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Invited review

Inorganic nanocrystals: From molecular design to systematic engineering☆

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ABSTRACT

Solution-based routes have been widely applied in the synthesis of nanostructures. It is desirable to choose or design precursors, ligands, and solvent molecules at the molecular level to allow the synthesis of low-dimensional nanocrystals with various shapes and sizes. The increasing requirements for the integration of the properties of nanocrystals have produced a high demand for the rational design and fine control of complex structures, in terms of both the composition and the structure. To meet this demand, researchers have developed new synthetic strategies to produce more complex and more functional nanocrystals. Typical procedures involve systematic engineering, which focuses on the whole synthetic procedure, instead of just the molecular details. This review focuses mainly on the work of Yadong Li's group over the last decade.

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Contents

☆ This is an invited review, reporting the ongoing research work on solution-based synthesis of inorganic nanocrystals in the research group of Professor Yadong Li, in Department of Chemistry, Tsinghua University. The review article, written by members of Li's group, focuses on the strategy—from molecular design for simple nanostructures to systematic engineering for more complex and functional nanostructures, developed in their research practice during the last decade.

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Introduction

In recent decades the nanoscience and nanotechnology fields have developed greatly. Various types of nanostructures with a wide distribution of sizes and shapes have been prepared by chemists and material scientists. Nanocrystals display a variety of outstanding properties, and have been applied in several fields, including biology, medicine (Wang, Bao, Wang, Zhang, & Li, 2006), nanocatalysis (Zhou, Wang, Sun, Peng, & Li, 2005), and assembly (Hu & Wang, 2013; Long et al., 2012; Luo, Wang, Jing, & Wang, 2014; Saleem et al., 2013; Wang, Sun, Ji, Li, & Wang, 2014; Xu et al., 2014). A large number of synthetic techniques have been developed, including hydrothermal, CVD, and sol–gel methods; however, it remains a challenge to precisely control the size, shape, and phase of nanocrystals. Among these methods, solution-based routes hold unique advantages; they can provide gram-scale samples, even in the laboratory, and can be easily used to investigate general formation mechanisms. Solution-based methods have therefore attracted increasing attention from synthetic scientists.

In solution-based routes, molecular design is typically used to design of precursor and/or ligand molecules that are applied for the synthesis of low dimensional nanocrystals. Different precursors—typically including organic and inorganic molecules—have a great influence on the nucleation and growth of these crystals. Organic molecules dissolve well in oils, and are easy to design through organic synthesis. Inorganic molecules, which are very cheap, are widely used in synthesis; however, their low solubility in oils limits their applications. It is therefore desirable to design the ligand molecules and the solvent for a particular reaction to optimize the reaction conditions. To achieve other synthetic routes—especially because of the continuous increases in the requirements in various fields in recent years—it is desirable to use systematic engineering processes to follow the whole crystal growth procedure, rather than simply designing some molecules. If these design and engineering processes can be applied, finally, it may be possible to control the size and shape of nanostructures flexibly and creatively.

Yadong Li's research group has developed a variety of solution-based routes in recent decades. In 2002 and 2003, Li et al. reported the use of solution-based routes to prepare a variety of rare earth compound nanostructures, including nanowires, and nanotubes (Wang & Li, 2002a, 2003a, 2003b; Wang, Sun, Yu, Zou, & Li, 2003). Besides rare-earth nanocrystals, CdE (E = S, Se, Te) nanorods (Deng, Li, & Li, 2003), $Mg(OH)_2$ nanodrods (Li et al., 2000), MnO_2 nanowires (Wang & Li, 2002b), and CaF_2 nanocubes (Sun & Li, 2003) were also synthesized before 2003. In 2005, Wang, Zhuang, Peng, and Li reported a general synthetic strategy for the production of various nanocrystals with different chemistries and properties. In recent years, Li's group has developed solution-based routes for the synthesis of more advanced functional nanostructures. In 2008, Wang, Zheng, Hao, Peng, and Li (2009) developed a synthetic method for a series of transition-metal chalcogenide semiconductor nanocrystals whose size and shape were well controlled. Various bimetallic catalysts (Wu, Cai, Wang, He, & Li, 2012a; Wu, Wang, et al., 2012; Wu et al., 2013) and concave nanomaterials (Li et al., 2013) were then reported, which exhibited excellent catalytic properties. In 2014, Duan et al. reported the synthesis of single-atom-layer rhodium nanosheets, which represented significant progress in the solution-based synthetic methods for the production of nanocrystals.

In this paper, we will review the recent progress made in solution-based synthesis strategies, which have been developed from molecular design for producing simple nanostructures to systematic engineering for producing more complex and functional nanostructures, highlighting the contributions of Li's group.

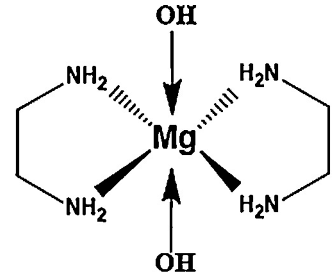

Fig. 1. A stable Mg^{2+} complex (Li et al., 2000).

This review is divided into two parts: molecular design, and systematic engineering. The first part reviews precursor molecular design and ligand molecular design, summarizing research into the synthesis of low-dimensional nanomaterials in which the precursors and some nanostructures were chosen or designed for biological applications by designing their ligands to change the surface properties.

Molecular design

Precursor molecular design

Precursors for nanoscale synthesis include inorganic compounds, organometallic coordination compounds, and polyacids, among other compounds. It is important to choose the organic functional groups for organometallic coordination compounds, as well as the solvent for inorganic compounds. We therefore review both the organic and the inorganic cases here.

Organometallic methods have been applied relatively successfully in recent decades (Murray, Norris, & Bawendi, 1993; Sun, Murray, Weller, Folks, & Moser, 2000). In these methods, the properties of the precursors typically depend on the organic part. Mai et al. (2006) developed an effective method for the synthesis of high-quality alkali-rare-earth complex fluoride ($AREF_4$) nanocrystals, when liquid precipitation methods prevailed at that time. One of the most significant factors influencing their success was that they carefully chose precursors which includes both metal and fluorine elements that made the reaction more controllable. In a typical procedure, $Na(CF_3COO)$ and $RE(CF_3COO)_3$ precursors are heated under an Ar atmosphere to achieve co-thermolysis, producing $NaREF_4$ (RE = Pr to Lu, Y), Yb^{3+}, and Er^{3+}/Tm^{3+} co-doped $NaYF_4$ nanocrystals (Mai et al., 2006). A similar result was reported in the same year (Zhang, Liu, Peng, Wang, & Li, 2006); in this case, the synthesis of nearly monodisperse Cu_2O and CuO nanospheres was performed using a $Cu(CH_3COO)_2$ precursor.

In general, inorganic compounds are cheap and easy to obtain, and are much simpler than organometallic coordination compounds; they are therefore widely used as precursors for the synthesis of nanocrystals. Li's group has successfully produced many nanostructures, including hydroxide and semiconductor nanorods, rare-earth nanorods, and nanowires, by choosing appropriate solvents in which the inorganic compounds formed special precursors with the solvent molecules.

Li et al. reported in 2000 that control over the nucleation and growth is important in the synthesis of $Mg(OH)_2$ nanorods; in their study, ethylenediamine was chosen as a solvent in which $Mg(OH)_2$ formed a relatively stable complex (Fig. 1). When the temperature was increased, the stability of complex decreased; hydroxyl groups may coordinate with Mg^{2+} and gradually replace

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