anisotropic NCHs of II-VI semiconductors with superparamagnetic Fe_3O_4 seeds that have been achieved recently in our laboratory. However, only a limited number of cases exist with well-defined geometries – i.e. heterodimers, trimers, etc. of nearly spherical NCs or selective growth at nanorod (NR) tips rather than random number and placement of second and/or additional components around the first material.

In developing any epitaxial NCHs from colloidal NC seeds, there are at least four general aspects to consider: (1) favorable interfacial chemistry, (2) compatible atomic arrangements/crystallography, (3) potential role(s) of surface capping molecules, and (4) growth kinetics. The favorable interfacial chemistry will often play the primary role in determining which materials can be brought together. The effects of capping molecules and growth kinetics may be varied by reaction conditions such as reagent concentrations and reaction temperature. Since no two distinct materials have exactly the same lattice parameters, even when materials with compatible crystal structures are brought together, there may be varying degree of lattice strain. Interfacial lattice strain may not only be composition dependent but also size-dependent. Especially in anisotropic NCHs, location and orientation of the growing second component can lead to different degree and direction of the strain. Such composition, size and topology dependent interfacial lattice strain can have profound effects in determining the resulting structure/shape and therefore the properties of NCHs. In this review, we discuss recent advances in both rod and spherical seed based NCHs with special attention to interfacial lattice strain and how it affects, and sometimes dictates, the overall structure of the products. Specific examples from our recent work are presented to highlight each area. While many different approaches such as vapor and electrochemical deposition methods have and continue to provide a multitude of possibilities especially in the area of nanowires [38–41], our discussion here is limited to NCHs synthesized by wet chemical means in the presence of surface capping molecules.

2. Nanorod-based heterostructures

With shape anisotropy already inherent, NRs may be the most obvious choice of seed materials for developing NCHs beyond the core/shell types. In NRs (and tetrapods), the underlying reduced symmetry of the seed facilitates the synthesis of well-defined anisotropic NCHs. There have been mainly two approaches for the NR-based materials or nanorod heterostructures (NRHs). The first approach exploits spatially selective growth at the more reactive tips [42]. Exclusive or near exclusive deposition of the second material at the tips may be achieved by direct extension of the initial NR growth as most often seen in II-VI systems such as CdTe growth on CdSe NRs [43–45] or by exploiting higher curvature/less perfect tips for enhanced reactivity as exemplified by selective tip growth of Au [42], PbSe [46], or Co [47] on CdS and/or CdSe NRs. The second approach takes advantage of chemical conversion

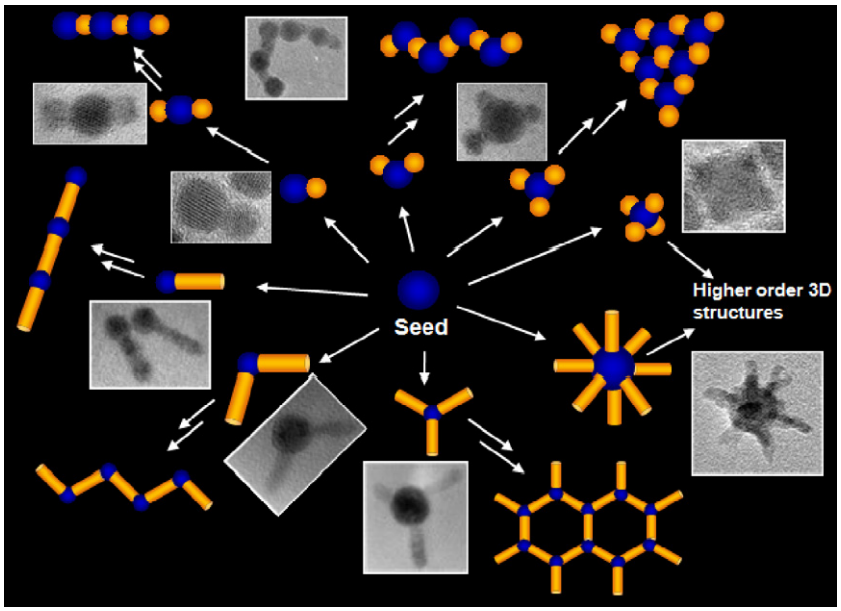

Fig. 1. Schematic of possible heterostructures that can be synthesized from a spherical or nearly spherical seed nanocrystal. TEM images of selected structures of Fe_3O_4/II–VI semiconductors that have been achieved are also shown. In all cases, the larger spherical component is the starting seed Fe_3O_4 nanocrystals with sizes ranging from ~5 to 15 nm in diameter.