

# **Advanced Shape, Composition, and Property Control in Colloidal Nanocrystal Synthesis**

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First, I would like to thank Prof. Jürgen Caro for the kind reception in his work group and for the opportunity to build up my own independent sub-group. Even though I had all freedom to conduct my research independently, Prof. Caro was always there as a mentor giving valuable strategic advices.

I would like to thank Prof. Liberato Manna and his research group for hosting my postdoctoral stay in Genoa and Prof. Uri Banin and his group for hosting my postdoctoral stay in Jerusalem, both stays were very educating not only from a scientific but also from a cultural point of view.

I thank Prof. Alexander Eychmüller for supervising my PhD thesis as well as his research group for the nice time in Dresden and in Hamburg.

Of course I have to sincerely thank all members of my own research group for the good work and the nice time in Hannover. I also would like to thank Nadja Bigall and her research group for fruitful cooperation and discussions.

I would like to thank all members of the research group of Prof. Caro; Prof. Armin Feldhoff for support concerning electron microscopy, Kerstin Janze and Yvonne Gabbey Uebe for valuable administrative support and of course all other members of the work group for the good time. Also all workers of the workshop of the Institute for Physical Chemistry are kindly acknowledged.

I would also like to thank my parents for support. Although my father may not read this thesis anymore, I sincerely hope he would have liked it.

Finally my wife Nadja is warmly acknowledged for all the help which she gave to me (scientifically as well as with her not ending patience and love).

## Preface

This thesis summarizes the results of 20 original publications authored or co-authored by me. All results included in these publications were obtained after my doctorate; accordingly none of these publications have been part of my dissertation. The results discussed were obtained partially during my postdoctoral research stay at the Hebrew University of Jerusalem where I worked in the group of Prof. Dr. Uri Banin, partially during my postdoctoral research stay at the Italian Institute of Technology where I worked in the group of Prof. Dr. Liberato Manna, and partially during my time at the Leibniz Universität Hannover where I was leading my own independent sub-group as *Habilitand* in the research group of Prof. Dr. Jürgen Caro. In the following section I will give a short summary of my individual contribution to each of the original publications included in this thesis chapter-wise:

Chapter 2:

- *Determination of all Dimensions of CdSe Seeded CdS Nanorods Solely via their UV/Vis Spectra*; Patrick Adel, Julian Bloh, Dominik Hinrichs, Torben Kodanek and Dirk Dorfs; *Zeitschrift für Physikalische Chemie* (2017), 231, 93:  
As corresponding author of this publication, I initiated, planned and coordinated all research activities. All co-authors were PhD students or undergraduate students under my supervision. I discussed and interpreted all data together with the co-authors. I also supervised and coordinated the writing of the manuscript and gave the ultimate approval to the final manuscript version before submission.
- *ZnSe Quantum Dots Within CdS Nanorods: A Seeded-Growth Type-II System*; Dirk Dorfs, Asaf Salant, Inna Popov and Uri Banin; *Small* (2008), 4, 1319:  
As first author of this publication I performed all synthetic work and most characterization work related to this publication, analyzed all data and discussed it with the co-authors, furthermore I wrote the manuscript. A. Salant and I. Popov performed TEM analysis. U. Banin supervised the work.
- *Determination of Band Offsets in Heterostructured Colloidal Nanorods Using Scanning Tunneling Spectroscopy*; Dov Steiner, Dirk Dorfs, Uri Banin, Fabio Della Sala, Liberato Manna and Oded Millo; *Nano Letters* (2008), 8, 2954:  
As second author of this publication I performed all synthetic work related to this publication and discussed the main results and proof read the manuscript. D. Steiner performed the scanning tunneling spectroscopy measurements and analyzed it. U. Banin and O. Milo supervised me and D. Steiner. F. Della Sala and L. Manna helped discussing and interpreting the data.
- *Selective Gold Growth on CdSe Seeded CdS Nanorods*; Gabi Menagen, David Mocatta, Asaf Salant, Inna Popov, Dirk Dorfs, and Uri Banin; *Chemistry of Materials* (2008), 20, 6900:  
As corresponding author of this publication, I initiated, planned and coordinated all research activities. The first author M.Sc. Gabi Menagen was co-supervised by me. I discussed and interpreted all data together with the co-authors. I also supervised and coordinated the writing of the manuscript and gave the ultimate approval to the final manuscript version before submission. D. Mocatta, A. Salant and I. Popov performed electron microscopy analysis, Uri Banin co-supervised G. Menagen and supervised me.

- *Aerogels from CdSe/CdS Nanorods with Ultra-long Exciton Lifetimes and High Fluorescence Quantum Yields*; Sara Sanchez-Paradinas, Dirk Dorfs, Sebastian Friebe, Axel Freytag, Andreas Wolf, Nadja C. Bigall, *Advanced Materials* (2015), 27, 6152:  
As second author of this publication I was in charge for coordinating and interpreting the optical characterization of the aerogel materials and was discussing these results, and was involved in writing the manuscript with S. Sanchez Paradinas and N. C. Bigall. S. Sanchez-Paradinas made all relevant synthesis work, which was partially started earlier by S. Friebe. A. Freytag and A. Wolf performed electron microscopy characterization. N.C. Bigall initiated and coordinated the research and supervised most co-authors.
- *Chloride Ion Mediated Synthesis of Metal/Semiconductor Hybrid Nanocrystals*; Dominik Hinrichs, Michael Galchenko, Torben Kodanek, Suraj Naskar, Nadja-C. Bigall and Dirk Dorfs; *Small* (2016), 12, 2588:  
As corresponding author of this publication, I initiated, planned and coordinated all research activities. Most co-authors were PhD students or undergraduate students under my supervision. I discussed and interpreted all data together with the co-authors. I also supervised and coordinated the writing of the manuscript and gave the ultimate approval to the final manuscript version before submission. Suraj Naskar supplied some of the metallic nanoparticles and was supervised by Dr. Nadja C. Bigall.
- *A Cast-Mold Approach to Iron Oxide and Pt/Iron Oxide Nanocontainers and Nanoparticles with a Reactive Concave Surface*; Chandramohan George, Dirk Dorfs, Giovanni Bertoni, Andrea Falqui, Alessandro Genovese, Teresa Pellegrino, Anna Roig, Alessandra Quarta, Roberto Comparelli, M. Lucia Curri, Roberto Cingolani, Liberato Manna, *Journal of the American Chemical Society* (2011), 133, 2205:  
Together with C. George I was involved in the synthesis of the nanoparticles and I was mainly in charge for the DLS characterization of the key-lock recognition reactions observed in this work.
- *Octapod-Shaped Colloidal Nanocrystals of Cadmium Chalcogenides via "One-Pot" Cation Exchange and Seeded Growth*, Sasanka Deka, Karol Miszta, Dirk Dorfs, Alessandro Genovese, Giovanni Bertoni, Liberato Manna, *Nano Letters* (2010), 10, 3770:  
Here I am author equally contributing to the first author. S. Deka initiated the synthetic work which I then continued together with K. Miszta after S. Deka left the research institution. I was mainly involved in studying the cation exchange mechanism and in the optical characterization of the system and discussed all results with all co-authors. I also wrote the manuscript. A. Genovese and G. Bertoni performed TEM investigations and L. Manna supervised and coordinated the research.
- *Birth and Growth of Octapod-Shaped Colloidal Nanocrystals Studied by Electron Tomography*; Rosaria Brescia, Karol Miszta, Dirk Dorfs, Liberato Manna, Giovanni Bertoni, *Journal of Physical Chemistry C* (2011), 115, 20128:  
Together with K. Miszta I was in charge for the synthesis of the investigated nanoparticles under supervision of L. Manna. R. Brescia and G. Bertoni performed the electron tomography measurements.
- *Phase transfer of 1-and 2-dimensional Cd-based nanocrystals*; Torben Kodanek, Hadeel M. Banbela, Suraj Naskar, Patrick Adel, Nadja C. Bigall and Dirk Dorfs, *Nanoscale* (2015), 7, 19300:

As corresponding author of this publication, I initiated, planned and coordinated all research activities. Most co-authors were PhD students or undergraduate students under my supervision. I discussed and interpreted all data together with the co-authors. I also supervised and coordinated the writing of the manuscript and gave the ultimate approval to the final manuscript version before submission. Suraj Naskar developed the transfer protocol for the 2D sheets and was supervised by Nadja C. Bigall.

#### Chapter 3:

- *Colloidal  $Cu_{2-x}(S_ySe_{1-y})$  alloy nanocrystals with controllable crystal phase: synthesis, plasmonic properties, cation exchange and electrochemical lithiation*; Enrico Dilena, Dirk Dorfs, Chandramohan George, Karol Miszta, Mauro Povia, Alessandro Genovese, Alberto Casu, Mirko Prato, Liberato Manna, *Journal of Materials Chemistry* (2012), 22, 13023:  
As author equally contributing like the first author to this publication I initiated all synthetic work which was then continued by E. Dilena after I left the research institution.
- *Cation Exchange Reactions in Colloidal Branched Nanocrystals*; Karol Miszta, Dirk Dorfs, Alessandro Genovese, Mee Rahn Kim, Liberato Manna, *ACS Nano* (2011), 5, 7176:  
As second author of this publication, I was in charge for the optimization of the synthesis procedure. Furthermore I wrote large parts of the manuscript.
- *Hierarchical self-assembly of suspended branched colloidal nanocrystals into superlattice structures*; Karol Miszta, Joost de Graaf, Giovanni Bertoni, Dirk Dorfs, Rosaria Brescia, Sergio Marras, Luca Ceseracciu, Roberto Cingolani, Rene van Roij, Marjolein Dijkstra, Liberato Manna, *Nature Materials* (2011), 10, 872:  
In this work I contributed by characterizing the temporal evolution of the assembly process by dynamic light scattering (DLS) measurements. Furthermore I conducted all cation exchange reactions performed on the superstructures. I was also involved in writing the manuscript.
- *Segmented CdSe@CdS/ZnS Nanorods Synthesized via a Partial Ion Exchange Sequence*; Patrick Adel, Andreas Wolf, Torben Kodanek, Dirk Dorfs, *Chemistry of Materials* (2014), 26, 3121:  
As corresponding author of this publication, I initiated, planned and coordinated all research activities. All co-authors were PhD students or undergraduate students under my supervision. I discussed and interpreted all data together with the co-authors. I also supervised and coordinated the writing of the manuscript and gave the ultimate approval to the final manuscript version before submission.

#### Chapter 4:

- *Reversible Tunability of the Near-Infrared Valence Band Plasmon Resonance in  $Cu_{2-x}Se$  Nanocrystals*; Dirk Dorfs, Thomas Härtling, Karol Miszta, Nadja C. Bigall, Mee Rahn Kim, Alessandro Genovese, Andrea Falqui, Mauro Povia and Liberato Manna, *Journal of the American Chemical Society* (2011), 133, 11175:  
As first author of this publication I performed all synthetic work and most characterization work related to this publication, analyzed all data and discussed it with the co-authors, furthermore I wrote the manuscript.
- *Plasmon Dynamics in Colloidal  $Cu_{2-x}Se$  Nanocrystals*; Francesco Scotognella, Giuseppe Della Valle, Ajay Ram Srimath Kandada, Dirk Dorfs, Margherita Zavelani-Rossi, Matteo Conforti,

Karol Miszta, Alberto Comin, Kseniya Korobchevskaya, Guglielmo Lanzani, Liberato Manna, and Francesco Tassone, *Nano Letters* (2011), *11*, 4711:

In this work I was in charge for the synthesis of the nanoparticles and also took part in the transient absorption measurements which were mainly conducted by F. Scotognella.

- *Synthesis of Plasmonic Cu<sub>2-x</sub>Se@ZnS Core@Shell Nanoparticles*; Andreas Wolf, Thomas Härtling, Dominik Hinrichs and Dirk Dorfs, *ChemPhysChem* (2016), *17*, 717:  
As corresponding author of this publication, I initiated, planned and coordinated all research activities. Most co-authors were PhD students or undergraduate students under my supervision. I discussed and interpreted all data together with the co-authors. I also supervised and coordinated the writing of the manuscript and gave the ultimate approval to the final manuscript version before submission. T. Härtling performed theoretical calculations on localized surface plasmon resonance positions.
- *Tuning the LSPR in copper chalcogenide nanoparticles by cation intercalation; cation exchange and metal growth*, Andreas Wolf, Torben Kodanek und Dirk Dorfs, *Nanoscale* (2015), *7*, 19519:  
As corresponding author of this publication, I initiated, planned and coordinated all research activities. All co-authors were PhD students or undergraduate students under my supervision. I discussed and interpreted all data together with the co-authors. I also supervised and coordinated the writing of the manuscript and gave the ultimate approval to the final manuscript version before submission.
- *Growth of Cu<sub>2-x</sub>Se-CuPt and Cu<sub>1.1</sub>S-Pt Hybrid Nanoparticles*; Andreas Wolf, Dominik Hinrichs, Joachim Sann, Jan F. Miethe, Nadja C. Bigall and Dirk Dorfs, *Journal of Physical Chemistry C* (2016), *120*, 21925:  
As corresponding author of this publication, I initiated, planned and coordinated all research activities. Most co-authors were PhD students or undergraduate students under my supervision. I discussed and interpreted all data together with the co-authors. I also supervised and coordinated the writing of the manuscript and gave the ultimate approval to the final manuscript version before submission. J. Sann performed XPS measurements, J. F. Miethe performed electrochemical measurements and was supervised by Nadja C. Bigall.
- *Plasmonic Semiconductor Nanoparticles in a Metal-Organic Framework Structure and their In Situ Cation Exchange*, Andreas Wolf, Lisa Diestel, Franziska Lübke, Torben Kodanek, Tarek Mohamed, Jürgen Caro and Dirk Dorfs, *Chemistry of Materials* (2016), *28*, 7511:  
As corresponding author of this publication, I initiated, planned and coordinated all research activities. Most co-authors were PhD students or undergraduate students under my supervision. I discussed and interpreted all data together with the co-authors. I also supervised and coordinated the writing of the manuscript and gave the ultimate approval to the final manuscript version before submission. L. Diestel advised during MOF preparation and was supervised by J. Caro who additionally helped me discuss and interpret the MOF related material properties.

## Abstract

Nanoscience is an emerging field of research in the last decades. Amongst other approaches like ball milling, ablation processes and various vapor deposition techniques, wet chemical approaches are one very prospering way to synthesize nanocrystals. The colloid chemical approach is dominated by surface coordinating ligands, which allow controlling size and shape of the resulting nanoparticles with extreme accuracy. The most fascinating point about nanoscale materials is that their properties can differ tremendously from those of the respective bulk materials. These properties are typically affected not only by size and composition of the nanoparticles but also by their shape.

This thesis summarizes the results of 20 original publications which are covering three closely connected aspects of modern colloidal nanochemistry. The chapters included are described in the following:

- Chapter one gives an overview over the colloidal synthesis of nanocrystals as well as their main properties which are relevant for this thesis. Hence, important synthesis and growth parameters are discussed. The size quantization effect in semiconducting nanoparticles and the localized surface plasmon resonance effect in conductive nanoparticles are explained in depth.
- Chapter two of this thesis deals with different aspects of shape control of colloidal nanoparticles. The advanced shape control developed in the various original publications in chapter two shows how far beyond simple (quasi)spherical nanoparticles colloid chemical synthesis can go today. A variety of differently shaped nanoparticles like rods, branched structures but also partially hollow or concave nanoparticles are introduced. All of them could be synthesized with very low degrees of polydispersity of the particle ensembles.
- Chapter three investigates cation exchange reactions with colloidal nanocrystals which are versatile approaches for composition control in these systems. These ion exchange reactions can either fully or also partially transform nanocrystals from one material to another without changing size or shape of the starting particles.
- Chapter four deals with property control in colloidal nanocrystals with a specific focus on nanoparticles with localized surface plasmon resonances in the near infrared spectral region. Here, nanoparticles from so-called degenerately doped materials are introduced as plasmonic materials which are a promising alternative for the traditional plasmonic noble metal nanoparticles.
- The thesis is finished by a conclusion and an outlook at future perspectives of colloid chemical nanoparticle synthesis.



## Erweiterte Zusammenfassung (deutsch)

Die Forschung an nanoskaligen Materialien und Festkörpern hat in den letzten Jahrzehnten deutlich an Bedeutung gewonnen. Dies beruht überwiegend auf dem Umstand, dass nanoskalige Festkörper neben einem zwangsläufig hohen Oberfläche-zu-Volumen Verhältnis oft auch spezielle physikalische und/oder chemische Eigenschaften besitzen können, welche im entsprechenden makroskopischen Festkörper überhaupt nicht beobachtet werden.

Heutzutage existieren zahlreiche unterschiedliche Herstellungsverfahren für nanoskalige Materialien mit sehr unterschiedlichen Vor- und Nachteilen. Die kolloidchemische Herstellung zeichnet sich dabei vor allem durch drei Vorteile aus:

- i) Die hergestellten Nanopartikel liegen in der Regel als gut voneinander separierte Objekte vor, d.h. Aggregation und Agglomeration können minimiert werden, hierdurch können ggf. die Eigenschaften einzelner Partikel bestimmt werden, falls diese durch dicht benachbarte Partikel beeinflusst werden.
- ii) Es kann (z.B. im Vergleich zu lithographischen Methoden) eine große Anzahl Nanopartikel auf einmal hergestellt werden.
- iii) Die Herstellungskosten sind im Vergleich zu z.B. lithographischen Methoden niedrig.

Diese Arbeit beleuchtet durch eine zusammenfassende Darstellung von insgesamt 20 Originalarbeiten im Wesentlichen drei miteinander in engem Zusammenhang stehende Aspekte moderner kolloidchemisch hergestellter Nanopartikel, mit denen ich mich in den letzten Jahren befasst habe. Nach einer kurzen Einführung, welche die wichtigsten größenabhängigen physikalischen Eigenschaften kolloidaler Nanopartikel zusammenfasst, beschäftigt sich Kapitel 2 dieser Arbeit mit Aspekten zur Formkontrolle von kolloidchemisch hergestellten Nanopartikeln. Kapitel 3 beleuchtet Kationenaustauschreaktionen an kolloidchemisch hergestellten Nanopartikeln, welche ein vielfältiges Instrument zur Zusammensetzungskontrolle von Nanopartikeln darstellen. Kapitel 4 beschäftigt sich mit lokalisierten Oberflächenplasmonenresonanzen in entartet dotierten Systemen, welche ein äußerst interessantes physikalisches Phänomen sind, das durch Form und Zusammensetzungskontrolle der Nanopartikel entscheidend manipuliert werden kann.

Die Eigenschaften nanoskaliger Partikel unterscheiden sich drastisch von denen makroskopischer Objekte. Ein wesentlicher Effekt der im Rahmen dieser Arbeit eine Rolle spielt ist dabei der sogenannte Größenquantisierungseffekt, welcher die Veränderung der Bandstruktur von Halbleitern im Nanometerbereich beschreibt. Im Bereich der metallischen Nanopartikel spielen hingegen sogenannte lokalisierte Oberflächenplasmonenresonanzen eine entscheidende Rolle für Ihre optischen Eigenschaften, welche zwar zunächst keinen quantenmechanischen Effekt darstellen, trotzdem jedoch in dieser Form nur in nanoskopischen Partikeln auftreten. Beide Effekte werden in dem für diese Arbeit nötigen Rahmen ausführlich im ersten einleitenden Kapitel dieser Arbeit erläutert. Weiterhin geht das erste Kapitel ausführlich auf die wesentlichen Aspekte der kolloidchemischen Nanopartikelsynthese ein, stellt die bekannten Verfahren zur Synthese von sphärischen und nicht sphärischen Partikeln vor und diskutiert wesentliche Syntheseparameter und Anwendungsaspekte.

Im Kapitel 2 werden meine Beiträge zur Formkontrolle im Rahmen der kolloidchemischen Synthese von Halbleiternanopartikeln ausführlich beleuchtet. Dabei werden sowohl stäbchenförmige Partikel als auch kontrolliert verzweigte Partikel behandelt, ebenso wie andere Formen, wie z.B. hohle oder konkave Partikel. Im Detail besteht Kapitel zwei dieser Arbeit aus den folgenden Arbeiten:

- *Determination of all Dimensions of CdSe Seeded CdS Nanorods Solely via their UV/Vis Spectra*; Patrick Adel, Julian Bloh, Dominik Hinrichs, Torben Kodanek and Dirk Dorfs; *Zeitschrift für Physikalische Chemie* (2017), 231, 93.

In dieser Arbeit werden die optischen Eigenschaften von kolloidalen CdSe/CdS Nanostäbchen ausführlich untersucht, und es wird ein Verfahren entwickelt um alle Abmessungen dieser Nanoheterostrukturen ausschließlich aus dem Absorptionsspektrum zu ermitteln.

- *ZnSe Quantum Dots Within CdS Nanorods: A Seeded-Growth Type-II System*; Dirk Dorfs, Asaf Salant, Inna Popov and Uri Banin; *Small* (2008), 4, 1319:

In dieser Arbeit werden die Auswirkung der internen Strukturierung von Nanostäbchen auf deren photophysikalischen Eigenschaften (z.B. Lebensdauer angeregter Ladungsträger) untersucht. Es wurde gezeigt, dass die interne Strukturierung die Fluoreszenzlebensdauer um mindestens eine Größenordnung beeinflussen kann.

- *Determination of Band Offsets in Heterostructured Colloidal Nanorods Using Scanning Tunneling Spectroscopy*; Dov Steiner, Dirk Dorfs, Uri Banin, Fabio Della Sala, Liberato Manna and Oded Millo; *Nano Letters* (2008), 8, 2954:

Diese Arbeit untersucht mittels Rastertunnelspektroskopie die absoluten Energieniveaulagen in intern strukturierten Nanostäbchen bestehend aus CdSe Keimen und CdS Stäbchen und liefert starke Hinweise auf eine Lokalisierung von sowohl Elektron als auch Loch in der Nähe des CdSe Kerns.

- *Selective Gold Growth on CdSe Seeded CdS Nanorods*; Gabi Menagen, David Mocatta, Asaf Salant, Inna Popov, Dirk Dorfs, and Uri Banin; *Chemistry of Materials* (2008), 20, 6900:

In dieser Arbeit wird der Einfluss der internen Strukturierung von CdS Stäbchen mit CdSe Kernen auf die Reaktivität und die Regioselektivität beim Aufwachsen von Golddomänen auf eben diese Stäbchen ausführlich untersucht. Es wurde ein entscheidender Einfluss des CdSe Kerns auf die Au Lokalisierung festgestellt.

- *Aerogels from CdSe/CdS Nanorods with Ultra-long Exciton Lifetimes and High Fluorescence Quantum Yields*; Sara Sanchez-Paradinas, Dirk Dorfs, Sebastian Friebe, Axel Freytag, Andreas Wolf, Nadja C. Bigall, *Advanced Materials* (2015), 27, 6152:

In dieser Arbeit werden die photophysikalischen Eigenschaften von Aerogelen aus miteinander verknüpften CdS Nanostäbchen mit CdSe Kernen untersucht. Es zeigt sich, dass vermutlich im angeregten Zustand Elektronen über größere Strecken delokalisiert werden, während Löcher in den CdSe Kernen lokalisiert bleiben.

- *Chloride Ion Mediated Synthesis of Metal/Semiconductor Hybrid Nanocrystals*; Dominik Hinrichs, Michael Galchenko, Torben Kodanek, Suraj Naskar, Nadja-C. Bigall and Dirk Dorfs; *Small* (2016), 12, 2588:

In dieser Arbeit werden die Synthesebedingungen für monodisperse Metall/Halbleiterhybridpartikel detailliert analysiert. Insbesondere wird gezeigt, dass

bereits Kleinstmengen von Chloridionen einen drastischen Einfluss auf die erhaltenen Heterostrukturen haben.

- *A Cast-Mold Approach to Iron Oxide and Pt/Iron Oxide Nanocontainers and Nanoparticles with a Reactive Concave Surface*; Chandramohan George, Dirk Dorfs, Giovanni Bertoni, Andrea Falqui, Alessandro Genovese, Teresa Pellegrino, Anna Roig, Alessandra Quarta, Roberto Comparelli, M. Lucia Curri, Roberto Cingolani, Liberato Manna, *Journal of the American Chemical Society* (2011), *133*, 2205:  
In dieser Arbeit wird ein Syntheseverfahren für teilweise hohle und teilweise konkave Eisenoxidnanopartikel entwickelt. Zusätzlich werden die Eigenschaften dieser Partikel untersucht.
- *Octapod-Shaped Colloidal Nanocrystals of Cadmium Chalcogenides via "One-Pot" Cation Exchange and Seeded Growth*, Sasanka Deka, Karol Miszta, Dirk Dorfs, Alessandro Genovese, Giovanni Bertoni, Liberato Manna, *Nano Letters* (2010), *10*, 3770:  
Diese Arbeit beschreibt die Synthese von kolloidalen achtarmigen Partikeln mit geringer Polydispersität. Im Verlauf der Synthese ist dabei ein Kationenaustauschprozess von entscheidender Bedeutung für das Gelingen: die für den Erfolg notwendigen 10-15 nm großen CdSe Nanopartikel mit kubisch flächenzentrierter Gitterstruktur sind anders als durch diesen Kationenaustauschschritt nicht herzustellen.
- *Birth and Growth of Octapod-Shaped Colloidal Nanocrystals Studied by Electron Tomography*; Rosaria Brescia, Karol Miszta, Dirk Dorfs, Liberato Manna, Giovanni Bertoni, *Journal of Physical Chemistry C* (2011), *115*, 20128:  
In dieser Arbeit wird die 3D Morphologie der oben beschriebenen achtarmigen Strukturen mittels Elektronentomographie exakt analysiert.
- *Phase transfer of 1-and 2-dimensional Cd-based nanocrystals*; Torben Kodanek, Hadeel M. Banbela, Suraj Naskar, Patrick Adel, Nadja C. Bigall and Dirk Dorfs\*, *Nanoscale* (2015), *7*, 19300:  
Diese Arbeit untersucht das Phasentransferverhalten (Transfer von unpolaren Medien in Wasser) von kolloidalen Nanopartikeln in Abhängigkeit ihrer Form. Dabei zeigt sich, dass das Phasentransferprotokoll für unterschiedliche Geometrien unterschiedlich angepasst werden muss, um optimale Ergebnisse zu erhalten.

Kapitel 3 dieser Arbeit beleuchtet die sich durch Kationenaustauschreaktionen ergebenden Möglichkeiten der Zusammensetzungskontrolle von kolloidalen Nanokristallen. Es werden verschiedene Beispiele von Mehrkomponentennanokristallen vorgestellt, die ohne diese Technik nicht hergestellt werden können. Im Detail sind die folgenden Arbeiten enthalten:

- *Colloidal  $Cu_{2-x}(S_ySe_{1-y})$  alloy nanocrystals with controllable crystal phase: synthesis, plasmonic properties, cation exchange and electrochemical lithiation*; Enrico Dilella<sup>‡</sup>, Dirk Dorfs<sup>‡</sup>, Chandramohan George, Karol Miszta, Mauro Povia, Alessandro Genovese, Alberto Casu, Mirko Prato, Liberato Manna, *Journal of Materials Chemistry* (2012), *22*, 13023:  
Diese Arbeit zeigt, dass Kationenaustauschreaktionen auch an Nanokristallen mit gemischten anionischen Gittern möglich sind und dabei das anionische Gitter nach wie vor vollständig erhalten bleibt.
- *Cation Exchange Reactions in Colloidal Branched Nanocrystals*; Karol Miszta, Dirk Dorfs, Alessandro Genovese, Mee Rahn Kim, Liberato Manna, *ACS Nano* (2011), *5*, 7176:

In dieser Arbeit wird sowohl der vollständige als auch der partielle Kationenaustausch an achtarmigen Nanopartikeln untersucht. Der partielle Kationenaustausch an diesen Strukturen geschieht dabei nicht an zufälligen Positionen sondern selektiv an den Spitzen der Arme.

- *Hierarchical self-assembly of suspended branched colloidal nanocrystals into superlattice structures*; Karol Miszta, Joost de Graaf, Giovanni Bertoni, Dirk Dorfs, Rosaria Brescia, Sergio Marras, Luca Ceseracciu, Roberto Cingolani, Rene van Roij, Marjolein Dijkstra, Liberato Manna, *Nature Materials* (2011), 10, 872:

In dieser Arbeit wird das komplexe Selbstanordnungsverhalten achtarmiger Nanopartikel untersucht. Darüber hinaus wird gezeigt, dass auch die angeordneten Strukturen Kationenaustauschreaktionen eingehen können, wobei sowohl die Struktur der Nanopartikelbausteine als auch die der Überstrukturen vollständig erhalten bleiben.

- *Segmented CdSe@CdS/ZnS Nanorods Synthesized via a Partial Ion Exchange Sequence*; Patrick Adel, Andreas Wolf, Torben Kodanek, Dirk Dorfs, *Chemistry of Materials* (2014), 26, 3121:

In dieser Arbeit wird gezeigt, dass auch Kationenaustauschreaktionen, die über einen einzelnen Schritt nicht möglich sind, gegebenenfalls über einen weiteren Kationenaustauschschritt realisiert werden können. Dies geschieht in dem untersuchten Beispiel im Fall des nicht kompletten Kationenaustauschs mit hoher Regioselektivität.

Weiterhin werden in Kapitel 4 ausführlich sogenannte lokalisierte Oberflächenplasmonenresonanzen behandelt. Dies sind resonante Ladungsträgeroszillationen von freien Ladungsträgern die in dieser Form im Festkörper nicht auftreten. In metallischen Nanopartikeln sind diese lokalisierten Oberflächenplasmonenresonanzen mittlerweile gut untersuchte Phänomene; die vorliegende Arbeit beleuchtet aber insbesondere das Phänomen, dass lokalisierte Oberflächenplasmonenresonanzen nicht nur in metallischen Partikeln auftreten, sondern auch in entartet dotierten Halbleitermaterialien. Die folgenden Originalarbeiten bilden das 4. Kapitel:

- *Reversible Tunability of the Near-Infrared Valence Band Plasmon Resonance in  $Cu_{2-x}Se$  Nanocrystals*; Dirk Dorfs, Thomas Härtling, Karol Miszta, Nadja C. Bigall, Mee Rahn Kim, Alessandro Genovese, Andrea Falqui, Mauro Povia and Liberato Manna, *Journal of the American Chemical Society* (2011), 133, 11175:

In dieser Arbeit werden Kupferselenidnanopartikel erstmalig als plasmonische Nanopartikel mit im Nahinfrarotbereich einstellbaren Oberflächenplasmonenresonanzen vorgestellt und der Zusammenhang zum Fehlstellendotierungsgrad wird untersucht und beschrieben.

- *Plasmon Dynamics in Colloidal  $Cu_{2-x}Se$  Nanocrystals*; Francesco Scotognella, Giuseppe Della Valle, Ajay Ram Srimath Kandada, Dirk Dorfs, Margherita Zavelani-Rossi, Matteo Conforti, Karol Miszta, Alberto Comin, Kseniya Korobchevskaya, Guglielmo Lanzani, Liberato Manna, and Francesco Tassone, *Nano Letters* (2011), 11, 4711:

In dieser Arbeit werden die Ladungsträgerdynamik der Kupferselenidnanopartikel nach Plasmonenanregung mit Pikosekundenzeitauflösung untersucht. Die Plasmonendynamik wird interpretiert, wobei teils sehr ähnliches, teils auch unterschiedliches Verhalten im Vergleich zu klassischen plasmonischen Edelmetallpartikeln gefunden wurde.

- *Synthesis of Plasmonic Cu<sub>2-x</sub>Se@ZnS Core@Shell Nanoparticles*; Andreas Wolf, Thomas Härtling, Dominik Hinrichs and Dirk Dorfs, *ChemPhysChem* (2016), 17, 717:  
 In dieser Arbeit wird gezeigt, dass eine dielektrische Schale aus ZnS um Kupferselenidnanopartikel gewachsen werden kann. Der Einfluss dieser Schale auf die spektrale Position der Plasmonenresonanz der Nanopartikel sowie auf die Beständigkeit der Partikel gegenüber Oxidationsmitteln und Reduktionsmitteln wird analysiert.
- *Tuning the LSPR in copper chalcogenide nanoparticles by cation intercalation; cation exchange and metal growth*; Andreas Wolf, Torben Kodanek und Dirk Dorfs, *Nanoscale* (2015), 7, 19519:  
 Diese Arbeit untersucht den Einfluss verschiedener Co-Dotierungen von Kupferselenid- und Kupfersulfidnanopartikeln mit z.B. Ag und Au Ionen, mit einem Hauptaugenmerk auf die dadurch erreichte erhöhte Stabilität gegenüber Sauerstoff.
- *Growth of Cu<sub>2-x</sub>Se-CuPt and Cu<sub>1.1</sub>S-Pt Hybrid Nanoparticles*; Andreas Wolf, Dominik Hinrichs, Joachim Sann, Jan F. Miethe, Nadja C. Bigall and Dirk Dorfs, *Journal of Physical Chemistry C* (2016), 120, 21925:  
 Diese Arbeit untersucht den Einfluss von Pt Domänen auf die Plasmonenresonanzen in Kupferchalcogenidnanopartikeln, welche die Plasmonenresonanz im Vergleich zu Golddomänen stark dämpfen.
- *Plasmonic Semiconductor Nanoparticles in a Metal-Organic Framework Structure and their In Situ Cation Exchange*, Andreas Wolf, Lisa Diestel, Franziska Luebke, Torben Kodanek, Tarek Mohamed, Jürgen Caro and Dirk Dorfs, *Chemistry of Materials* (2016), 28, 7511:  
 In dieser Arbeit wird eine Methode zum Einbringen von Kupferselenid und ITO Nanopartikeln in poröse metallorganische Gerüstverbindungen entwickelt. Es konnte gezeigt werden, dass die Plasmonenresonanzen dabei fast unverändert erhalten bleiben und die Nanopartikel innerhalb der MOF Partikel immer noch zugänglich sind (z.B. für Kationenaustauschreaktionen).

Die Arbeit schließt mit einem Kapitel mit Schlussfolgerungen und einem Ausblick. Darin werden die erzielten Möglichkeiten zur Form-, Zusammensetzungs- und Eigenschaftskontrolle zusammengefasst. Weiterhin wird die Bedeutung der Ergebnisse für die zukünftige Forschung auf diesem Gebiet und für mögliche Anwendungen diskutiert.

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# 1. Introduction

## 1.1. General Introduction

Nanostructures are defined as structures with at least one dimension being smaller than 100 nm. Such structures are of high research interest since in this size regime some of the material properties alter significantly from the properties of the bulk material. One of the first examples where these different properties were (unknowingly) applied are e.g. colored church windows and other ancient colored glasses whose violet or red colors originate from gold nanoparticles dispersed in these glasses.

Today, nanoscience is one of the most emerging fields in research with potential applications in many different sectors, like e.g. applications in optoelectronics, photovoltaics and catalysis (see chapter 1.5).<sup>1,2</sup> Nanoscopic structures can in principle be produced either by so-called top down approaches starting from bulk materials which are transformed to nanomaterials (e.g. ball milling, laser ablation, various lithographic and similar techniques) or via so-called bottom up approaches starting from molecular precursors. Among the different bottom up approaches one might further distinguish typical physical methods (various vapor deposition techniques, molecular beam epitaxy and alike) and chemical approaches.

Colloidal nanoparticles are particles which are individually dispersed in a liquid phase and which are stabilized either by their surface charge or by steric repulsion due to surface bound ligands. In principle, the colloid chemical synthesis of nanoparticles is a precipitation reaction occurring in oversaturated solution, which is hindered from proceeding to larger particles by e.g. the addition of surface active molecules (surfactants) binding to the surface of the particles formed and decelerating the particle growth (see figure 1 for schematic illustration). At the same time the surfactants hinder particle fusion. The colloid chemical approach to synthesize nanostructures is a typical wet chemical approach with the advantage that typically much larger amounts of nanostructures can be produced compared to most physical methods, and that the surface of the synthesized structures can be directly modified using the rich versatility of wet chemical organic and inorganic synthesis.

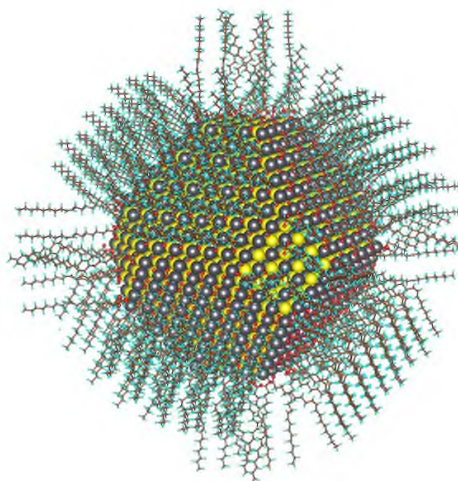


Figure 1: atomistic model of a 5 nm PbS nanocrystals covered with oleic acid as surface bound ligand. Adapted from ref [3]. Reprinted with permission from AAAS.

## *1. Introduction*

Colloid chemistry nowadays allows the synthesis of a very large variety of nanocrystals with various compositions (oxides, semiconductors, metals, and magnetic materials) and sizes (from clusters with few atoms up to 100 nm or larger). In this thesis, my contributions to the field of shape and composition control in colloid chemical nanoparticle synthesis are summarized with a strong focus on multi-component nanoparticles comprised of two or more semiconductor materials and on multi-component nanoparticles comprised of a metal domain and a semiconductor domain. Especially particles with well-defined shapes beyond simple quasi-spherical shape are investigated. It is shown, that the advanced shape and composition control can result in an advanced property control which can be utilized for a variety of applications.

Before summarizing my own original contributions to the field of shape control (chapter 2), composition control (chapter 3) and property control (chapter 4) of colloidal nanocrystals in a cumulative way, the following sub-chapters will briefly introduce into the colloid chemical synthesis of nanoparticles (chapter 1.2), the most important properties of colloidal metal and semiconductor nanocrystals (chapter 1.3), and colloidal multi-component nanoheterostructures (chapter 1.4) as well as their applications (chapter 1.5).

## 1.2. Colloid Chemical Synthesis of Nanocrystals

Nowadays, a large variety of methods to produce nanoparticles is available ranging from mainly physical (like e.g. ball milling, laser ablation, vapor deposition techniques) to various chemical routes.<sup>4</sup> All these synthetic techniques have their own advantages and disadvantages. The colloid chemical approach produces typically nanoparticles with some sort of surface passivation, and therefore is one of the most powerful approaches when non-aggregated or non-agglomerated individual nanocrystals shall be produced. Furthermore the surface passivation can be altered, and this way it allows to fine tune surface properties such as hydrophobicity or hydrophilicity.

Since many properties of nanocrystals can be drastically size and shape dependent, it is obvious that in order to synthetically control the properties of a nanocrystal batch, it is necessary to control the polydispersity of the particles as good as possible. In most colloid chemical reactions, this is reached by as good as possible separating the nucleation and growth steps of the nanocrystals. In other words it is necessary to keep the nucleation phase as short as possible (see figure 2).

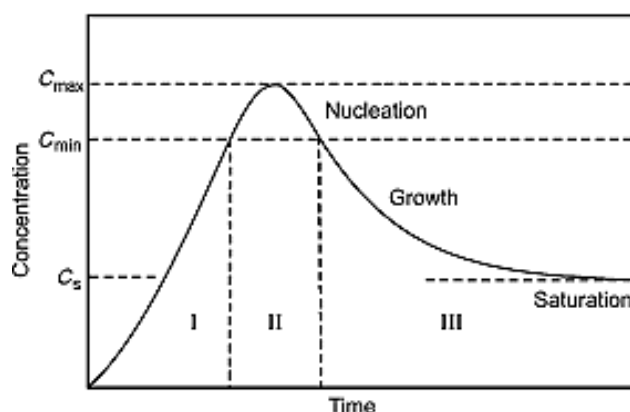


Figure 2: Diagram showing monomer concentration as a function of time according to the La Mer growth model for colloids. Adapted from ref [5]. Copyright (1950) American Chemical Society.

The earliest wet chemical synthetic approaches go back more than 100 years when Michael Faraday described the synthesis and optical properties of colloidal solutions of Au nanoparticles. Some of the first size quantized colloidal quantum dots (QDs, that is semiconductor nanoparticles within the size regime of the Bohr exciton radius, see chapter 1.3.1.1 for details) have been synthesized by the Henglein group in the early 1980s.<sup>6,7</sup> The aqueous synthesis of a variety of colloidal nanocrystals has been optimized since these first steps, and many materials are available via direct aqueous synthesis with high quality nowadays. This is of course especially important when nanoparticles with a hydrophilic surface are desired for a specific application, since nanocrystals synthesized in water are either stabilized by short and polar ligands or are stabilized via surface charges. Both cases give rise to a hydrophilic surface. Therefore a lot of effort was put in the development of aqueous synthesis of e.g. high quality quantum dots, and to date especially CdTe quantum dots capped with short thiol ligands can be synthesized in water with very good optical properties as shown by Rogach et al.<sup>8,9</sup>

However, the aqueous colloid chemical synthesis of nanoparticles has the inherent disadvantage that reaction temperatures are limited to maximum 100°C as long as

## 1. Introduction

atmospheric pressure reactions are performed. Higher reaction temperatures are however very much desired when highly crystalline nanoparticles with low amounts of defects or crystal twinning shall be obtained. In a pioneering work by Murray et. al in 1993 the synthesis of extremely “monodisperse” (that is a low degree of polydispersity) cadmium chalcogenide nanocrystals CdE (E = S, Se or Te) in high boiling organic solvents/surfactants was demonstrated for the first time.<sup>10</sup> In this synthesis n-trioctylphosphine and n-trioctylphosphine oxide were used as solvent and coordinating agents at the same time yielding particles with a “monodispersity” not known before. It should be noted that it was found later, that the commercially available n-trioctylphosphine oxide usually contains a small amount of phosphonic acids which have later been shown to be one vital compound for the successful synthesis of CdSe quantum dots (and that the until then used extremely toxic dimethylcadmium is not necessary as Cd precursor but can be replaced e.g. by CdO).<sup>11</sup> All syntheses had in common that organometallic precursors of the respective semiconductor material are injected quickly and at as high as possible temperature (that is close to the boiling point of TOPO, ca. 350°C) into the solvent/surfactant mixture. This so-called “hot injection” approach was subsequently extended to a large variety of accessible materials and also to multi-component nanocrystals.

Also multi-component nanocrystals have been widely studied.<sup>12,13</sup> The easiest examples are simple core/shell nanoparticles which have early been shown to have e.g. significantly enhanced photoluminescence quantum yields when compared to simple single component quantum dots. This is due to the fact that photogenerated charge carriers can effectively be hindered from reaching the particle surface by growing a shell material with an energetically wider band gap onto the quantum dot (see chapter 1.4.1 for details). First examples for the successful synthesis of high quality core/shell quantum dots were e.g. CdSe/CdS and CdSe/ZnS core/shell quantum dots.<sup>14,15</sup> The latter examples are still the gold standard when quantum dots with reproducibly high photoluminescence quantum yields (PLQY) are required. Nevertheless, more recent results suggest that the PLQY can be further increased (and reproducibly approach values >90%) when core/shell/shell structures are employed in which the intermediate material acts as a lattice buffer layer<sup>16</sup> and the different interfaces in these structures are not sharp but controlledly alloyed.<sup>17</sup> The latter findings show that in order to reach high PLQYs not only a good electronic passivation is required, but also too strong lattice strain within a heterostructure must be avoided in order to avoid defects at the interface(s) which could themselves act as trap states for photogenerated charge carriers and hence reduce the PLQY (see chapter 1.3.1.2. for details on quantum dot (QD) photoluminescence properties).

Also shape control beyond simple quasi spherical colloidal nanocrystals was introduced in colloid chemistry via the “hot injection” approach. E.g. CdSe quantum rods have been synthesized by Peng et al. in 2000 using phosphonic acids which bind stronger to the mantle facets than to the terminating facets of the rods with a hexagonal crystal phase.<sup>18</sup> In the very recent past also 2D nanostructures (nanosheets) have been synthesized using “hot injection” approaches as demonstrated e.g. by Weller et al for PbS.<sup>19</sup> Also branched nanostructures have been synthesized using the “hot injection” method e.g. by Manna et al. in 2003.<sup>20,21</sup>

A recently often applied synthesis approach is the so-called seed mediated growth (often also referred to as “seeded growth”) technique in which a well-defined nanocrystal serves as a seed for the growth of a more sophisticated structure.<sup>22,23</sup> This method was applied for the formation of homogeneous nanorods, heterogeneous nanorods as well as for the formation of

e.g. tetrapods and octapods.<sup>20,22-25</sup> The big advantage of the seeded growth approach compared to non-seeded synthesis of e.g. rods or tetrapods is the inherent separation of nucleation and growth in this type of synthesis. In a one-step procedure for the synthesis of e.g. a nanorod, the parameters have to be optimized in a way, that shortly after the first nucleation event the nucleation rate drops to a negligible value, in order to obtain an ensemble with a narrow size distribution. When heterostructures are synthesized by a seed mediated growth approach, mainly the rates of primary to secondary nucleation have to be considered. In this case the reaction conditions should be tuned in such a way that the primary nucleation of the second material is as good suppressed as possible in order to obtain an as uniform as possible ensemble of heteroparticles.

After the development of colloid synthesis for quantum rods, the combination with metal compartments was one of the next steps developed in colloid chemistry of nanoparticles. For example, the selective gold growth on one or both sides of a CdSe quantum rod was achieved<sup>26</sup> as well as other region selective metal growth reactions onto semiconductor nanocrystals.<sup>27-29</sup>

Yet another approach for the production of more elaborate shapes of nanocrystals especially like particles with concave compartments is based on the usage of metal seeds for the growth of a second material with a subsequent removal of the templating metal seed. This so-called “cast mold” approach was studied for e.g. Fe<sub>3</sub>O<sub>4</sub>-Au composites and SiO<sub>2</sub>-Au composites,<sup>30,31</sup> and the resulting particles show various interesting properties like e.g. size selective formation of key-lock assemblies with nanoparticles matching exactly the cavity size.<sup>32</sup>

While the synthesis routes in high boiling organic solvents mentioned above often yield particles with higher crystallinity as well as with better defined and controlled shapes than those particles synthesized in water, these routes naturally yield particles with hydrophobic surfaces which are typically covered by long chained organic ligands. For several applications this is not beneficial (e.g. for basically all biomedical applications hydrophobic particles cannot be used). Therefore, after the development of these synthesis procedures much research effort was put into the development of phase transfer protocols for such type of nanocrystals. Such phase transfer protocols can either invoke the replacement of the original capping ligands of the nanocrystals by more hydrophilic ligands<sup>33</sup> or the enwrapping of the whole particle in e.g. amphiphilic polymers.<sup>34</sup>

Chapter two of this thesis will summarize my own contributions to the field of shape control in colloidal nanocrystal synthesis.

Thus indeed a lot of progress was made in the controlled growth of various types of nanocrystalline materials. However, one drawback until today is that in most cases shape control has to be reached for each material individually. That means usually one has to first find a procedure to synthesize quantum dots of a given material and then develop synthetic conditions which are capable of producing controlled shapes of nanocrystals of the respective material. Recently the very interesting alternative route in form of cation exchange reactions is reported frequently. Even though these have been introduced quite early in colloid chemical synthesis,<sup>35</sup> these types of reactions have been investigated in depth and systematically only in the recent past.<sup>36</sup> Especially the works of Alivisatos and co-workers demonstrate nicely how powerful this synthetic pathway can be.<sup>37</sup> When applying the right conditions, these types of reactions can transform one nanocrystalline material completely into another one without affecting the size or shape distribution of the ensemble of nanocrystals. Ion exchange can also

## 1. Introduction

be a synthetic pathway for post synthetic doping of a given set of nanocrystals, or it can be used to regioselectively exchange the cations in a specific region of a given nanocrystal.

Chapter three of this thesis will summarize my own contributions to the field of composition control in colloidal nanocrystals applying cation exchange reactions.

Localized surface plasmon resonances (which can be simplest envisioned as a resonant density oscillation of free charge carriers, see chapter 1.3.2 for details) are known for a long time in metallic nanoparticles and were widely and exhaustively studied. The spectral position of the resonance depends in principle on the change of the dielectric function from the metal particle to the dielectric function of its surrounding, and hence strongly on the vicinity of the nanoparticle. This effect has been exploited in a large variety of biosensing applications alike DNA sensing, enzymatic activity sensing, protein catabolism sensing and antigen-antibody recognition sensing.<sup>38-40</sup> Even though localized surface plasmon resonances are mostly studied in metallic nanoparticles, it is well known that highly doped semiconductors or oxides can show partially metallic behavior (they become so-called degenerately doped semiconductors, which means that formerly localized dopant states merge into a band-like structure). However, only in the very recent past, some types of heavily doped NCs have been synthesized and shown to exhibit LSPRs. Until now, these materials are mainly strongly self-doped nanoparticles like  $\text{Cu}_{2-x}\text{S}$  and  $\text{Cu}_{2-x}\text{Se}$ <sup>41,42</sup> and some conductive glasses like indium tin oxide (ITO).<sup>43</sup>

My contributions regarding the plasmonic behavior of non-metallic (namely heavily doped semiconducting or oxide) nanoparticles together with different ways to tune the plasmon resonances in these particles is presented in chapter 4 of this thesis.

### 1.3. Properties of Colloidal Nanocrystals

Nanocrystals show a large variety of properties which are not at all or only to a much smaller extent observed in their macroscopic counterparts. Many of these properties such as the enhanced catalytic activity are related to the greatly enhanced surface-to-volume ratio in nanocrystals, which is inversely proportional to the radius of the nanocrystals. However, in the following part of the introduction, I will focus on three properties which are inherently connected to nanocrystals of different material types and which are not observed in bulk materials.

#### 1.3.1. Semiconductor Nanocrystals

Quasi-spherical semiconductor nanocrystals are often also referred to as quantum dots when their diameter is small enough so that a significant size quantization effect (see 1.3.1.1.) occurs. They are characterized mainly by a strongly size dependent electronic structure and often also by a pronounced photoluminescence (1.3.1.2.). Both effects are absent in the bulk material.

##### 1.3.1.1. The Size Quantization Effect

In semiconductor materials with not too small values of the permittivity at high frequencies (formerly often referred to as high frequency dielectric constant), the absorption of a photon with energies higher than the band gap typically results in the formation of a so-called Mott-Wanier exciton (which I will refer to from here on only as exciton, since the so-called Frenkel exciton, which occurs in insulators and high band gap semiconductors with low permittivity plays no role within this thesis). It can be envisioned easiest as a bound state composed of an electron and an electron vacancy (a hole) which can be described similar to a hydrogen atom. Therefore, one can easily assign a radius to this type of quasi particle which is derived from the Bohr radius of the hydrogen atom, with the only difference being the different masses of the electron and the hole in the crystal compared to a free electron and a proton (which form the hydrogen atom) and the different permittivity (which is the permittivity of vacuum in case of the hydrogen atom and the permittivity of the semiconductor material in case of an exciton). The masses of electron and hole (with the latter one having no rest mass anyway) are expressed by the so-called effective masses. Effective masses are derived from a semi-classical model, and are basically the inert masses of the respective free charge carrier within a given crystal when applying an external electric field. They can be derived from the curvature of the dispersion relation of the respective charge carrier near the band gap. Thus, the so-called Bohr exciton radius is given by the following expression (equation 1):

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} \quad r_{\text{Bohr-Exziton}} = \frac{4\pi\epsilon_0\epsilon_r\hbar^2}{e^2} \left( \frac{1}{m_e^*} + \frac{1}{m_h^*} \right) = a_0 \cdot \epsilon_r \cdot m_e \left( \frac{1}{m_e^*} + \frac{1}{m_h^*} \right)$$

Equation 1: Bohr radius of the hydrogen atom  $a_0$  and Bohr radius of an exciton  $r_{\text{Bohr-Exziton}}$ .  $m_e^*$  and  $m_h^*$  are the effective masses of the electron and the hole in the respective material,  $\epsilon_r$  is the relative permittivity of the material.

As I wrote in a recent manuscript for a book chapter on nanoparticles: "It can be intuitively understood, that the electronic properties of the crystal change dramatically, when the radius of the whole crystal reaches the same order of magnitude as the Bohr exciton radius (which is larger for materials with low effective masses of the charge carriers and high relative

## 1. Introduction

permittivity according to equation 1 and is for typical semiconductor materials in the range of 2 to 30 nm).

Combining the solid state physical approximation of the effective masses of the charge carriers with the quantum mechanical model of the particle in the box, the change in energy for each charge carrier can be derived as a function of the particle radius. This most simple way of a quantitative description of the size quantization effect is called the Brus equation (equation 2):<sup>(44)</sup>

$$E_{gap}(r) = E_{gap(bulk)} + \frac{h^2}{8r^2} \cdot \left( \frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - \frac{1,8e^2}{4\pi\epsilon_r\epsilon_0r}$$

Equation (2): Brus equation for calculating the energy band gap  $E_{gap}$  of a quantum dot as a function of its radius ( $r$ ). Necessary material constants are the effective masses of the charge carriers ( $m_e^*$  and  $m_h^*$ ) in the material, the relative permittivity ( $\epsilon_r$ ) of the material and the bulk band gap ( $E_{Gap(bulk)}$ ) of the material.

The Brus equation in this form contains one term derived from the particle in the box model (for both charge carriers) and an additional term which is a correction term for the attractive Coulomb interaction between the two charge carriers.”<sup>4</sup>

As a consequence of this simple model, the band gap of a semiconductor nanoparticle increases with decreasing particles size (see schematic illustration in figure 3).

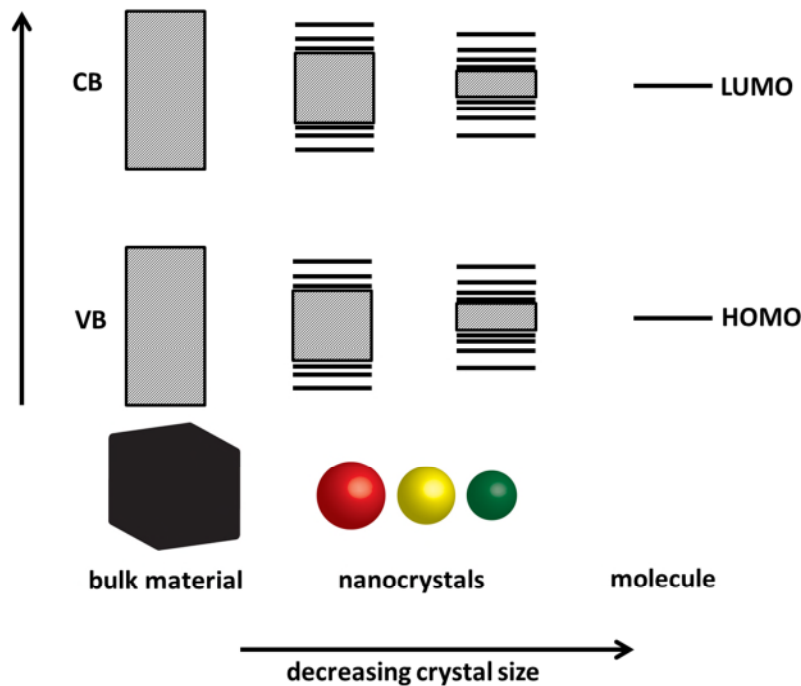


Figure 3: Schematic diagram of the size dependence of the energy levels in a semiconductor material. Note that the changes in conduction band (CB) and valence band (VB) are in most cases not symmetric but depend on the relative effective masses of electron and hole.<sup>4</sup>

However, this effect becomes detectable only in the nanometer size regime. It is also important to note, that the energetic shift of the valence band edge and of the conduction band edge can be very differently pronounced (with the ratio of the two shifts depending on the ratio of the effective mass of electron and hole in the material which can easily vary up to one order of magnitude or more). While the latter effect is not important for e.g. the optical properties of one isolated nanocrystal (here only the energy differences between conduction



band edge and valence band edge matter) it can be important when a nanocrystal is in contact with another material (e.g. another nanocrystal of a different semiconducting or metallic material or also an electrode, see also section 1.4 on nanoheterostructures) or when excited charge carriers are participating in redox reactions.<sup>45</sup>

It should be noted that the Brus equation (equation 2) is derived from the very simplistic model of a particle in the box with infinite potential barriers at the edge and therefore tends to overestimate the effect of size quantization slightly, as in real systems the surrounding of the nanoparticle (which is typically some sort of insulating solvent) represent a high but not infinite potential barrier for the charge carriers. It was shown that calculations with more or less arbitrarily chosen high but not infinite potential barriers for the surrounding (e.g. 8 eV) often yield more accurate predictions of the degree of size quantization than the actual Brus formula. These considerations of none infinite potential barriers become extremely important when trying to understand the behavior of e.g. various types of core/shell quantum dots (see chapter 1.4.1.).<sup>46</sup>

All above considerations were derived for spherical semiconductor nanoparticles or so-called quantum dots. In non-spherical systems the situation is slightly more complicated but shall also be discussed briefly. For 1D semiconductor nanoparticles generally quantum wires can be distinguished from quantum rods: quantum wires are structures with two dimensions being within the quantized regime (that is at least of the same order of magnitude than the Bohr exciton radius) and the third one being orders of magnitude larger than the Bohr exciton radius (typically on the micrometer scale), while quantum rods are structures with still all three dimensions in the quantized regime but nevertheless one of them being significantly different from the other two. Interestingly, in both cases the size of the band gap of the object is determined mainly by the strongest quantized dimensions of the rod or wire. For example, quantum rods of similar diameter have similar band gaps more or less independently of their length. The same approximation holds for 2D so-called quantum wells of similar thickness which have similar band gaps more or less independently of their thickness. Even though 2D quantum wells are not a research focus of this thesis, it should be noted that this type of 2D structures has been a material class which has for a long time only been synthesized using physical deposition techniques (various vapor deposition or molecular beam techniques), and that in the last 5 years a significant amount of publications also report the synthesis of 2D structures via colloid chemical approaches. While for 1D and 2D structures the band gap can be easily derived from the strongest quantized dimension in a first approximation, the density of states and also the number of degenerated states near the band gap can become a complicated function of the particle dimension for all types of anisotropic nanocrystals. A more detailed discussion of the shape related properties can be found in the original publications in chapter 2 of this thesis.

### 1.3.1.2. Fluorescence in Semiconductor Nanocrystals

Additionally to the size quantization effect which makes the band gap a function of particle size, yet another property of semiconductor nanocrystals can be observed which is not observed in bulk semiconductor materials: often semiconductor nanocrystals show a prominent photoluminescence. Simply spoken, the boundaries of the nanoparticle prevent the photogenerated charge carriers (electron and hole) from dissipating after excitation, even if the photoexcitation occurs with energies much higher than the band gap, increasing the

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probability of a radiative recombination by orders of magnitude. If such photoluminescence is observed, the wavelength of the emitted light is naturally similarly dependent on the particle size as the band gap as described above (with a small so-called Stokes shift of the photoluminescence with respect to the lowest energy absorption band due to phononic energy losses), making semiconductor nanocrystals very promising and unique tunable fluorophores.

Nevertheless, not all semiconductor nanoparticles show photoluminescence and those that do so, have a so-called photoluminescence quantum yield (PLQY, that is the ratio of emitted photons to absorbed photons) of less than 100%. Hence, obviously loss mechanisms exist which have to be understood and controlled in order to design efficient fluorophores. It was found early in nanocrystal research that the most prominent loss mechanisms (that is concurrence processes to radiative charge carrier recombination) are defect and/or surface related.<sup>47</sup> Here it is worth to note that sufficiently small nanocrystals are (apart from the surface) often defect free single crystals, since the thermodynamic defect equilibrium concentration per particle is often much smaller than one defect per particle (e.g. if an equilibrium concentration of 0.01 defects per particle is calculated that means that on average in a nanocrystals ensemble 99% of the particles are defect free while one percent contains a defect).

The PLQY can be simply derived from the rate constant of the radiative charge carrier recombination and the rate constants of all non-radiative and radiative recombination pathways by equation 3.

$$PLQY = \frac{k_{rad}}{k_{rad} + \sum_i k_{non-rad,i}}$$

Equation 3: Photoluminescence quantum yield expressed by the rate constant of the radiative charge carrier recombination  $k_{rad}$  and the rate constants of the different possible non-radiative recombination rates  $k_{non-rad,i}$ .

Defect or surface states are often energetically located within the band gap and can therefore function as efficient electron or hole “traps”.<sup>47</sup> Each of these trap states can open up a non-radiative recombination pathway for the excited charge carriers and therefore decrease the PLQY. Since such trapping processes typically have rate constants which are orders of magnitude larger than typical radiative recombination rates, one single trap state can already result in a PLQY of a specific quantum dot close to zero.

Compared to molecular dyes, there is one important difference when looking at ensembles of quantum dots. While in an ensemble of molecular dyes, each molecule is a perfect copy of one another, this is not the case in a nanoparticle ensemble since each particle has an individual composition (size, surface saturation etc.). Therefore also each particle has its own specific PLQY and the one measured for the ensemble is just an average value. The research as it stands today suggests that e.g. a quantum dot ensemble with PLQY = 50% is more likely to consist of about 50% quantum dots with a PLQY close to 100% and 50% quantum dots with a PLQY close to 0%, rather than only consisting of quantum dots with 50% PLQY (as it would be in case of a molecular dye). Summarizing the last paragraph, the optical properties of

individual nanoparticles can differ significantly from one another as well as from the ensemble properties.

Logically, in order to enhance the PLQY, quantum dots have to be single crystals and charge carriers have to be kept away from the particle surface. The latter can e.g. be accomplished by growing a shell of a higher band gap material around the particles (see chapter 1.4.).

### 1.3.2. Conductive Nanocrystals – Localized Surface Plasmon Resonances

While the dominant size dependent effect for semiconductor nanoparticles is the size quantization effect, metal nanoparticles show another property which cannot be observed in bulk materials, the so-called localized surface plasmon resonance. Although the absorption spectra of an ensemble of e.g. CdSe (semiconductor) quantum dots and e.g. Au nanoparticles can look quite similar on a first glance (see figure 4 for exemplary spectra), the underlying physical phenomena are indeed extremely different. Very simply spoken, the absorption band in a quantum dot sample is caused by photon absorption of single electrons which are promoted from the valence band to the conduction band (from a stronger bound state to a more delocalized state) while in the case of localized surface plasmon resonances, all free movable charge carriers within one particle are excited simultaneously (see figure 5).

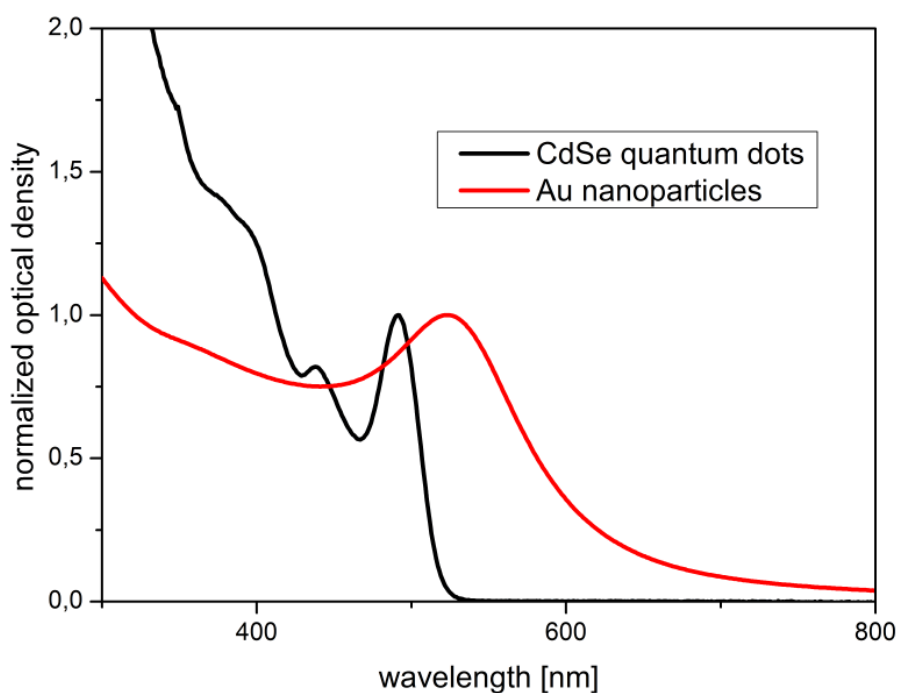


Figure 4: Absorption spectra of a sample of quantum dots and of a sample of metallic (Au) nanoparticles.

A plasmon is a quasi-particle which is basically a quantum of free charge carrier density oscillation within a conductive material (the word plasmon originates from plasma oscillation). In principle three different types of plasmons can be distinguished: volume plasmons, (propagating) surface plasmon polaritons and localized surface plasmon polaritons (sometimes also referred to as “particle plasmon” to distinguish more clearly from the propagating surface plasmon polariton). Naturally, since optical photons cannot penetrate into metals far beyond the surface, volume plasmons cannot be excited by absorption of photons. (Propagating) surface plasmon polaritons can normally also not be excited by direct photon absorption due to the fact that the dispersion relation of the more or less free conduction band electrons and

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the dispersion relation of a photon do not intercept. In contrary, the so-called localized surface plasmon resonances (LSPRs) occurring in conductive nanoparticles typically have very high oscillator strengths and can easily be excited by direct photon absorption. Within this thesis all plasmon resonances discussed fall under this category. The LSPR is a phenomenon which only occurs in nanostructured materials, since the localization of the surface plasmon is only possible by restricting the material dimensions and therefore in bulk materials only propagating surface plasmon resonances can be observed.

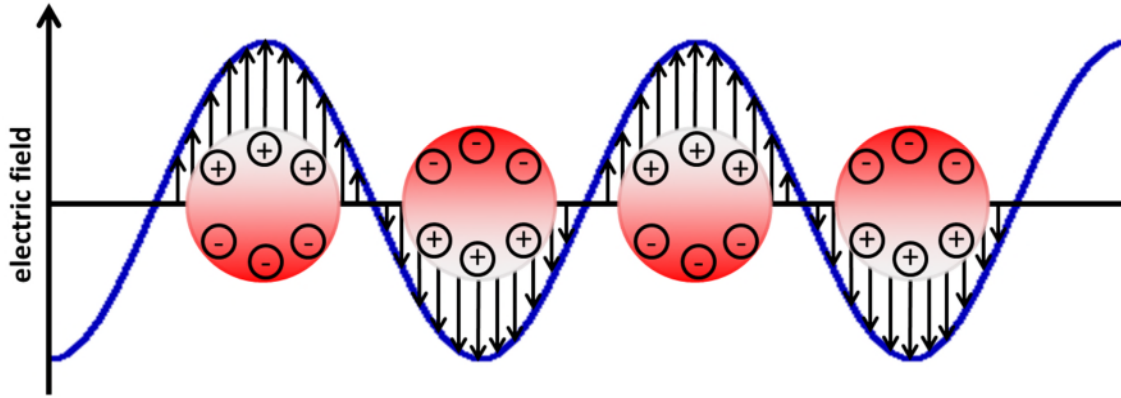


Figure 5: Scheme of the excitation of a localized surface plasmon resonance (LSPR) by an electromagnetic wave (only electric field oscillation shown here). The LSPR is a resonant charge carrier density oscillation of the free charge carriers within the conductive particle.

It is however important to note that in a first approximation the resonance condition for a LSPR can be calculated using classical physics only (while in the case of the size quantization effect even the simplest possible description is based on quantum mechanics).

$$\omega_{LSPR} = \sqrt{\frac{\omega_p^2}{1 + 2\epsilon_m} - \gamma^2} \quad \text{with} \quad \omega_p = \sqrt{\frac{ne^2}{\epsilon_0 m_{eff}}}$$

Equation 4: resonance frequency of a localized surface plasmon resonance  $\omega_{LSPR}$  according to the Drude model and the quasi static approximation.  $\omega_p$  is the plasma frequency,  $\epsilon_m$  the relative permittivity of the surrounding medium, and  $\gamma$  a damping factor.  $n$  is the charge carrier density,  $e$  the elemental charge,  $m_{eff}$  the effective mass of the oscillating charge carriers and  $\epsilon_0$  the permittivity of the vacuum.

Equation 4 gives the resonance frequency of a localized surface plasmon resonance of a conductive sphere according to the Drude model within the framework of the so-called quasi static approximation. The latter is that the sphere is much smaller than the wavelength of the resonantly interacting electromagnetic wave and hence the electric field can be regarded as constant over the whole particle at fixed time (note that for the sake of clarity the sphere shown in figure 5 is enlarged so that the electrostatic approximation would not be applicable). Although the Drude model implements several quite drastic simplifications (e.g. electron-electron interactions are ignored), these equations often provide good agreement with the measured resonance frequencies. Notably, according to equation 4 the resonance condition is size independent. Indeed also experiments show that the LSPR of metallic nanoparticles is almost size independent over a large size range (roughly the regime of 5 nm to 30 nm for particles with LSPR in the visible part of the spectrum). However, of course the LSPR becomes size dependent when the particles become so large that the quasi static approximation cannot

be applied anymore. At this stage also higher order LSPRs like quadrupole resonances become important while they are negligible for particle sizes which are much smaller than the wavelength of the resonant photons. The LSPR also becomes size dependent for very small particles ( $< 5$  nm), since in this case the dielectric function of the nanocrystalline material starts to differ from the one of the bulk material.

As just discussed, for sufficiently small nanoparticles, LSPR are only slightly dependent on the particle size. However, also for very small nanoparticles, a very strong dependency of the LSPR frequency on the particle shape can be observed. Basically every divergence from a perfect sphere causes an alteration of the LSPR frequency and often also results in a splitting of the LSPR into two different LSPRs with different resonance frequencies. This effect can be envisioned best for cylindrical shaped nanorods. In such systems typically two distinct LSPRs can be observed for sufficiently high aspect ratios of the rods, one LSPR belonging to the so-called transversal and one to the so-called longitudinal LSPR mode of the rod (see figure 6).

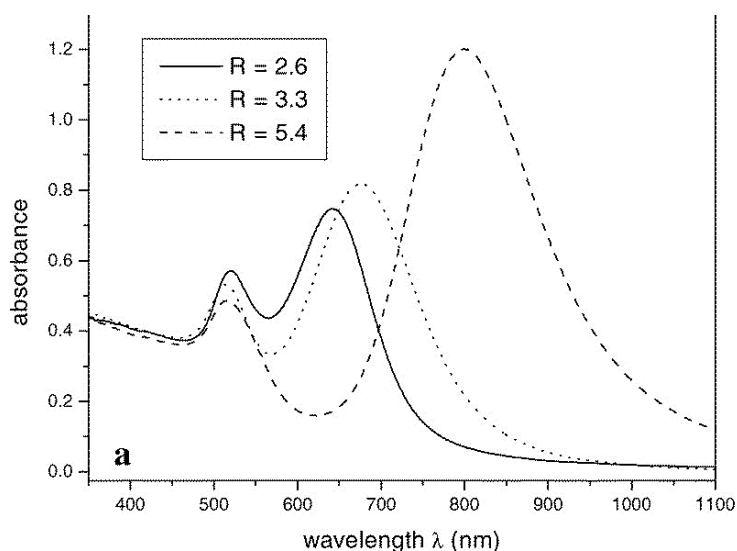


Figure 6: Transversal (around 525 nm in all cases) and longitudinal LSPR (dependent on aspect ratio) band of gold nanorods with different aspect ratios (R). Reprinted from [48].

It should be mentioned that in the case of nanorods the positions of the two LSPRs in a first approximation do not depend on the absolute dimensions of the rod, as long as all dimensions are sufficiently small compared to the wavelength of the resonant photon (similar to spherical particles) but it is rather the aspect ratio of the nanorods which mainly determines the position of the two LSPRs. Figure 6 shows absorption spectra consisting of the one transversal LSPR absorption band at higher energies (lower wavelength) and one longitudinal LSPR absorption band at lower energies (higher wavelength) for gold nanorods with three different aspect ratios.

Since LSPRs require a significant amount of free charge carriers per particle, they are best known for metal nanoparticles and here specifically for noble metal nanoparticles (also less noble metal particles can of course show LSPRs but are often very difficult to handle due to their extremely high chemical reactivity e.g. towards oxygen). However, metals are not the only material class with a high amount of free charge carriers. Also so-called degenerately doped materials can have sufficiently high charge carrier densities to exhibit LSPRs. When

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compared with metals, (degenerately) doped semiconductors have an intrinsic downside with respect to their applicability as plasmonic materials, which is the comparably low charge carrier density (which results in a less strong oscillator strength of the plasmon resonance). However, this type of material has also the major advantage of a tunability of exactly this charge carrier density, which is a material constant in the case of metals. Thus, while doped semiconducting materials will surely not be a replacement for the traditional metallic plasmonic materials, they might very well be complementary components in all types of applications where a simple and wide spectral tunability of a plasmon resonance is more important than its actual oscillator strength (e.g. in many sensing applications). Additionally, the relatively low charge carrier density in doped semiconductors (compared to metals) is naturally more sensitive towards external influences which might increase the sensitivity of such a system for sensoric applications. Furthermore, non-metallic plasmonic materials grant easier access to spectral regions which are not easily covered by metallic nanoparticles (NIR and mid-IR spectral regions due to the lower charge carrier density, see equation 4). Figure 7 summarizes the expected LSPR position as a function of carrier density and particle diameter (and therefore charges carriers per particle).

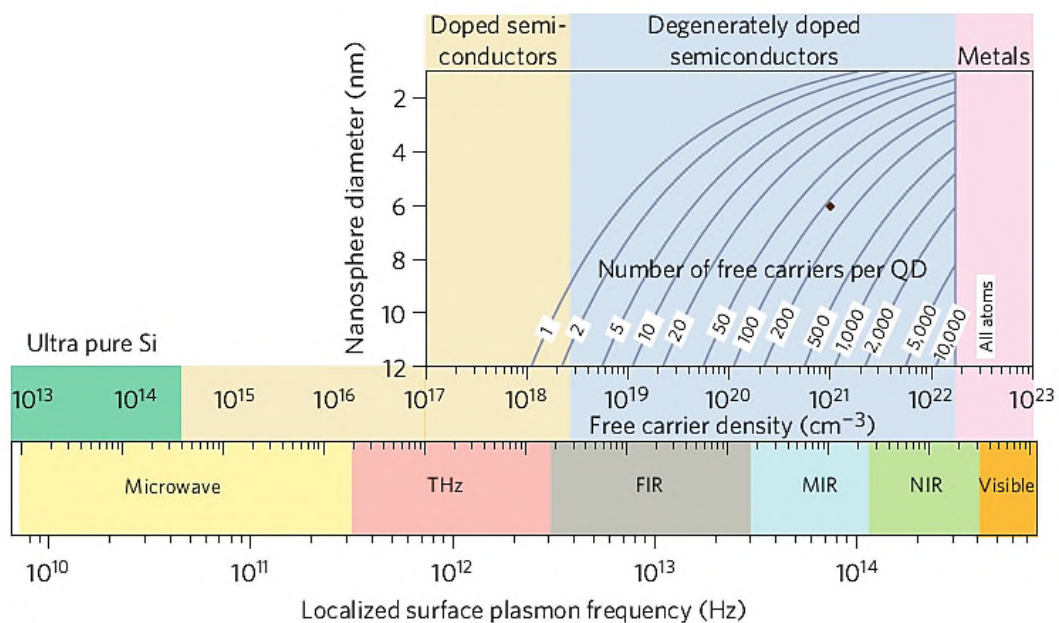


Figure 7: Expected spectral position of the LSPR (bottom) correlated to charge carrier density (middle) and correlated to particle diameter and charge carriers per particle (top).<sup>49</sup> Reprinted by permission from Macmillan Publishers Ltd: Nature Materials (2011), 10, 361. Copyright (2011).

Thus, in principle nanoparticles from strongly doped materials are interesting alternatives for classical plasmonic nanoparticles, especially since the degree of doping can in several cases be easily tuned. This opens up access to LSPRs which are very easily tunable in their spectral position. In chapter 4 of this thesis this effect will be discussed in depth.

## 1.4. Properties of Nanoheterostructures

While the preceding subchapter summarized the main properties of single component nanocrystals, this subchapter will focus on the properties of multicomponent nanoparticles and is subdivided in one subchapter on semiconductor/semiconductor heterostructures and one on metal/semiconductor heterostructures.

### 1.4.1. Semiconductor/Semiconductor Heterostructures

When two semiconductor materials are brought in contact with each other, the two most important factors to consider are the sizes of the band gaps of the two materials as well as the relative positions of the Fermi levels of the two components to one another. Figure 8 shows in a very simple manner the two cases which have to be considered.

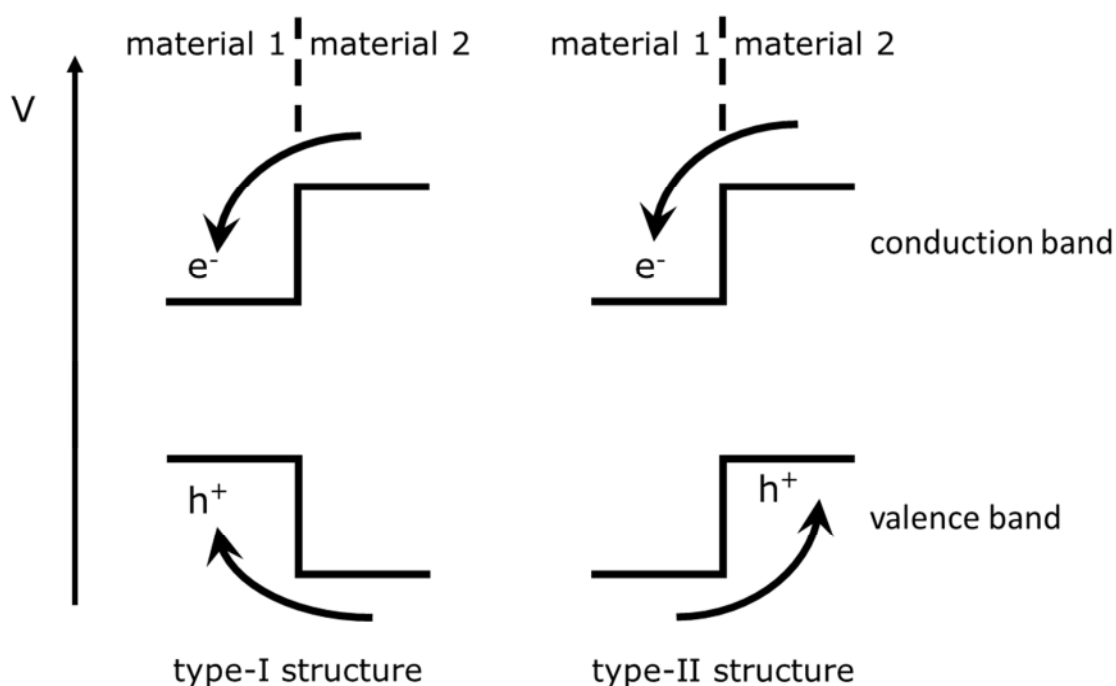


Figure 8: schematic description of type-I and type-II band gap alignment for two semiconductor materials.

The band gaps can either be aligned in a way that a larger band gap envelops a smaller one (type-I situation, figure 8 left) resulting in excited (free) charge carriers being located in one part of the heterostructure, or in a staggered way (type-II situation, figure 8 right) resulting in both charge carriers being spatially separated from each other. It is important to note that figure 8 depicts the situation in a bulk-like semiconductor. As mentioned before, the absolute positions of valence and conduction band edge can shift significantly as a function of the particle size (and as mentioned in 1.3.1, this shift is normally not symmetric). In a heterostructure the band edges of both materials can change in position as a function of the size of the respective compartment but also as a function of the overall size of the heterostructure (especially when the whole structure is in a size regime with strong quantum confinement).<sup>50</sup> The lowest possible energy states of free electrons in the conduction band and of free holes in the valence band can still be calculated using the particle in the box model as mentioned in chapter 1.3. However, several potential steps have to be considered within the box. Nevertheless also here the extension of the simple particle in the box model for

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core/shell particles can predict the expected lowest energy value often quite precisely.<sup>46,51</sup> For the degree of electron and hole localization respectively delocalization, not only the band alignment is important, but also the effective masses of the charge carriers in both materials.

As mentioned in chapter 1.3.1.2 quantum dots often show prominent band gap fluorescence, and surface trapping of charge carriers is one of the major mechanisms decreasing the PLQY of a QD. Therefore, type-I heterostructures with an outer material with a larger band gap are often materials with way higher PLQYs than QDs made from just one material, since the photoexcited charge carriers can be effectively hindered from reaching the particle surface and hence cannot be trapped at surface states. Hence, type-I core/shell particles are until today the QD “gold standard” when high PLQYs are required.

Type-II semiconductor heterostructures on the other hand lead to an intrinsic spatial separation of photoexcited charge carriers which e.g. results in a prolonged radiative charge carrier recombination lifetime. Such types of heterostructures are typically not first choice as normal fluorophores but have different application fields such for active materials in QD based lasers (see chapter 1.5 for details).

### 1.4.2. Semiconductor/Metal Heterostructures

In bulk materials, a metal semiconductor contact is typically described as a so-called Schottky barrier. In this case, the behavior is again dominated by the relative position of the Fermi level of the metal and the semiconductor, typically resulting in a depletion zone within the semiconductor close to the interface to the metal. However, the simple bulk model of a Schottky barrier is based on the assumption that the metal is an infinite electron reservoir in comparison to the depletion zone (simpler spoken, the metal volume is much larger than the volume of the depletion zone). This approximation obviously must fail when the dimensions of the whole nanoheterostructures are on the nanometer scale, since in bulk interfaces typical depletion zones have thicknesses of several tens of nanometers.<sup>52</sup>

In a metal/semiconductor hybrid nanoparticle in which both parts are in direct contact, typically the photoexcited electron is quickly (picosecond timescale) transferred to the metallic part. Since this charge carrier transfer is orders of magnitude faster than the radiative recombination of electron and hole in the semiconductor part, this typically leads to efficient fluorescence quenching in cases where the original semiconductor particle was fluorescent. As a consequence such structures are typically not useful as fluorophore but instead are more efficient in e.g. photocatalysis applications since radiative charge carrier recombination is effectively suppressed, and the separated charge carriers can be used for redox reactions.<sup>52</sup>



## 1.5. Application Perspectives for Colloidal Nanoparticles

Colloidal nanoparticles have a wide range of possible applications of which some of the most important are exemplarily highlighted in the following:

- **Cosmetic products:** Colloidal nanoparticles have very high molar extinction coefficients as well as high UV scattering cross sections, making e.g. TiO<sub>2</sub> nanoparticles efficient ingredients for sun blocking skin products.<sup>53</sup>
- **Surface treatment:** The controlled adsorption/deposition of colloidal nanocrystals on e.g. glass surfaces can be used to control the hydrophobicity/hydrophilicity of the surface and results in e.g. self-cleaning or easier to clean surfaces (e.g. superhydrophobic surfaces).<sup>54</sup>
- **Color conversion:** Color conversion is possibly the only application of QDs which reached the brought consumer market with a final product, namely in form of flat screen color television with currently highest color brilliance. This is possible since QDs have narrower emission spectra than conventional organic dyes and can furthermore be excited over the whole range of the UV and blue spectral region, whereas organic dyes typically have narrow excitation windows. Furthermore the QD emission lines can be extremely fine-tuned by simply adapting the QD size to match the absorption maxima of the three different color sensitive dyes in the human eye. This way very strong “felt brightness” can be generated with a relatively low amount of light, making this type of display also very energy efficient.<sup>55,56</sup> This might also be an application for some of the nanoparticles synthesized within chapter 2 of this thesis (e.g. CdSe seeded CdS nanorods).
- **LEDs:** While in the above described color conversion application the quantum dots are still optically excited and only convert the absorbed light into light with the desired wavelength, quantum dots can also serve as active layer in a light emitting diode. Therefore charge carriers have to be injected in the quantum dots.<sup>56,57</sup> Until today quantum dot driven LEDs cannot compete with the often employed organic LEDs (OLEDs). Nevertheless it can be seen from figure 9 that especially such QD based LEDs which combine organic as well as inorganic charge transporting layers (type IV in figure 9) have experienced a tremendous development in external quantum efficiency (EQE) as well as in brightness, and the gap to the OLEDs is closing. In some more specific applications like e.g. NIR emitting diodes, state of the art QD LEDs already outperform OLEDs.

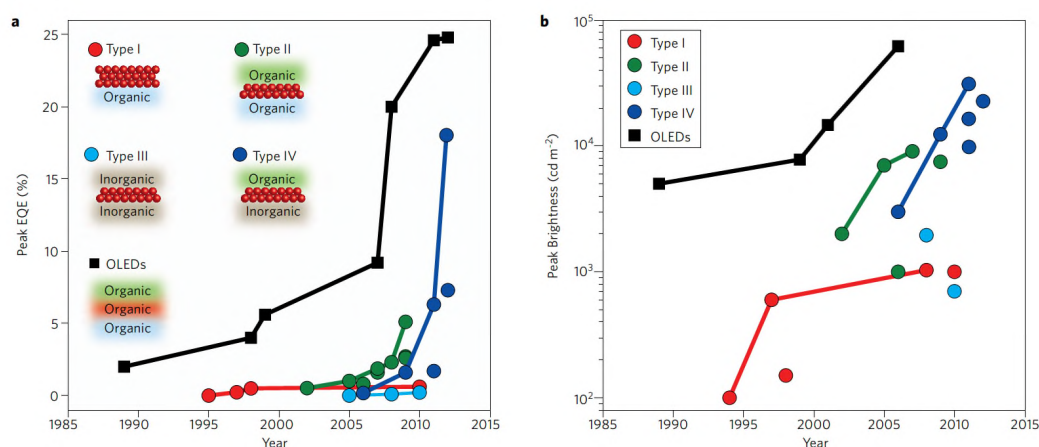


Figure 9: (left) peak external quantum efficiencies (EQE) and (right) peak brightness of QD based LEDs with different principle set-ups (different LED set-ups as depicted in the left panel), development over the last 20 years (OLEDs are shown for comparison as black line). Reprinted from ref. [56] with permission from Nature Publishing Group.

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Some of the particles investigated in chapter 2 of this thesis have already been investigated towards their suitability as active layer in LEDs, however this research is still ongoing.<sup>58</sup>

- Solar cells: Semiconductor materials are an integral component of solar cells. Accordingly intensive studies focus on using quantum dots in solar cells. The QDs can be incorporated in a variety of different solar cell concepts e.g. in Grätzel type cells (replacing the dye in a dye sensitized solar cell) but also in other solar cell types.<sup>59</sup>
- Laser materials: Size quantized semiconductor nanoparticles are under intense investigation as active materials in lasers. The basically arbitrary free tunable emission wavelength would give a significant advantage compared to many conventional laser dyes. However, also several significant challenges have to be overcome. One fundamental problem is that in normal quantum dot ensembles, on average more than one exciton per particle is required to built-up a population inversion which is fundamentally required for any type of stimulated emission (which in turn is the fundamental requirement for lasing). However, more than one exciton per particle open up the way for fast (picosecond timescale) recombination processes.<sup>60,61</sup> Several of the nanorods and nanoplatelets (especially CdSe seeded CdS but also ZnSe seeded CdS) shown in chapter 2 of this thesis are under current investigation for a variety of lasing applications.
- Biomedical applications: A variety of biomedical applications of colloidal nanoparticles are investigated. Superparamagnetic iron oxide nanoparticles are e.g. already in use as MRI contrast agents<sup>62-64</sup> and similar particles are also in focus of research for hyperthermia treatment of e.g. cancer, as they can be selectively and strongly heated when applying an alternating magnetic field.<sup>64</sup> For the latter application, also plasmonic particles are of high interest, in that case for photothermal therapies in which particles are heated using laser irradiation.<sup>65</sup> For the latter applications especially near infrared plasmonic particles (see chapter 4 of this thesis) are attracting considerable attention since NIR radiation can penetrate deeper in human tissues.<sup>66</sup> Other applications of e.g. fluorescent quantum dots include the so-called “bio-labeling” in which a single quantum dot is connected to some biomedical target which shall be traced via e.g. confocal fluorescent microscopy. Here, QDs have one strong advantage in comparison to organic dyes since they have a much lower tendency to photobleach even under strong laser irradiation.<sup>67</sup> On the other hand, simple QDs can show strong fluorescence intermittency (so-called QD “blinking”) which can be problematic in such applications but which can be partially overcome by special design of the QD (e.g. core/(giant)shell particles).<sup>68</sup>
- Sensors: Colloidal nanoparticles and especially colloidal plasmonic nanoparticles can be used in sensors due to the sensitivity of the LSPR to the permittivity of the close vicinity of the particle and also due to the sensitivity of the LSPR to surface bound ligands. Furthermore the LSPR of plasmonic particles is highly sensitive to the distance between two or more individual plasmonic particles.<sup>69</sup> All these effects can be used in sensory applications.<sup>70</sup> NIR plasmonic particles as shown in chapter 4 are also here an interesting alternative for traditional noble metal nanoparticles.
- Photocatalysis: The high molar absorption coefficients together with the fast charge carrier separation especially in metal/semiconductor hybrid materials (see also chapter 2 of this thesis) can make these interesting and effective photocatalysts.<sup>52,71</sup>

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## 2. Shape Control – Nanoheterostructure Synthesis

### 2.1. Outline

Especially when looking at the synthesis of multicomponent anisotropic nanoparticles, the so-called seed mediated growth approach (shortly often referred to as “seeded growth”) is a very powerful one yielding samples with extraordinary control over size and shape of the whole particle as well as of all constituting compartments of the particle, as already established within the introduction. For CdSe/CdS dot in rod nanorods the publication in chapter 2.2 demonstrates that indeed all size dimensions of such a CdSe seeded CdS nanorod (namely CdSe core size as well as CdS rod length and width) can be determined solely via optical spectroscopy without the need for additional characterization (e.g. electron microscopy) which greatly facilitates the applicability of such materials.

The seed mediated growth approach was extended to ZnSe/CdS nanorods in a further work included in this thesis. The ZnSe/CdS systems differs significantly from the preceding CdSe/CdS systems, since ZnSe/CdS has a so-called type-II band gap alignment (a p/n junction) between the two materials which changes the material properties upon photoexcitation dramatically. Namely, the charge carriers in such systems are spatially separated from each other, resulting in a prolonged lifetime of the excited state by at least one order of magnitude (from 13 to 105 ns). Even more surprisingly this enhanced lifetime does not necessarily go along with a decrease in fluorescence quantum yield as shown in the publication in chapter 2.3. While optical spectroscopy as a characterization tool allows easily and accurately the determination of differences between two energy levels, it does not (or only indirectly) allow to measure the absolute positions of these energy levels. Therefore, the work included in this thesis in chapter 2.4 describes an in depth comparative characterization of ZnSe/CdS and CdSe/CdS nanorods using scanning tunneling microscopy and scanning tunneling spectroscopy, which was the first work directly revealing the absolute band alignments in these two different colloidal nanoheterostructures. These results are furthermore in good agreement with the site selective metal deposition of Au nanoparticles on top of CdSe/CdS nanorods, which was found to occur regio-selectively at the location of the CdSe seed. This behavior is very different from pure CdSe rods, on which Au was shown to grow preferentially at the tips of the rods (shown in chapter 2.5). Another possibility to strongly alter the charge carrier localization in a nanocrystal can be to connect it to other nanocrystals. The influence of such an assembling of nanocrystals into so-called aerogels on the lifetime of the excited charge carriers was studied in the publication in chapter 2.6 of this thesis, giving strong evidence that in an aerogel-type assembly of CdSe core / CdS shell nanorods the photoexcited electrons are delocalized within the CdS network while the photogenerated holes remain confined in the CdSe cores of the structure.

Another recent work included in this thesis in chapter 2.7 emphasizes the role of also simple coordinating agents like e.g. chloride ions on the ratio of primary to secondary nucleation in a seed mediated growth approach, showing in detail that the shape and composition of Au/CdS hybrid nanoparticles can be tuned over a large range by simply changing the amount of Cl<sup>-</sup> ions during the reaction. This influence was revealed to occur also in other hybrid systems containing an Au domain. Beneath the typical applications in e.g. photocatalysis, metal/semiconductor

and metal/oxide heteroparticles can also serve as starting materials for the synthesis of hollow and concave nanoparticles via a so-called “cast mold” approach. In this reaction scheme, a material is grown onto another material and then the original seed material is selectively and quantitatively etched away giving rise to partially concave particles as shown in the publication in chapter 2.8 of this thesis. This type of concave iron oxide nanoparticles is also promising for sensory applications since the particles show selective reactions with gold nanoparticles which exactly match the void of the particles.

Even more sophisticated shaped heteronanoparticles are discussed in chapter 2.9, demonstrating that also eight armed branched nanocrystals (so-called “octapods”) can be synthesized applying a seed mediated growth approach, if seeds with eight well developed 111 facets and a face centered cubic symmetry are employed. These structures were further investigated in depth using electron tomography in the publication in chapter 2.10.

The nanoparticles described so far in this chapter are typically covered with hydrophobic ligands as synthesized. For several applications however, hydrophilic nanoparticles are needed. This can be achieved via ligand exchange of the original hydrophobic ligands against shorter hydrophilic ligands. In the publication in chapter 2.11 of this thesis the influence of the geometry of a given nanoscopic system on the optical properties after the transfer to aqueous solution was studied, revealing that indeed differently shaped nanocrystals behave very differently when transferred from unpolar to polar environment even though the inorganic materials and the organic ligands employed are the same.

**2.2. Determination of All Dimensions of CdSe Seeded CdS Nanorods Solely via Their UV/Vis Spectra**

Patrick Adel, Julian Bloh, Dominik Hinrichs, Torben Kodanek and [Dirk Dorfs](#)

Zeitschrift für Physikalische Chemie (2016), published online.

Article DOI: [10.1515/zpch-2016-0887](https://doi.org/10.1515/zpch-2016-0887)

Supplementary material is available online from the publisher.



**2.3. ZnSe Quantum Dots Within CdS Nanorods: A Seeded-Growth Type-II System**

Dirk Dorfs, Asaf Salant, Inna Popov and Uri Banin

Small (2008), 4, 1319.

Article DOI: 10.1002/smll.200800084

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**2.4. Determination of Band Offsets in Heterostructured Colloidal Nanorods Using Scanning Tunneling Spectroscopy**

Dov Steiner, [Dirk Dorfs](#), Uri Banin, Fabio Della Sala, Liberato Manna and Oded Millo

Nano Letters (2008), 8, 2954.

Article DOI: [10.1021/nl801848x](https://doi.org/10.1021/nl801848x)

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**2.5. Selective Gold Growth on CdSe Seeded CdS Nanorods**

Gabi Menagen, David Mocatta, Asaf Salant, Inna Popov, Dirk Dorfs and Uri Banin

Chemistry of Materials (2008), 20, 6900.

Article DOI: 10.1021/cm801702x

Supplementary material is available online from the publisher.

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**2.6. Aerogels from CdSe/CdS Nanorods with Ultra-Long Exciton Lifetimes and High Fluorescence Quantum Yields**

Sara Sanchez-Paradinas, [Dirk Dorfs](#), Sebastian Friebe, Axel Freytag, Andreas Wolf, Nadja C. Bigall,

Advanced Materials (2015), 27, 6152.

Article DOI: [10.1002/adma.201502078](https://doi.org/10.1002/adma.201502078)

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## **2.7. Chloride Ion Mediated Synthesis of Metal/Semiconductor Hybrid Nanocrystals**

Dominik Hinrichs, Michael Galchenko, Torben Kodanek, Suraj Naskar, Nadja-C. Bigall and Dirk Dorfs

Small (2016), 12, 2588.

Article DOI: 10.1002/smll.201600430

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**2.8. A Cast-Mold Approach to Iron Oxide and Pt/Iron Oxide Nanocontainers and Nanoparticles with a Reactive Concave Surface**

Chandramohan George, [Dirk Dorfs](#), Giovanni Bertoni, Andrea Falqui, Alessandro Genovese, Teresa Pellegrino, Anna Roig, Alessandra Quarta, Roberto Comparelli, M. Lucia Curri, Roberto Cingolani, Liberato Manna

Journal of the American Chemical Society (2011), 133, 2205.

Article DOI: [10.1021/ja108781w](https://doi.org/10.1021/ja108781w)

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**2.9. Octapod-Shaped Colloidal Nanocrystals of Cadmium Chalcogenides via "One-Pot" Cation Exchange and Seeded Growth**

Sasanka Deka, Karol Miszta, [Dirk Dorfs](#), Alessandro Genovese, Giovanni Bertoni, Liberato Manna

Nano Letters (2010), 10, 3770.

Article DOI: [10.1021/nl102539a](https://doi.org/10.1021/nl102539a)

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**2.10. Birth and Growth of Octapod-Shaped Colloidal Nanocrystals Studied by Electron Tomography**

Rosaria Brescia, Karol Miszta, [Dirk Dorfs](#), Liberato Manna, Giovanni Bertoni

Journal of Physical Chemistry C (2011), 115, 20128.

Article DOI: [10.1021/jp206253w](https://doi.org/10.1021/jp206253w)

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### **2.11. Phase Transfer of 1- and 2-Dimensional Cd-Based Nanocrystals**

Torben Kodanek, Hadeel M. Banbela, Suraj Naskar, Patrick Adel, Nadja C. Bigall and Dirk Dorfs

Nanoscale (2015), 7, 19300.

Article DOI: [10.1039/c5nr06221g](https://doi.org/10.1039/c5nr06221g)

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### 3. Post Synthesis Composition Control - Cation Exchange Reactions in Nanocrystals

#### 3.1. Outline

It took the colloid chemists community more than three decades to achieve the sophisticated shape control which has partially been described above. However, the development of new colloidal synthesis procedures remains a highly empirical task. Especially the transfer of a specific synthesis procedure for a specific particle shape from a given material A to another material B is often not possible due to e.g. differences in coordination chemistry etc. The development of a new synthetic procedure for similarly shaped nanoparticles of material B however may take a very long time or may fail completely when appropriate ligand mixtures cannot be found. Therefore, all sorts of chemical reactions which can transform a given nanocrystal into another material while conserving the shape of the original crystals are extremely interesting, since they allow to access completely new types of NCs which cannot be achieved by direct colloidal synthesis. Ion exchange reactions are one important type of such reactions which are investigated in depth in the publications described and attached in the following.

When looking at a specific ion exchange reaction in a colloidal suspension of nanocrystals, several parameters have to be considered in order to decide whether a specific ion exchange reaction in principle can take place and how long it would take to be completed. First we will have a look at the equilibrium position of a given reaction (thermodynamic considerations). The most apparent parameter is of course the lattice energy of the starting material compared to this of the product material, the higher the lattice energy of the product material in comparison to the lattice energy of the starting material, the more favorable a specific cation exchange reaction becomes. In a colloidal suspension also the hydration/solvation/complexation energies of the two cations in the respective solvent have to be considered. However, especially in the case of a reaction in an unpolar solvent (like e.g. octadecene) the ions always have to be stabilized in solution by some sort of complexing ligand. Of course the complexation energy for both cations can significantly differ, and a sufficiently high complexation energy for the exchanged cation in comparison to the exchanging cation in a given reaction mixture can help significantly to facilitate a cation exchange reaction. Additionally to the change in energy of the system, also the change of the entropy of the system has to be considered. As a very rough approximation the changes in entropy can be neglected for ion exchange reactions in which one ion  $A^+$  or  $A^{2+}$  is exchanged by another cation of the same charge  $B^+$  or  $B^{2+}$ . In ion exchange reactions where one ion  $A^{2+}$  is exchanged by two ions  $B^+$ , the entropy change of the system is typically strongly negative, and in the vice versa case, the entropy change is strongly positive. According to the Gibbs Helmholtz equation, the entropy changes of course become much more important at higher reaction temperatures. Apart from thermodynamic considerations also kinetics has to be considered in order to judge whether a thermodynamically allowed ion exchange reaction also occurs on an acceptable time scale. Here, the ion diffusivities of both cations in both lattices play a major role. Naturally, kinetic considerations are more important in larger (nano)crystals as the diffusion length to achieve a full ion exchange increases.

The first work included here in chapter 3.2 shows that cation exchange reaction can also be applied to nanocrystals with a mixed anionic framework with complete retention of the anionic lattice and composition.

Obviously, cation exchange reactions become very interesting when being applied to complicated shaped nanoparticles, as they can allow transforming these particles into other materials while retaining the shape. The work dealing with the synthesis of octapods (see chapter 2.9) was one first example within this thesis where an ion exchange reaction (which in this case happened in situ together with a seeded growth reaction) played a key role in order to synthesize a specific and complex nanocrystal shape. In the publication in chapter 3.3 this approach was extended and the  $\text{Cu}^+$  to  $\text{Cd}^{2+}$  ion exchange was shown to be reversible. Interestingly, the  $\text{Cd}^{2+}$  to  $\text{Cu}^+$  ion exchange occurs with a high regio selectivity starting from the tips of the nanocrystals. This gives rise to sophisticated ternary nanocrystalline compounds consisting of a CdSe core and arms made of CdS close to the core and  $\text{Cu}_{2-x}\text{S}$  at the tips. The phase boundary between CdS and  $\text{Cu}_{2-x}\text{S}$  can be fine-tuned by adapting the amount of  $\text{Cu}^+$  ions invoked during the ion exchange reaction. Here, the interface is always sharp even on the nanometer scale with almost no alloying of the two phases showing that ion exchange reactions can open up pathways to high quality and epitactic nanoscaled interfaces.

Also superstructures of nanocrystals can be subjected to complete ion exchange as shown in the publication in chapter 3.4 as part of this thesis. Here it was shown that self-assembled structures of octapod shaped nanocrystals with a size of several micrometers can still undergo complete cation exchange from  $\text{Cd}^{2+}$  to  $\text{Cu}^+$  under retention of the shape of the individual octapods as well as of the superstructures. It should be pointed out that this finding can be of utmost general importance for all types of nanoparticle assemblies and/or deposition techniques as together with the publication in chapter 3.3 it implies that in the sequence 1. synthesis 2. ion exchange 3. deposition/assembly the steps 2 and 3 can be simply exchanged, which might be of use when the materials show different deposition/assembly behavior before and after cation exchange.

Furthermore, ion exchange reactions can also be extended to such types of exchange reactions which might not be possible in one step due to thermodynamic considerations by applying a sequence of two different ion exchange reactions at different temperatures or in a different ligand environment. In cases where a direct cation exchange is not possible, an intermediate step might still allow the complete ion exchange to the desired material. For example, the ion exchange of CdS to ZnS, which cannot be achieved in one single step, is possible by first exchanging  $\text{Cd}^{2+}$  with  $\text{Cu}^+$  (transforming CdS in  $\text{Cu}_2\text{Se}$ ) at room temperature (driven by the higher  $\text{Cu}_2\text{Se}$  lattice energy), and subsequently exchanging the  $\text{Cu}^+$  ions with  $\text{Zn}^{2+}$  ions at elevated temperature (250°C) and with an additional ligand (*n*-trioctylphosphine (TOP)) being present in the reaction mixture (driven by the complexation of  $\text{Cu}^+$  by TOP). In the publication in chapter 3.5 it was further shown that this sequential ion exchange can also be used to regio-selectively exchange only the tips of e.g. CdS nanorods with ZnS, since in the second ion exchange step only the  $\text{Cu}_2\text{Se}$  part of the rod (whose dimensions can be tuned according to the publication in chapter 3.3) undergoes ion exchange, while the CdS part of the rod stays untouched in this second step even if a large excess of  $\text{Zn}^{2+}$  ions is invoked (which is necessary to quantitatively exchange  $\text{Cu}^+$  to  $\text{Zn}^{2+}$ ).

**3.2. Colloidal  $\text{Cu}_{2-x}(\text{S}_y\text{Se}_{1-y})$  Alloy Nanocrystals with Controllable Crystal Phase: Synthesis, Plasmonic Properties, Cation exchange and Electrochemical Lithiation**

Enrico Dilella, [Dirk Dorfs](#), Chandramohan George, Karol Miszta, Mauro Povia, Alessandro Genovese, Alberto Casu, Mirko Prato, Liberato Manna

Journal of Materials Chemistry (2012), 22, 13023.

Article DOI: [10.1039/c2jm30788j](https://doi.org/10.1039/c2jm30788j)

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### **3.3. Cation Exchange Reactions in Colloidal Branched Nanocrystals**

Karol Miszta, [Dirk Dorfs](#), Alessandro Genovese, Mee Rahn Kim, Liberato Manna

ACS Nano (2011), 5, 7176.

Article DOI: [10.1021/nn201988w](https://doi.org/10.1021/nn201988w)

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### **3.4. Hierarchical Self-Assembly of Suspended Branched Colloidal Nanocrystals into Superlattice Structures**

Karol Miszta, Joost de Graaf, Giovanni Bertoni, [Dirk Dorfs](#), Rosaria Brescia, Sergio Marras, Luca Ceseracciu, Roberto Cingolani, Rene van Roij, Marjolein Dijkstra, Liberato Manna

Nature Materials (2011), 10, 872.

Article DOI: [10.1038/NMAT3121](https://doi.org/10.1038/NMAT3121)

Supplementary material is available online from the publisher.

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**3.5. Segmented CdSe@CdS/ZnS Nanorods Synthesized via a Partial Ion Exchange Sequence**

Patrick Adel, Andreas Wolf, Torben Kodanek, [Dirk Dorfs](#)

Chemistry of Materials (2014), 26, 3121.

Article DOI: 10.1021/cm500431m

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## 4. Property Control – Plasmon Resonances in Non-Metallic Nanocrystals

### 4.1. Outline

The previous two chapters in depth highlight my contribution to shape and composition control in colloidal nanocrystal synthesis. This chapter will show how composition control of nanocrystals can be used to tune their physical properties. Here the influence of the composition on the LSPR of nanoparticles is shown with a focus on degenerately doped nanoparticles.

In the introduction part of this manuscript, the occurrence of localized surface plasmon resonances was purposely not assigned to metallic nanoparticles, but instead to conductive nanoparticles. Indeed LSPRs are well known and well researched in most noble metal nanoparticles such as Ag, Au and Pt. Nevertheless, also other materials with a sufficiently high density of free movable charge carriers can exhibit LSPRs. Also in the introduction it was derived that the LSPR resonance frequency depends directly on the charge carrier density of the nanoparticles which is typically a material constant in metals but a tunable value in degenerately doped materials. Thus tuning the charge carrier density would allow to easily tuning the LSPR frequency.

This is exactly what was investigated in the publication in chapter 4.2 of this thesis. Herein it was demonstrated, that  $\text{Cu}_{2-x}\text{Se}$  nanocrystals exhibit an LSPR in the near infrared part of the spectrum (1000 – 1700 nm). The LSPR position can be easily tuned by varying the amount of copper vacancies in the structure (which in turn directly influences the amount of free p-type charge carriers in the valence band of the particles). This work also nicely demonstrates that the phenomenon of LSPRs is not limited to n-type conductive materials (like e.g. metals) but can also occur in p-type conductive materials when the free charge carrier density is sufficiently high. In the publication in chapter 4.3 the charge carrier dynamics of the NIR plasmon resonance in  $\text{Cu}_{2-x}\text{Se}$  nanoparticles has been further characterized using pump probe transient absorption spectroscopy with sub picosecond time resolution. The data was interpreted in the framework of the so-called two temperature model. This model is based on the assumption that right after the excitation only the free electron gas is heated on a fs timescale, and the heat then thermalizes via electron/phonon and phonon/phonon coupling on a time scale of few picoseconds (electron/phonon coupling) to several hundreds of picoseconds (phonon/phonon coupling). The main conclusion is the fact that the charge carrier dynamics of the NIR LSPRs observed are quite similar to the LSPRs of noble metals in the visible spectral regime.

It should be noted, that the degenerately doped copper chalcogenides represent a very versatile system with respect to a simple tunable LSPR in the near infrared spectral regime but typically suffer from a quite high sensitivity towards oxygen. This sensitivity might significantly limit their applicability under ambient conditions. Therefore, in order to increase the stability, the influence of various chemical modifications to the copper chalcogenide nanocrystals was studied. Namely the influence of the growth of an additional inorganic shell composed of ZnS (publication in chapter 4.4), as well as partial ion exchange with Ag and Au ions, and growth of metallic Au domains (publication in chapter 4.5) or of metallic Pt domains (publication in chapter 4.6.). While even closed dense ZnS shells were not capable to completely protect the particles from oxidation (even though the oxidation kinetics were significantly decelerated), the



partial ion exchange of Ag and Au ions into the  $\text{Cu}_{2-x}\text{Se}$  lattice allowed to significantly enhance the stability of these particles under ambient conditions.

Plasmonic nanoparticles are often discussed as possible sensory materials. However, while the LSPR of a plasmonic nanoparticle is typically very sensitive to all kinds of changes at the particle surface or in its vicinity, these changes in LSPR positions are typically not selective to specific analytes. Therefore, selectivity has to be introduced somehow else. One possible approach could be a size discriminating surrounding material. In the publication in chapter 4.7 the possibility to include e.g.  $\text{Cu}_{2-x}\text{Se}$  nanoparticles into mesoporous metal organic framework (MOF) ZIF-8 particles has been shown. This might enable specific sensing applications in the future in which the plasmonic particles serve as sensor and the MOF serves as size discriminator which allows only sufficiently small entities to reach the plasmonic particles.

#### 4.2. Reversible Tunability of the Near-Infrared Valence Band Plasmon Resonance in $\text{Cu}_{2-x}\text{Se}$ Nanocrystals

Dirk Dorfs, Thomas Härtling, Karol Miszta, Nadja C. Bigall, Mee Rahn Kim, Alessandro Genovese, Andrea Falqui, Mauro Povia and Liberato Manna

*Journal of the American Chemical Society* (2011), 133, 11175.

Article DOI: 10.1021/ja2016284

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### **4.3. Plasmon Dynamics in Colloidal Cu<sub>2-x</sub>Se Nanocrystals**

Francesco Scotognella, Giuseppe Della Valle, Ajay Ram Srimath Kandada, [Dirk Dorfs](#), Margherita Zavelani-Rossi, Matteo Conforti, Karol Miszta, Alberto Comin, Kseniya Korobchevskaya, Guglielmo Lanzani, Liberato Manna, and Francesco Tassone

Nano Letters (2011), 11, 4711.

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#### **4.4. Synthesis of Plasmonic Cu<sub>2-x</sub>Se@ZnS Core@Shell Nanoparticles**

Andreas Wolf, Thomas Härtling, Dominik Hinrichs and Dirk Dorfs

ChemPhysChem (2016), 17, 717.

Article DOI: 10.1002/cphc.201500907

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**4.5. Tuning the LSPR in copper chalcogenide nanoparticles by cation intercalation, cation exchange and metal growth**

Andreas Wolf, Torben Kodanek und Dirk Dorfs

Nanoscale (2015), 7, 19519.

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**4.6. Growth of  $\text{Cu}_{2-x}\text{Se-CuPt}$  and  $\text{Cu}_{1.1}\text{S-Pt}$  Hybrid Nanoparticles**

Andreas Wolf, Dominik Hinrichs, Joachim Sann, Jan F. Miethe, Nadja C. Bigall and Dirk Dorfs

Journal of Physical Chemistry C (2016), 120, 21925.

Article DOI: [10.1021/acs.jpcc.6b05574](https://doi.org/10.1021/acs.jpcc.6b05574)

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**4.7. Plasmonic Semiconductor Nanoparticles in a Metal-Organic Framework Structure and their In Situ Cation Exchange**

Andreas Wolf, Lisa Diestel, Franziska Luebke, Torben Kodanek, Tarek Mohamed, Jürgen Caro and Dirk Dorfs

Chemistry of Materials (2016), 28, 7511.

Article DOI: [10.1021/acs.chemmater.6b03425](https://doi.org/10.1021/acs.chemmater.6b03425)

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## 5. Conclusions and Outlook

This thesis cumulatively summarizes my contributions to the field of nanoparticle shape, composition and property control.

In chapter two several original publications are shown and put into context, which dealt with the advanced shape control in nanocrystal synthesis going far beyond simple spherical nanoparticles. A plurality of sophisticated shaped nanoparticles like dot-in-rod type structures, highly symmetric eight armed structures (octapods), and partially hollow or concave particles were synthesized. It was shown how the different shapes of the nanoparticles influence especially not only the optical properties but also e.g. the self-assembly behavior.

Chapter three summarizes those publications dealing with cation exchange reactions as a very elegant way to tune nanoparticle compositions without altering their size and shape. The major result here is that a large variety of nanocrystals can be transformed from one material to another without altering size or shape of the particles.

Finally chapter four summarizes those publications which dealt with localized surface plasmon resonances in degenerately doped nanocrystals. Most importantly, it is shown that LSPRs not only occur in metal nanoparticles but also in degenerately doped semiconductors giving the advantage of adjustability of the plasmon by the degree of doping. Furthermore, investigations towards chemical passivation of these nanoparticles were undertaken, and it is demonstrated that porous surroundings of such particles can contribute on the way for sensory applications in future.

Summarizing overall, it can be stated that the possibilities of colloid chemical synthesis have been extended significantly in the past decade, influenced strongly by the results presented in this thesis. A broad variety of shapes and compositions of materials can be realized nowadays by applying the introduced concepts (seed mediated growth, cation exchange, “hot injection” etc.).

Therefore, in future colloidal nanoparticle research, a strong focus will have to be put on designing nanocrystals with tailor-made shape and composition for specific applications. Chapter 4 of this thesis already gave an impression how already tiny changes in composition can drastically change nanocrystal properties. Having this in mind, the future challenge will be to develop and fine-tune composition and shape of colloidal nanocrystals for the various application fields, which are optical (like e.g. LEDs, Lasers), biomedical (like e.g. fluorescence labels and plasmonic hyperthermia), catalytic (like e.g. heterogeneous catalysis and photocatalysis), sensing (like e.g. plasmon-based sensing) and cosmetic fields of applications. A big advantage is that many of the results described in this work can contribute to overcome this challenge, since the synthetic strategies often do not depend on a specific compound class and therefore can be applied to the development for tailored components for each specific application.



## 6. Annex

### 6.1. Publications

In the following (inverse chronological) complete list of my publications, the publications included in this thesis are highlighted using blue letters.

- 1) *Synthesis of Ternary and Quaternary Au and Pt Decorated CdSe/CdS Heteronanoplatelets with Controllable Morphology*  
Naskar, S. ; Lübke mann, F. ; Hamid, S.; Freytag, A.; Wolf, A.; Koch, J. ; Ivanova, I.; Pfnür, H.; Dorfs, D.; Bahnemann, D. W.; Bigall, N. C.;  
**Adv. Func. Mater.**, **2017**, 27, 1604685.
- 2) *Determination of all Dimensions of CdSe Seeded CdS Nanorods Solely via their UV/Vis Spectra*  
Adel, P.; Bloh, J.; Hinrichs, D.; Kodanek, T.; Dorfs, D.;  
**Z. Phys. Chem.**, **2017**, 231, 93  
(\*corresponding author)
- 3) *Plasmonic Semiconductor Nanoparticles in a Metal–Organic Framework Structure and Their in Situ Cation Exchange*  
Wolf, A.; Diestel, L.; Lübke mann, F.; Kodanek, T.; Mohamed, T.; Caro, J.; Dorfs, D.\*  
**Chem. Mater**, **2016**, 28, 7511.  
(\*corresponding author)
- 4) *Growth of  $Cu_{2-x}Se$ -CuPt and  $Cu_{1.1}S$ -Pt Hybrid Nanoparticles*  
Wolf, A.; Hinrichs, D.; Sann, J.; Miethe, J.F.; Bigall, N.C.; Dorfs, D.\*  
**J. Phys. Chem. C**, **2016**, 120, 21925.  
(\*corresponding author)
- 5) *Chloride Ion Mediated Synthesis of Metal/Semiconductor Hybrid Nanocrystals*  
Hinrichs, D.; Galchenko, M.; Kodanek, T.; Suraj, N.; Bigall, N.C.; Dorfs, D.\*;  
**Small**, **2016**, 12, 2588.  
(\*corresponding author)
- 6) *Synthesis of Plasmonic  $Cu_{2-x}Se@ZnS$  Core@Shell Nanoparticles*  
Wolf, A.; Hartling, T.; Hinrichs, D.; Dorfs, D.\*;  
**ChemPhysChem**, **2016**, 17, 717.  
(\*corresponding author)
- 7) *Tuning the LSPR in copper chalcogenide nanoparticles by cation intercalation, cation exchange and metal growth*  
Wolf, A.; Kodanek, T.; Dorfs, D.\*;  
**Nanoscale**, **2015**, 7, 19519.  
(\*corresponding author)
- 8) *Phase transfer of 1-and 2-dimensional Cd-based nanocrystals*  
Kodanek, T.; Banbela, H.M.; Naskar, S.; Adel, P.; Bigall, N.C.; Dorfs, D.\*  
**Nanoscale**, **2015**, 7, 19300.  
(\*corresponding author)

- 9) *Aerogels from CdSe/CdS Nanorods with Ultra-long Exciton Lifetimes and High Fluorescence Quantum Yields*  
Sanchez-Paradinas, S.; Dorfs, D.; Friebe, S.; Freytag, A.; Wolf, A.; Bigall, N.C.;  
**Advanced Materials**, 2015, 27, 6152.
- 10) *Hollow Iron Oxide Nanoparticles in Polymer Nanobeads as MRI Contrast Agents*  
Bigall N.C.; Dilena, E. Dorfs, D.; Beoutis, M.; Pugliese G.; Wilhelm, C.; Gazeau, F.; Khan, A.A. Bittner, A.M.; Garcia, M.A.; Garcia-Hernandez M.; Manna, L.; Pellegrino, T.;  
**J. Phys. Chem. C**, 2015, 119, 6246.
- 11) *Segmented CdSe@CdS/ZnS Nanorods Synthesized Via a Partial Ion Exchange Sequence*  
Adel, P.; Wolf, A.; Kodanek, T.; Dorfs, D.\*;  
**Chem. Mater.**, 2014, 26, 3121.  
(\*corresponding author)
- 12) *Quantum-Dot-Based Photoelectrochemical Sensors for Chemical and Biological Detection*  
Yue, Z.; Lisdat, F.; Parak, W.J.; Hickey, S.G.; Tu, L.P.; Sabir, N.; Dorfs, D.; Bigall, N.C.;  
**ACS Applied Materials & Interfaces**, 2013, 5, 2800.
- 13) *Fluorescent, Magnetic and Plasmonic – Hybrid Multifunctional Colloidal Nano Objects*  
Bigall, N.C.; Parak; W.J.; Dorfs, D.\*;  
**Nano Today**, 2012, 7, 282.  
(\*corresponding author)
- 14) *Colloidal Cu<sub>2-x</sub>(S<sub>y</sub>Se<sub>1-y</sub>) Alloy Nanocrystals with Controllable Crystal Phase: Synthesis, Plasmonic Properties, Cation Exchange and Electrochemical Lithiation*  
Dilena, E.†; Dorfs, D.†; George, C.†; Miszta, K.; Povia, M., Genovese, A.; Casua, A.; Prato, M.; Manna, L.  
**J. Mater. Chem.**, 2012, 22, 13023.  
(†equally contributing authors)
- 15) *Application Prospects of Spray-Assisted Layer-by-Layer Assembly of Colloidal Nanoparticles*  
Otto, T.; Mudra, P.; Schelter, M.; Frolova, E.; Dorfs, D.; Gaponik, N.; Eychmüller, A.;  
**ChemPhysChem**, 2012, 13, 2128.
- 16) *Birth and Growth of Octapod-Shaped Colloidal Nanocrystals Studied by Electron Tomography*  
Brescia, R.; Miszta, K.; Dorfs, D.; Manna, L.; Bertoni, G.;  
**J. Phys. Chem. C**, 2011, 115, 20128.
- 17) *Plasmon dynamics in colloidal Cu<sub>2-x</sub>Se nanocrystals*  
Scotognella, F.; Della Valle, G.; Kandada, A.R.S.; Dorfs, D.; Zavelani-Rossi, M.; Lanzani, G.; Manna, L.; Tassone, F.;  
**Nano Lett.**, 2011, 11, 4711.
- 18) *Hierarchical self-assembly of suspended branched colloidal nanocrystals into superlattice structures*  
Miszta, K.; de Graaf, J., Bertoni, G. Dorfs, D.; Brescia, R.; Marras, S.; Ceseracciu, L.; Cingolani, R.; van Roij, R.; Dijkstra, M.; Manna, L.;  
**Nat. Mater.**, 2011, 10, 872.

- 19) *Cation Exchange Reactions in Colloidal Branched Nanocrystals*  
Miszta, K.; Dorfs, D.; Genovese, A.; Kim M.R.; Manna, L.;  
**ACS Nano**, 2011, 5, 7176.
- 20) *Steady-state photoinduced absorption of CdSe/CdS octapod shaped nanocrystals.*  
Antognazza, M.R.; Scotognella, F.; Miszta, K.; Dorfs, D.; Zanella, M.; Zavelani-Rossi, M.;  
Manna, L.; Lanzani, G.; Tassone, F.;  
**Phys. Chem. Chem. Phys. : PCCP**, 2011, 13, 15326.
- 21) *Reversible Tunability of the NIR Valence Band Plasmon Resonance in Cu<sub>2-x</sub>Se Nanocrystals*  
Dorfs, D.; Härtling, T.; Miszta, K.; Bigall, N.C.; Kim, M.R.; Genovese, A.; Falqui, A.; Povia, M.;  
Manna, L.;  
**J. Am. Chem. Soc.**, 2011, 133, 11175.
- 22) *Ultrafast Exciton Dynamics in Colloidal CdSe/CdS Octapod Shaped Nanocrystals*  
Scotognella, F.; Miszta, K.; Dorfs, D.; Zavelani-Rossi, M.; Brescia, R.; Marras, S.; Manna, L.;  
Lanzani, G.; Tassone, F.;  
**J. Phys. Chem. C**, 2011, 115, 9005.
- 23) *A Cast-Mold Approach to Iron Oxide and Pt/Iron Oxide Nanocontainers and Nanoparticles with a Reactive Concave Surface*  
George, C.; Dorfs, D.; Bertoni, G.; Falqui, A.; Genovese, A.; Pellegrino, T.; Roig, A.; Quarta, A.; Comparelli, R.; Lucia Curri, M.; Cingolani, R.; Manna, L.;  
**J. Am. Chem. Soc.**, 2011, 133, 2205.
- 24) *Multifunctional Nanobeads Based on Quantum Dots and Magnetic Nanoparticles: Synthesis and Cancer Cell Targeting and Sorting*  
Di Corato, R.; Bigall, N.C.; Ragusa, A.; Dorfs, D.; Genovese, A.; Marotta, R.; Manna, L.; Pellegrino, T.;  
**ACS Nano**, 2011, 5, 1109.
- 25) *Octapod-Shaped Colloidal Nanocrystals of Cadmium Chalcogenides via "One-Pot" Cation Exchange and Seeded Growth*  
Deka, S.†; Miszta, K.†; Dorfs, D.†; Genovese, A.; Bertoni G.; Manna L.;  
**Nano Lett.**, 2010, 10, 3770.  
(†equally contributing authors)
- 26) *Progress in the Light Emission of Colloidal Semiconductor Nanocrystals*  
Gaponik, N.; Hickey, S.G.; Dorfs, D.; Rogach, A.L.; Eychmüller A.;  
**Small**, 2010, 6, 1364.
- 27) *Hydrogels and Aerogels from Noble Metal Nanoparticles*  
Bigall, N.C.; Herrmann, A.K.; Vogel, M.; Rose, M.; Simon, P.; Cabrera, W.C.; Dorfs, D.; Kaskel, S.; Gaponik, N.; Eychmüller, A.;  
**Angew. Chem. Int. Ed.**, 2009, 48, 9731.
- 28) *Synthesis of Extremely Small CdSe and Bright Blue Luminescent CdSe/ZnS Nanoparticles by a Pre-Focused Hot-Injection Approach*  
Capek, R.; Lambert, K.; Dorfs, D.; Smet, P.; Poelman, D.; Eychmüller, A.; Hens, Z.;  
**Chem. Mater.**, 2009, 21, 1743.

- 29) *Selective Gold Growth on CdSe Seeded CdS Nanorods*  
Menagen, G.; Mocatta, D.; Salant, A.; Popov, I.; Dorfs, D.\*; Banin, U.;  
**Chem. Mater.**, **2008**, *20*, 6900.  
(\*corresponding author)
- 30) *Determination of Band Offsets in Heterostructured Colloidal Nanorods Using Scanning Tunneling Spectroscopy*  
Steiner, D.; Dorfs, D.; Banin, U.; Della Sala, F.; Manna, L.; Milo, O.;  
**Nano Lett.**, **2008**, *8*, 2954.
- 31) *ZnSe Quantum Dots Within CdS Nanorods - a Seeded Growth Type-II System*  
Dorfs, D.; Salant, A.; Inna, P.; Banin, U.;  
**Small**, **2008**, *4*, 1319.
- 32) *Type-I and Type-II Nanoheterostructures Based on CdTe Nanocrystals – a Comparative Study*  
Dorfs, D.; Franzl, T.; Osovsky, R.; Brumer, M.; Lifshitz, E.; Klar, T.A.; Eychmüller, A.;  
**Small**, **2008**, *4*, 1148.
- 33) *Multilayered Semiconductor Nanoheterostructures*  
Dorfs, D.; Eychmüller, A.;  
**Z. Phys. Chem.**, **2006**, *220*, 1539.
- 34) *Multilayered Nanoheterostructures: Theory and Experiment*  
Dorfs, D.; Henschel, H.; Kolny, J.; Eychmüller, A.;  
**J. Phys. Chem. B.**, **2004**, *108*, 1578.
- 35) *Photoemission Study of Onion Like Quantum Dot Quantum Well and Double Quantum Well Nanocrystals of CdS and HgS*  
Borchert, H.; Dorfs, D.; McGinley, C.; Adam, S.; Moeller, T.; Weller, H.; Eychmüller, A.;  
**J. Phys. Chem. B.**, **2003**, *107*, 7486.
- 36) *A Series of Double Well Semiconductor Quantum Dots*  
Dorfs, D.; Eychmüller A.;  
**Nano Lett.**, **2001**, *1*, 663.

## 6.2. Curriculum vitae



**Dr. Dirk Dorfs**

**Date and place of birth:**

26<sup>th</sup> of December 1976  
in Hamburg

**Address:**

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**Marital status:**

married

**Citizenship:**

German

Hannover, 28<sup>th</sup> of March 2017

## Working experience

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Since 10/2011	Researcher ( <i>Habilitand</i> ) at the Leibniz Universität Hannover, Institute of Physical Chemistry and Electrochemistry
01/2009 – 09/2011	Postdoc at the Istituto Italiano di Tecnologia, Nanobiotech Facilities, Nanochemistry (Prof. Liberato Manna), Genoa, Italy
07/2008 – 12/2008	Postdoc at the Technische Universität Dresden, Institute for Physical Chemistry (Prof. Alexander Eychmüller), Dresden, Germany
04/2007 – 06/2008	Postdoc at the Hebrew University of Jerusalem, Department for Physical Chemistry (Prof. Uri Banin), Jerusalem, Israel
05/2006 – 03/2007	Research associate (PhD student) at the Technische Universität Dresden, Institute for Physical Chemistry (Prof. Alexander Eychmüller), Dresden, Germany
03/2003 – 04/2006	Research associate (PhD student) at the Universität Hamburg, Institute for Physical Chemistry (Prof. Alexander Eychmüller), Hamburg, Germany

## Academic studies

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03/2007	<b>Conferral of a doctorate</b> at the Technische Universität Dresden. Dissertation: <i>Synthesis and Characterization of Type-II Semiconductor Nanoheterostructures</i> (grade: summa cum laude)
04/2003	<b>Diploma in chemistry</b> at the Universität Hamburg Diploma thesis: <i>Synthesis and Characterization of Multilayered Nanoheterostructures</i> (grade: 1,0 (very good))
1997 – 2003	Studies of chemistry at the Universität Hamburg

## Civil service

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1996 – 1997	<b>Civil service</b> at the Deutsches Rotes Kreuz, Hamburg
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## School

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1996	<b>Abitur</b> (university entrance diploma) at the Gymnasium Alstertal, Hamburg
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## Awards

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07/2008	Professor-Schwabe-Award of the Professor-Schwabe-Foundation at the Technische Universität Dresden for outstanding performance during the making of the dissertation
04/2007	Minerva fellowship of the Minerva foundation of the Max Planck Society for a 15 month postdoctoral research stay at the Hebrew University of Jerusalem
03/2003	Award of the friends and supporters' association of the Department of Chemistry of the University of Hamburg for the best diploma thesis of the year (2. place)

## Teaching experience

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**Lecturer** for general chemistry for chemistry as a minor subject and several master courses

**Head of practical training** for general chemistry for chemistry as a minor subject

**Supervision** of PhD students, master students and bachelor students

**Standing-in as lecturer** in nanochemistry

**Teaching assistant** in physical chemistry and in mathematics for chemists

## Language skills

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**German** native speaker

**English** fluent

**French** good knowledge

**Italian** good knowledge

## Summary of authoring activities

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- 36 peer reviewed publications
- 8 of these as first (or equally contributing) author
- 9 of these as corresponding author
- > 1600 citations (without self-citation)
- h-index = 20
- 3 book chapters
- 2 patents
- Reviewer for J. Am. Chem. Soc., Nano Lett., ACS Nano, Chem. Mater., J. Mater. Chem. and other journals

### **6.3. Erklärung**

Hiermit erkläre ich, dass ich die vorliegende Arbeit selbstständig und ohne fremde Hilfe verfasst, keine anderen als die angegebenen Quellen und Hilfsmittel benutzt und die den benutzten Werken entnommenen Stellen sowie bereits veröffentlichte Teile als solche kenntlich gemacht habe.

Die Arbeit wurde bisher weder im Inland noch im Ausland in gleicher oder ähnlicher Form einer anderen Prüfungsbehörde vorgelegt.

Es sind keine anderen Promotions- oder Habilitationsverfahren anhängig.

Hannover, März 2017

Dr. Dirk Dorfs