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Metal-semiconductor hybrid nanoparticles

Halogen induced shape control, hybrid synthesis and electrical transport

Contents

List of Abbreviations

BE	Binding energy
CB	Conduction band
COD	1-Chlorooctadecane
Cub.	Cubic
DBE	Dibromoethane
DCE	1,2-Dichloroethane
DDA	Dodecylamine
DDT	Dodecanethiol
DEG	Diethyleneglycol
DFT	Density functional theory
DIE	1,2-Diiodoethane
DTAB	n-Dodecyltrimethylammonium bromide
DTAC	n-Dodecyltrimethylammonium chloride
EDX	Energy dispersive X-ray spectroscopy
FWHM	Full width at half maximum
Hex.	Hexagonal
HDA	Hexadecylamine
HOPG	Highly oriented pyrolitic graphite
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
MIGS	Metal induced gap state
Monocl.	Monoclinic
NNH	Nearest-neighbour hopping
OAc	Oleic acid
OAm	Oleylamine
Orthorhomb.	Orthorhombic
PMMA	Polamethylmetacrylate
QY	Quantum yield

STEM	Scanning transmission electron microscopy
TBAB	Tetra-n-butylammonium borohydride
TCE	1,1,2-Trichloroethane
TEM	Transmission electron microscopy
Tetr.	Tetragonal
TOP(O)	Tri-n-octylphosphine (oxide)
TXRF	Total reflection X-ray fluorescence spectroscopy
UV-Vis	Ultraviolet-visible
VB	Valence band
VRH	Variable-range hopping
XPS	X-ray Photoelectron Spectroscopy
XRD	Powder X-ray diffractommetry

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1 Introduction

Based on their outstanding properties, nanoparticles have entered broad areas of research related to (photo)catalysis [1], energy conversion [2], optoelectronics [3], and biomedicine [4, 5]. A major factor determining these properties and the reactivity of nanoparticles is their size and related to it their large surface-to-volume ratio. The small dimensions cause quantum mechanical confinement of electrons and thus altered physical conditions compared to bulk materials [6]. The reduction in size is also advantageous to save precious materials such as catalytic metals. With proceeding climate change and pollution, high hopes rest on developments in solar energy conversion. Nanoparticles offer a variety of solutions for related applications in photovoltaics and photocatalytic conversion of solar into chemical energy.

During the past decades, the preparation of nanostructures consisting of single and multiple components has developed into a tool box for the creation of purpose-designed materials. Especially the colloidal synthesis can be applied to prepare nanoparticles in a large variety of shapes and sizes with comparatively low effort and costs. With the introduction of high temperature preparation methods twenty years ago [7], a way to obtain highly monodisperse nanoparticles was paved. From then on, the control over size and shape of the particles has grown steadily.

Another strong impulse was the selective formation of multicomponent nanostructures that combine materials with different physical properties [8]. In secondary steps other materials can be grown onto prepared nanoparticles with high precision [9, 10]. Metallic nanostructures deposited onto semiconductors, for instance, facilitate the separation of charges that are photogenerated in the semiconductor [11]. This fundamental process is the basis for improved efficiencies in fields such as photocatalytic water splitting [12]. An interesting feature of metal domains on semiconductor nanoparticles is their ability to improve electrical contacts to the latter [13]. This might be utilised to increase the charge transport in semiconductor nanoparticle arrays and affect the photocurrent obtained under illumination.

Creating and characterising such a nanoparticle array requires a high degree of control over all steps involved, from semiconductor synthesis over metal deposition to the final assembly. To reach this control, an understanding of the fundamental processes accompanying each step is necessary. By modulating the shape of the semiconductor material, for example, the number of sites reactive towards the deposition of metals can be varied which affects the whole architecture. Their comparatively large surface results in lowered melting points of nanoparticles and furthermore makes them susceptible for fast dissolution, the adsorption of molecules and reactions with the surrounding medium [14]. To prevent them from coagulation, nanoparticles are coated by a layer of surfactants, also referred to as ligands or stabilisers. Apart from exhibiting a stabilising effect, the adsorption of such ligands may play an important role in the shape evolution of wet-chemically prepared nanostructures. In connection with the preparation of CdSe-carbon nanotube composites 1,2-dichloroethane was observed to induce the formation of hexagonal pyramidally shaped CdSe nanoparticles [15, 16]. A mechanism involving chloride ions was presumed.

The peculiar pyramidal geometry provides a high number of sites prone to metal deposition and is thus an ideal candidate for an envisaged synthesis of hybrid nanoparticles with several defined metal domains in an oligomeric structure. The control of the shape evolution in reactions without carbon nanotubes and a possible adaptation of the method to develop different morphologies is desired. For this reason, a better understanding of the influence of the di-halogen alkane on the shape evolution shall be gained in this work. Another goal is the preparation of hybrid nanoparticles with oligomeric structure for the electrical characterisation in two-dimensional arrays. Finally, the obtained material shall be assembled and pioneering electrical studies shall be conducted to find out how the interplay of the domains influences two-dimensional conductance and the generation of photocurrents.

Following these steps, this thesis is separated into three chapters, each with a theoretical introduction, a results and discussion as well as a conclusions section. In the concluding sections, specific aspects concerning the results of the corresponding chapter will be treated.

In chapter 2, the interactions between ligands and the nanoparticle surface play an important role. The shape control of the semiconductor component by halogenated additives is examined. To better understand why 1,2-dichloroethane induces such a peculiar shape and if the effect may be exploited to tune the size and shape of nanoparticles, experimental and theoretical studies are combined. Systematic variations of halogenated additives as well as elemental and surface analysis are applied. In the theoretical part, calculations

based on the density functional theory and parallels to a classical crystal growth model are presented.

In chapter 3, the seeded-growth deposition of four metals, Au, Ag, Pd and Pt, onto hexagonal pyramidal CdSe nanoparticles in organic solution is examined. The reasons for the formation of a presumed shell-like Au structure with undefined composition observed in preliminary work ([17]) are scrutinised. Among the conducted experiments are studies concerning the influence of the oxidation state of the precursor on the morphology of forming hybrids. The oxidation state of the metal in the shell is examined by X-ray photo-electron spectroscopy. The deposition behaviour of the other three metals is tested by a new common synthetic method with oleylamine as ligand and reducing agent for the metal.

Chapter 4 deals with electrical properties of nanoparticles and specifically two-dimensional Pt-CdSe hybrid nanoparticle arrays. Nanoparticles with two sizes of Pt domains are examined. The assemblies are prepared with the Langmuir-Blodgett technique and measured in a probe station under vacuum. Current-voltage curves are recorded in darkness and under illumination conditions with different irradiation sources. Additionally, the temperature is varied down to cryogenic conditions. In comparison to literature data of related systems observations concerning the transport mechanisms are made.

Experimental details of all chapters are summarised in a joined experimental chapter (chapter 5). A general summary with outlook for the work follows in chapter 6, while chapter 7 contains a summary in German. Additional data for chapters 2, 3 and 4 is provided in the appendix.

2 Halogen induced shape control of CdSe nanoparticles

Due to their special size dependent optical and electronic properties semiconductor nanoparticles find application in photovoltaics [18, 19], (photo)catalysis [1, 12], light emitting devices [20] and biological labelling [21, 22], among others [23].

In these contexts, the shape of the nanoparticles may become important due to physical properties depending on the dimensionality of quantum confinement in the nanostructure or simply their packing behaviour [3, 24, 25, 26]. Apart from their morphology, an aspect that is critical for applications is the passivation of the nanoparticle surface by stabilisers.

Owing to the successful implementation of nanoparticles partially capped by or post synthetically treated with halides into solar cells with increased efficiency [27, 28], incorporation of atomic halogen ligands has attracted much attention recently [29, 30, 31, 32, 33]. In addition to enhancing physical properties in nanoparticle arrays, halides show interesting effects on the shaping of nanoparticles. With metal nanoparticles they are deliberately employed to control the growth with influences on the shape formation [34, 35]. For semiconductor nanoparticles, several cases of wurtzite structures with hexagonal bullet, pyramid, pencil or diamond shape were reported which had in common that chloride precursors were present [36, 37, 38]. A few studies showed an increase of morphological uniformity in branched cadmium chalcogenides with wurtzite arms growing on seeds of deviating crystal structures when halides were added [39, 38, 40]. Juárez and co-workers observed how traces of 1,2-dichloroethane employed as solvent for carbon nanotubes added *in situ* to a synthesis of CdSe nanorods induced a shape evolution [15, 16]. Hexagonal pyramidal nanoparticles with wurtzite structure evolved, which then formed composites with the nanotubes. Chloroalkanes were furthermore reported to aid the preparation of sheet-like lead sulfide nanostructures with the chemical structure of the molecules influencing the dimensions of the crystals [41, 42]. These circumstances built a promising foundation for further studies on the shape control of semiconductor nanoparticles by halogen compounds

with CdSe as a model system with well-known properties. An extension of feasible morphologies presents an attractive goal with respect to increasing demands on the control of nanoparticle shapes for application in thin film arrays or as seed material with controllable reactive sites for heteronanoparticle formation.

In the following, the most important theoretical aspects of the wet-chemical nanoparticle synthesis and methods of semiconductor nanoparticle shape control will be introduced. They will lay the basis for the discussion of aspects of the shape control of CdSe nanoparticles aided by (organo) halogen compounds examined in this work. For more detailed insights into properties and preparation of nanoparticles, references [23, 43, 44, 45, 46] are suggested. A substantial part of the chapter is based on and reproduced in part with permission from [Meyns, M., Iacono, F., Palencia, C., Geweke, J., Coderch, M. D., Fittschen, U. E. A., Gallego, J. M., Otero, R., Juárez, B. H., Klinke, C. *Chem. Mater.* **2014**, *26*, 1813-1821.] Copyright [2014] American Chemical Society.

2.1 Properties and synthesis of semiconductor nanoparticles

The field of semiconductor nanoparticle synthesis offers a wide and growing variety of synthetic protocols and factors that can be tuned to influence and design the dimensions and shapes of the crystals. Known morphologies range from zero- to two-dimensional in terms of bulk-like dimensions (quantum dots [47], nanotubes and nanowires [48, 49], tetrapods [50], nanosheets [51, 52]). This is appealing in so far as the shape of nanoparticles influences physical and chemical properties through changes in electric fields and crystal facet dependent surface reactivity [14, 53, 54, 55].

2.1.1 Properties of semiconductor (CdSe) nanoparticles

In terms of electrical properties, semiconductors take a middle position between highly conducting metals and insulating materials such as glasses or polymers. The reason for this is that they are able to conduct electricity only when activated by thermal energy or light. This additional energy allows electrons to move from the lower valence to the upper conduction band across the band gap; in metals there is no gap between the bands, whereas insulators are defined as having a band gap bigger than 4 eV. These bands, formed by energetically close lying electron orbitals, are delocalised over the whole crystal and

excited electron-hole pairs (excitons) are free to move in all directions in bulk materials. In nanoparticles, the number of atoms, each contributing one orbital to the band, is much smaller (between 100 and a few 10000), which causes an increase of the gap with decreasing nanoparticle size and the formation of discrete states at the band edges [6, 24]. At sizes of a few nanometres, the wave functions of electron and hole become confined in the dimensions of the semiconductor nanoparticles, now called quantum dots, and the gap is strongly size dependent (quantum size effect). The number of nanoparticle dimensions ranging in the confinement regime determines the density of available energetic states. This way, the shape and directed growth of a nanostructure may influence its band gap [56]. In spherical nanoparticles all three dimensions are affected and the electronic levels develop into discrete states. This is visible by blue shifts in absorption and emission spectra, in which the first maximum at lower wavelengths in the absorption spectra can be employed to directly relate size and band gap of the nanoparticles [57, 58]. Due to the high surface-to-volume ratio, the configuration of the outer layer of atoms and the ligand sphere protecting the nanoparticles from coagulation make a large impact on the overall properties. For example, the quantum yield of emission and the electrical transport in nanoparticle arrays can be significantly deteriorated by charge trapping sites in form of dangling bonds.

The medium valued direct band gap of II-VI semiconductor CdSe (1.74 eV in bulk [59]) makes it one of the few materials whose nanoparticles can be tuned in size to absorb and emit light throughout the visible spectrum. The electrical properties of CdSe nanoparticles will be addressed in Chapter 4. CdSe crystals occur in the cubic zinc blende or in the hexagonal wurtzite structure. The latter is depicted in Figure 2.1. At room temperature the cubic phase is slightly more stable by 1.4 meV per atom [61]. Polytypism occurs at higher temperatures and the crystal structure depends on the reaction conditions. In the presence of halogens a preferential formation of the wurtzite phase was observed, the reason for which has not been clarified so far [40, 62, 63]. The wurtzite structure is anisotropic, which becomes apparent by differences in the number of bonds per element when counting in opposite directions of the c-axis. In the positive direction Cd has one bond pointing upwards whereas Se has three. For this reason, hexagonal CdSe crystals are usually terminated by a positively charged Cd-rich (0001) and a negatively charged Se-rich (000$\bar{1}$) facet to minimise the number of dangling bonds [64, 65, 66]. This anisotropic charge distribution creates a dipole moment in the nanoparticles [67, 68].
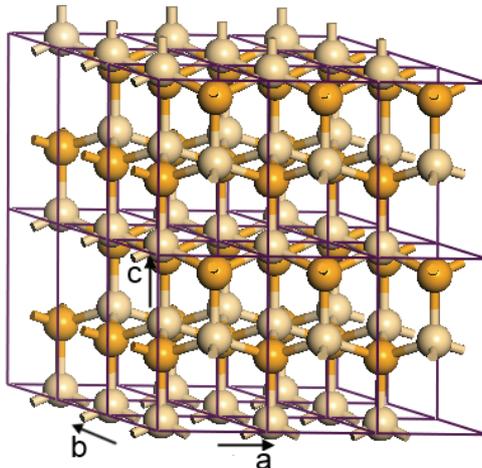
Figure 2.1: Hexagonal wurtzite crystal structure of CdSe composed from unit cells with the lattice constants a, b: 4.30 Å, c: 7.01 Å [60]; Cd atoms are beige, Se atoms are orange. The upper (0001) layer consists of Cd-atoms with one dangling bond, the lower (000$\bar{1}$) facet is usually terminated by Se with one dangling bond. Created with *Materials studio*.

CdSe nanoparticles alone or as cores coated with inorganic or organic shell materials, are applied in solar cells [18], light emitting diodes [20], and biological imaging [4]. Furthermore, they have acted as model systems for the exploration of properties in a variety of contexts. Among these are optical and electrical studies as well as investigations of shape control during synthesis [69, 70, 71].

2.1.2 Colloidal semiconductor nanoparticle synthesis and shape control

For further processing and efficient applications nanoparticles should be homogeneous in their size and shape. The method of choice to obtain nanoparticles with the highest precision in terms of size and shape is the wet-chemical bottom-up approach, where crystals are prepared from molecular precursors of the components. Semiconductor nanoparticles with small size distributions of below 10% are mainly obtained by hot-injection syntheses with separated nucleation and growth stages as pioneered by Murray, Norris and Bawendi in 1993 [7]. Before going into detail, the basics of nanoparticle formation and different models of shape control will be presented briefly.

2.1.2.1 Basics of nanoparticle nucleation

For the formation of nanoparticles starting materials are mixed and react to a solute form of the crystal[1], not yet considered as a solid phase, which evolves into nuclei once a critical supersaturation is reached. The activation energy necessary for nucleation is provided when the change of the overall free energy

$$\Delta G = -\frac{4}{V_{m,NP}}\pi r^3 k_B T \ln(S) + 4\pi r^2 \gamma \tag{2.1}$$

reaches a maximum. In Equation (2.1) $V_{m,NP}$ is the molecular volume of the material in the crystal, r is the radius of the spherical nuclei, k_B is the Boltzmann constant, S is the saturation ratio and γ is the surface free energy per unit surface area [14]. The maximum is reached for a critical radius r^* when the saturation ratio $S = \frac{c_{solute}}{k_{sp}}$ with the solute concentration c_{solute} and the solubility product of the crystal material k_{sp} is larger than one [72]. The critical radius is obtained as

$$r^* = \frac{2V_{m,NP}\gamma}{3k_B T \ln(S)} \tag{2.2}$$

by derivation of Equation 2.1. During nucleation, the supersaturation depletes until no further nuclei form. These nuclei continue to grow towards nanoparticles whose size and shape can be controlled by growth parameters such as concentration, temperature and the choice of ligands. Finally, the solute concentration will approach the level of the material's solubility and the critical radius will shift to larger values so that smaller particles dissolve in favour of further growth of bigger ones, a process known as Ostwald ripening [73].

2.1.2.2 Mechanisms of shape control

Non-spherical shapes form whenever the facets of a crystal exhibit different growth rates; fast growing facets are eliminated and slowly growing facets eventually determine the shape or *Tracht*, the entirety of the facets that form the crystal surface. Growth rates can be governed by thermodynamic or kinetic influences, depending on the growth conditions. Apart from temperature and concentration, a major role in size and shape control is played by

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[1] In literature the terms *solute* and *monomer* are employed to describe a small unit consisting of at least one of each crystal components. Solute is the term found in works on classical crystal growth and is less limited, since the solute form must not necessarily be a single formula unit.

organic surfactants, which are employed to stabilize the solid nanoparticle phase against dissolution and coagulation [74, 75, 76]. The most commonly employed types of ligands to stabilise semiconductor nanoparticles are amphiphilic organic molecules counted to the groups of neutral L-type or negatively charged X-type ligands. The first group may co-ordinate both cationic and anionic crystal components, while the second one selectively balances positively charged surface atoms to reach overall charge neutrality. If both types are present, the interaction with X-type ligands will dominate due to stronger interactions with the surface [29, 31, 77, 78]. L-type ligands provide additional stability but are more easily washed away during purification. A breakthrough observation regarding selective X-type adsorption is the case of phosphonic acid impurities in a CdSe synthesis with oth-erwise neutral tri-n-octylphosphane (TOP) ligands in tri-n-octylphosphane oxide (TOPO), which coordinated the nanoparticles in form of phosphonates [79]. As mentioned earlier, halide ions acting as atomic X-type ligands gain increasing popularity.

The terms *surfactant*, *stabiliser* and *ligand* are often used interchangeably in the lit-erature. Since surfactants and stabilising molecules usually are amphiphilic compounds with alkyl chains, the term ligand will be applied here within the meaning of a potentially surface bound constituent including short molecules and halides.
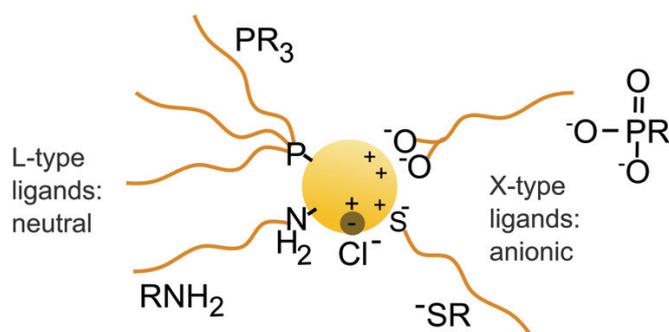
Figure 2.2: Most of the ligands employed in semiconductor nanoparticle stabilisation belong to the groups of neutral L-type ligands, which bind to cations and anions of the crystal (a dative bond to the metal cation is shown here), and X-type ligands that selectively bind to the cationic component. The named examples are tri-n-alkylphosphanes (R_3P), primary amines (RNH_2), thiolates (RS^-) and phosphonates ((RPO_3)$^{2-}$). Halides can act as atomic X-type ligands. In metallic nanoparticles with negative surface charges cationic ligands are another important group of surfactants.