



Core and surface engineering in binary, ternary and quaternary semiconductor nanocrystals—A critical review



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ABSTRACT

In the past two decades significant research efforts of chemists, physicists, materials scientists and electronic engineers have been devoted to the elaboration of semiconductor nanocrystals with controlled optoelectronic properties and dispersible in various media, including aqueous ones. This review discusses problems of the inorganic nanocrystals synthesis with special emphasis on the role of initial ligands *i.e.* ligands originating from the reaction mixture in this process. Chemical nature of initial ligands and their topology have a profound effect on the nanocrystals' shape and size, as well as on their physical properties. Also methods for identification of initial ligands are outlined. Classification of these ligands is presented and their interactions with nanocrystal surface is discussed in the frame of HSAB (hard and soft (Lewis) acid and bases) theory. Since exchange of initial ligands for functional ones, which could tune electrical transport and other properties of the resulting nanomaterials, is crucial for nanocrystals engineering, effective ligands exchange procedures are also described, including exchange for organic ligands of semiconductor nature. Not neglecting initially developed nanocrystals (CdSe and PbS), frequently considered as “model” systems, in this review special interest is focused on heavy metal-free nanocrystals, attracting increasing scientific interests in recent years, namely binary InP NCs, ternary stoichiometric (CuInS₂) and nonstoichiometric (Cu-In-S) NCs, and quaternary Cu-In-Zn-S ones. To enhance practical utility of this review, recommended nanocrystals preparation methods, resulting in different initial ligands, as well as ligands exchange procedures are presented for each group of the discussed nanocrystals.

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1. Introduction

Specific properties of inorganic semiconductor nanocrystals are determined not only by the composition and structure of their inorganic core but also by the type of surficial ligands assuring their colloidal stability. The so called “initial” or “primary” ligands, introduced to the reaction mixture in a form of a solvent or as a part of the used precursors, frequently strongly affect the size, shape and composition of the resulting colloidal nanoparticles. Moreover, the chemical constitution of the ligand shell additionally influences the properties of the ligand-capped nanocrystals and to a large extent determines their interactions with the environment. Initial ligands such as thiols, amines or carboxylic acids containing long aliphatic substituents usually efficiently assure colloidal stability of the prepared nanoparticles in organic solvents. However, in some applications of nanocrystals they have to be

exchanged for functional ligands bringing new functions to these inorganic/organic hybrids and tuning their selected properties.

In the case of binary nanocrystals such as CdSe, CdS, PbSe, PbS, synthesized and exhaustively studied for over 20 years, several procedures of the nanocrystals synthesis and the initial ligands exchange have been elaborated leading to hybrids with a large variety of organic and even inorganic ligands [1–3]. Among the above listed binary nanocrystals, cadmium selenide is frequently considered as a model system as far as both the control of the nanocrystals size and shape and the mechanism of their growth are considered [4–7]. CdSe nanocrystals stabilized by a large variety of primary ligands have successfully been prepared. These embrace alkylphosphines (trioctylphosphine, TOP) and alkylphosphine oxides (trioctylphosphine oxide, TOPO) [8], phosphonic acids (octadecylphosphonic acid) [9], (hexylphosphonic acid, tetradecylphosphonic acid) [10], amines (hexadecylamine) [11], (octadecylamine and dioctylamine) [12], fatty carboxylic acids (oleic acid) [13], myristic acid [14], stearic acid [15]. Moreover, the methods of the molar absorption coefficients determination, elaborated for CdSe nanocrystals, can be considered as model procedures [16].

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One of the most popular ligand exchange strategy, which involves the use of pyridine as a labile, intermediate ligand in its initial form was also first applied to CdSe nanocrystals. In this approach the primary ligands are first exchanged for pyridine and in the second step pyridine is exchanged for the target ligand [17,18].

Several methods of surficial ligands identification in CdSe nanocrystals have been proposed. One of the oldest is based on the dissolution of the nanocrystal inorganic core with subsequent free ligands recovery and their identification by classical methods used in organic chemistry [5]. Newer methods exploit special spectroscopic techniques such as diffusion-ordered NMR spectroscopy (DOSY), for example [19].

Ligands exchange procedures *via* intermediate, labile pyridine ligands were also used to fabricate hybrids of CdSe nanocrystals and polymeric electroactive ligands [2]. Nanocomposites exhibiting no phase separation between nanocrystals and the polymeric component were obtained by introducing amine coordinating functions as end groups of polythiophene macromolecules [20]. This interesting approach has however its limitation to polythiophenes of a rather low molecular mass. Alternatively, coordinating functions, for example carboxylic ones, were introduced to the polythiophene chain as side groups through copolymerization of ethyl-3-thiopheneacetate and 3-alkylthiophene, leading to a copolymer which forms practically homogeneous nanocomposites with CdSe nanocrystals [21]. The same simple ligand exchange approach was used in the preparation of CdSe nanocrystals hybrids with thiophene oligomers [22].

In addition to the above described, pyridine-based ligand exchange procedures other strategies have been proposed. One of them involves the initial ligands exchange for a bifunctional linker ligand containing a coordinating function and a reactive one. In the first step initial ligands are exchanged for the linker ligands to which electroactive molecule (macromolecules) is then grafted through an appropriate reaction with the linker ligand reactive end group. Grafting of aniline tetramer to CdSe nanocrystals is an instructive example of this approach. In this case initial ligands are first exchanged for 4-formyldithiobenzoic acid, which $-C(S)SH$ group forms a chelate-type complex with the surficial atoms of the nanocrystal. In the next step the tetraaniline grafting takes place through a condensation reaction between the aldehyde group of the linker ligands and the terminal amine group of tetraaniline with the terminal amine group of aniline tetramer [23].

The formation of inorganic/organic hybrids with the use of linker ligands is also possible by exploiting the molecular recognition phenomena [24]. A specific example of this approach is briefly discussed here. Initial ligands in CdSe nanocrystals are exchanged for mercaptohexylthymine ones. These nanocrystals are then mixed with polythiophene containing alkyl and diaminopyrimidine side groups. Molecular recognition of diaminopyrimidine and thymine moieties through three hydrogen bonds leads to a homogeneous nanocomposite with no phase separation. This molecular recognition can also be exploited in the *layer by layer* (LbL) fabrication of hybrid materials consisting of alternating nanocrystals and polymer layers [25].

The problem associated with many electroactive ligands is the presence of long solubilizing groups in these molecules (macromolecules) which presence may impede the transport of charge carriers in the hybrid materials. As a result, improvement of electrical parameters in electronic devices where these materials are used is frequently rather limited. Application of simple ligands of thiol- or amine-type which do not contain long substituents frequently leads to much better results [26]. Exchange of primary ligands in oleic acid-capped CdSe nanocrystals for 1-octylamine and 1-butylamine, using pyridine intermediate labile ligand, led to the fabrication of photovoltaic cells of 1.2% and 2.0% power

conversion efficiencies, respectively [27]. Layers of CdSe nanocrystals capped with *tert*-butylthiol, annealed at temperatures exceeding 200 °C, showed n-type conductivity with ($\mu_e = 1.3 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). Films of pyridine-capped CdSe nanocrystals prepared in the same manner were ambipolar with much lower charge carriers mobilities ($\mu_e = 8.0 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) [28]. Much better results were obtained for sintered pyridine-capped CdSe nanocrystals. Electron mobilities measured for thin films in the field effect transistor (FET) configuration reached $1.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [29].

More recently, inorganic ligands were introduced through the ligand exchange process, yielding CdSe nanocrystals dispersable in highly polar solvents. Historically, first inorganic ligands used for nanocrystals stabilization were $\text{Sn}_2\text{S}_6^{4-}$ and $\text{Sn}_2\text{Se}_6^{4-}$ (with N_2H_5^+ counterion). As a result of the primary ligand exchange for the inorganic ones CdSe nanocrystals could be transferred to anhydrous hydrazine or DMSO, still retaining their shape and size. Thermal annealing of thin layers of CdSe nanocrystals capped with these inorganic ligands resulted in the formation of SnS_2 or SnSe_2 shells. The annealed layers showed reasonable electron mobility ($\mu_e \sim 3 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), essentially independently from the type of the inorganic ligand [30,31].

Much higher electron mobilities were obtained for thiocyanate-capped CdSe nanocrystals (in a form of $\text{NH}_4^+ \text{SCN}^-$). Small size of these ligands limited the separation of individual nanocrystals and promoted inter-particles charge transport. As a result, the measured electron mobility reached $3.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in the field effect transistor configuration [32].

Several simple inorganic anions such as S^{2-} , HS^- , Se^{2-} , HSe^- , Te^{2-} , HTe^- , TeS_3^{2-} , OH^- and NH_2^- were introduced to CdSe nanocrystals as ligands inducing their colloidal stability in polar solvents, for example in formamide which is characterized by one of the highest dielectric constants [33].

According to HSAB theory, the discussed ligands can be divided into soft bases of high polarizability (S^{2-} , HS^- , Se^{2-}) and hard bases, whose polarizability is much lower (OH^- and NH_2^-). Stable colloidal dispersion in formamide were obtained for CdSe nanocrystals capped with all above listed inorganic ligands. Moreover, the ligand exchange process did not alter the nanocrystals spectroscopic properties, as evidenced by the comparison of the corresponding UV-vis spectra. High electron mobility of CdSe nanocrystals, after the exchange of the initial ligands for S^{2-} (applied as $(\text{NH}_4)_2\text{S}$) should be pointed out— $0.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in the FET configuration [33]. Core/shell nanocrystals of CdSe/CdS and CdSe/ZnS capped with the same ligands showed significantly lower electron mobility.

The possibility of practical application of nanocrystals containing toxic elements such as Cd or Pb is, however, severely limited. According to the rules of the European Union on Restriction of Hazardous Substances, imposed in 2006, cadmium is considered as one of the most dangerous elements and its admissible content in a given, separable element of a device should not exceed 0.01%. This toxicity of cadmium is mainly associated with its high tendency to be accumulated in mammal organs [34]. From this point of view, gradual surficial oxidation of CdSe nanocrystals, leading to a release of cadmium to the environment [35], seems extremely dangerous. Taking into account the above outlined restrictions, it seems obvious that the research in this area has to be extended to nanocrystals which do not contain toxic elements, especially if their biological and biomedical applications are envisioned. In addition, such binary (InP) and ternary nanocrystals (CuInS_2) are presently being tested as components of photovoltaic end electroluminescence devices. In both families of nanocrystals their properties can be controllably tuned by exploiting the quantum confinement effect, adjusting surficial ligands and in the ternary system by changing their composition.

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