Semiconductor nanocrystals – versatile building blocks for innovative microsystems

Alexander Weiß[1], Joern Langenickel[2], Kathleen Heinrich[1], Joerg Martin[1], _Thomas Otto_[1], Thomas Geßner[1,2]

[1] Fraunhofer Institute for Electronic Nanosystems, Technologie-Campus 3, 09126 Chemnitz, Germany,
thomas.otto@enas.fraunhofer.de
[2] Technische Universität Chemnitz, Reichenhainer Straße 70, 09126 Chemnitz, Germany

Abstract

Semiconductor nanocrystals, so-called quantum dots, with a typical diameter range of 3-7 nm exhibit several exceptional properties. Among them is high quantum efficiency regarding fluorescence, but also high sensitivity against electrical charges and fields. Consequently, quantum dots are not only innovative light emitters, but also excellent building blocks for nanosensors. In this paper some basics of electro- and photoluminescence of semiconductor nanocrystals are described. Further we present some results on the preparation and characterization of CdSe nanocrystal-polymer composites. Finally, examples concerning the use of nanocrystals as light emitters in a quantum dot LED and nanosensors will be given.

Key words: semiconductor nanocrystals, photoluminescence, electroluminescence, quenching

Nanocrystal luminescence

Since _Efros et al_. in 1982 described some unique properties of small semiconductor spheres, they have gained much interest [1]. Especially, the observation of fluorescence coming from silicon nanostructures in 1990 opened a completely new field in science [2]. The starting material for semiconducting nanocrystals often consists of a II-VI compound, that is a composite of the cations of the second subgroup with the anions of the sixth main group. In general, these semiconductors crystallize either as face centered cubic or hexagonal (wurtzite) crystal system. The different crystal structures have a strong influence on the properties of the seminconductor nanocrystals [3]. The most common material for colloidal quantum dots (QDs) is the II-VI semiconductor CdSe with wurtzite crystal structure. It has a direct band gap of 1.79 eV [4] and an exciton Bohr radius of 5.6 nm [5]. The exciton Bohr radius describes the distance of the bound electron-hole pair. If the size of the nanocrystal is smaller than the exciton Bohr radius the possible energy states quantize, the so-called 'quantum confinement'. As a result it is possible to adjust the photoluminescence (PL) or electroluminescence (EL) from blue to red simply by changing the size of the nanostructures. The larger the nanostructure, the smaller the widening of the band gap is. Thus the emission wavelength shifts to larger wavelengths. Also the phenomenon of 'blinking' has been detected from various single semiconductor nanocrystals, e.g. Si or CdSe [6]. 'Blinking' is understood as statistical transition between bright and dark periods in photoluminescence under continuous excitation. Dark periods are usually observed for charged particles [7]. An additional delocalized charge inside a particle leads to a non-radiative recombination of the excited exciton (see Fig. 1b).

a) quantum dot photo-luminescence

b) quenching of photo-luminescence due to delocalized charge
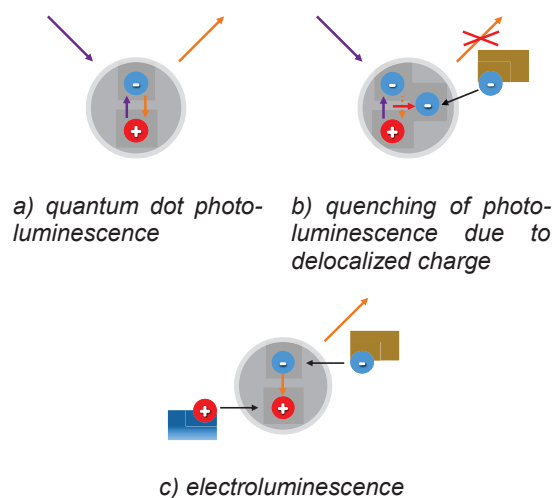
c) electroluminescence

Fig. 1. Schematics of different luminescence behaviors.

The extra-charge inside the particle can be created by direct or Auger photoionization or can even be injected electrically from the surrounding matrix [8]. A possible application of luminescence bleaching is on the one hand the detection, storage and visualization of charge carriers. On the other hand, semiconductor nanocrystals are due to their exceptional properties, prominent candidates for light emitting diodes, laser sources or photo detectors [9, 10]. In our current work we focus on the application of quantum dots for spectral light sources and as sensor elements. Special focus is on the usage of sol-gel coating processes for the realization of either n-type or p-type semiconductors for charge carrier transport.

Charge carrier materials and deposition technologies

Figure 2 gives an overview of charge carrier materials used for quantum dot LEDs and nanosensors in this study. Hence both inorganic and organic charge carrier materials were used.
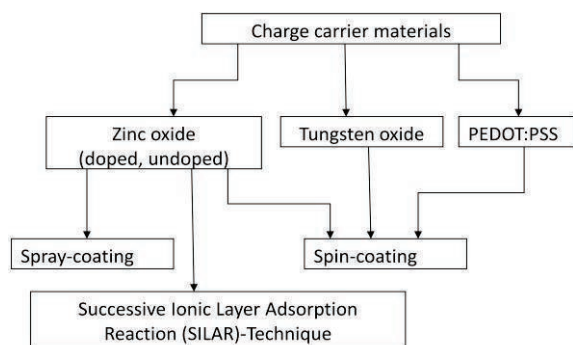

Fig. 2. Overview of materials and deposition methods used for quantum dot LED and nanosensors.

Poly(3,4-ethylenedioxythiophene) Polystyrene sulfonate (PEDOT:PSS) is an intrinsically conductive organic polymer which can be easily processed from dispersion using spin-coating technique. To improve the interaction of polymer and substrate organic solvents, e.g. ethanol was added to the aqueous polymer dispersion before spin-coating. As a result homogeneously distributed films were obtained.

Besides zinc oxide and tungsten oxide were synthesized via the sol-gel-process. The zinc oxide sol was obtained by dissolving zinc acetate dihydrate in 2-methoxyethanol and ethanolamine at 60 °C for several hours [11]. The as prepared sol was aged between 4 – 36 hrs, deposited by spin-coating on glass-ITO substrates and annealed at 200 °C.

Zinc oxide layers were also deposited via successive ionic layer adsorption reaction (SILAR) at temperatures below 100 °C and spray coating [12, 13]. SILAR deposition leads to a densely-packed crystalline film whereas spray-coated films show a high surface roughness with porous and fiber-like areas. Therefore just SILAR-deposited and spin-coated zinc oxide layers were used for the above mentioned applications. Because zinc oxide layers resulting from the SILAR-deposition process needs low temperatures also polymer substrates have been successfully coated.

Tungsten oxide films were also obtained via the sol gel process. For preparing the sol, tungsten powder was carefully dissolved in hydrogen peroxide. The sol was spin-coated onto glass-ITO substrates whereas polymers like polyvinyl alcohol or polar solvents, e.g. ethanol or 2-propanol, were added in order to get a homogeneously distributed film [14].

Zinc oxide layers can be doped with aluminium or boron whereas tungsten oxide films can be doped with titanium to improve their charge carrier properties.

Semiconductor nanocrystals as part of light sources

In general, 4 types of QD-LEDs can be distinguished [15]. Especially type IV (hybrid) hold several advantages over type I and type II QD-LEDs. By replacing the organic matrix with inorganic components a significant improvement in the stability of the devices under ambient conditions is expected. In addition, the higher current densities allow an increase in efficiency. Using colloidal metal oxides or sol-gel technologies enables the preparation of fully solution processed QD-LEDs, which may be useful for mass production. In this study, in addition to standard hole injection layer (HIL) like PEDOT:PSS inorganic alternatives are studied. These were reduced graphene oxide (rGO) and tungsten oxide (WO_3). In order to apply the rGO, ascorbic acid was added to the aqueous solution containing the graphene flakes [16]. The resulting rGO was then applied directly from solution to the ITO substrate. In order to apply WO_3 a tungstic acid solution obtained from tungsten powder dissolved in hydrogen peroxide was deposited on the substrate, which was afterwards annealed at 250 °C. Thus, a WO_3 layer which lowers the work function of the anode is formed [17]. Then Poly(9-vinylcarbazole) (PVK) acting as hole transport layer (HTL), double shell CdSe/ZnSe/ZnS QDs (peak wavelength 610 nm) as emitting layer

and zinc oxide (ZnO) nanoparticles as electron transport layer (ETL) were added by spin-coating and a 100 nm high and 1 mm thick aluminium cathode was deposited by vapor deposition (FHR MS 150 x 4 AE). The nanoparticles were doped with 2% aluminium to increase the conductivity. Due to the valence band energy of 4.0 eV ZnO is well suited to inject electrons in CdSe QDs [18]. To disperse the ZnO nanoparticles in ethanol, polyvinyl pyrrolidone (PVP) was added to the solution. PVP stabilizes the nanoparticles sterically in ethanol [19]. Since PVP is non-conductive, the current transport occurs exclusively through the ZnO nanoparticles. By adsorption of the PVP to the nanoparticles the properties of the layer, such as stability in air and a lower roughness could be improved [20]. Figure 3 shows the corresponding band structure.
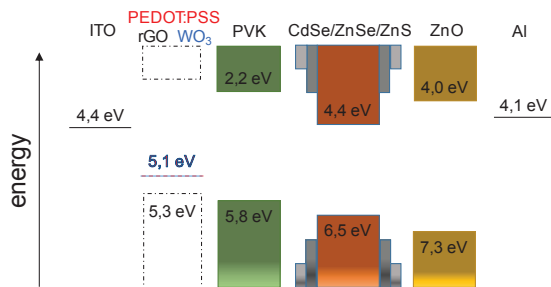

Fig. 3. Band structure for QD-LEDs with different hole injection layers [21, 17, 22].

Figure 4 shows that the sample with PEDOT:PSS can carry higher amounts of current than rGO and WO_3 after turn on voltage. It is assumed, that this is due to the higher conductivity of PEDOT:PSS. The currents of the QD-LEDs with rGO and WO_3 as HIL are in the same range. At 10 V the sample with rGO however collapses.
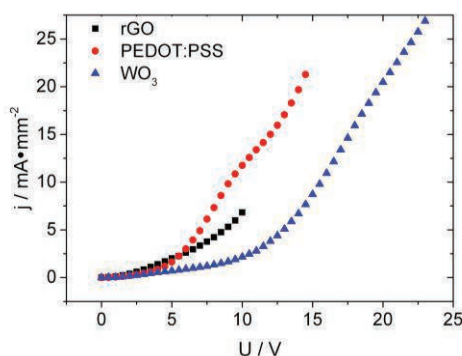

Fig. 4. Current density j vs. voltage U for QD-LEDs with different HILs.

As shown in Fig. 5, the maximum power density of the QD-LEDs with PEDOT:PSS and WO_3 as HIL are nearly equal, but is for PEDOT:PSS reached at a lower voltage. For rGO the luminous efficiency is in the same range of PEDOT:PSS, although current density is lower after turn on voltage. This is caused by the decreased energy barrier for hole injection into PVK. In addition it is assumed, that rGO can block electrons more efficient than WO_3.
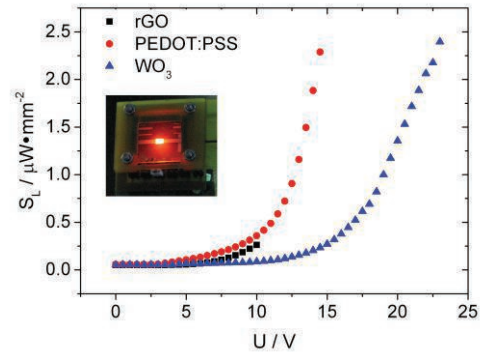

Fig. 5. Power density of the emitted light S_L vs. voltage U for QD-LEDs with different HILs.

Semiconductor nanocrystals as part of a load sensor

A relative new application of luminescence bleaching is the detection, storage and visualization of mechanical overloads especially on lightweight structures. Key feature of the setup is a double layer consisting of a piezoelectric foil and a quantum-dot-based layer stack which are laminated on the mechanical structure. In case of mechanical impacts or overloads, electrical charges will be generated by the piezoelectric foil and transferred as well as injected to the quantum dots. Because an additional delocalized charge within a nanocrystal leads to photo-luminescence quenching, mechanical loads are direct transformed to a reduced photo-luminescence, visible as optical contrast (see Fig. 1 b).

Figure 6 shows a typical integrated photoluminescence signal of a quantum dot composite layer. At an observation time of 10 seconds various external voltages are applied, leading to a considerable reduction of PL intensity due to charge injection. The achievable optical contrast depends on several factors, such as applied voltage, layer thickness, and charge mobility/current. Removal of the external voltage (at 35 seconds) is followed by an increase of PL up to the initial value. Charges - and thus the optical contrast - are stored a certain time within the QDs depending on barriers around the QDs (shells) and the electronic band level alignment between QDs and matrix material. The relative short recovery time is very suitable for investigation of photo physical processes as

well as demonstration purposes, and can be extended by alternative material combinations of QDs and matrix material.
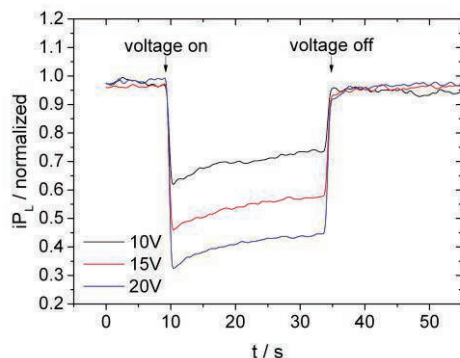

Fig. 6. Integrated photoluminescence iP_L of CdSe-CdS quantum rods biased with external voltages.

Summary

Semiconductor nanostructures have great potential for system integration - not only as light sources, but also as smart nanosensors. There exists a wide range of applications for both fields. We presented some aspects of realizing load sensors and solution processable QD-LEDs. The preparation of high quality layer stacks is of essential importance regarding devise performance. But also the quantum dot environment plays a crucial role with respect to light emitting properties. Further we have shown intended quenching of quantum dot fluorescence by application of different external voltages on an appropriate sensor layer. This mechanism will be used for detection and visualization of mechanical loads on light-weight structures.

Acknowledgement

References

[1] Al. L. Efros, and A. L. Efros; *Sov. Phys. Semicond.* 16, p. 772 (1982).

[2] L. T. Canham; *Appl. Phys. Lett.* 57, p. 1046 (1990).

[3] D. Bera, L. Qian, T.-K. Tseng, and P. H. Holloway, *Materials* 3, 2260–2345 (2010).

[4] Y. Shirasaki, PhD thesis, Massachusetts Institute of Technology (2013).

[5] [5] D. Norris and M. Bawendi, *Physical review. B, Condensed matter* 53, 16338–16346 (1996).

[6] M. Nirmal, B. O. Dabbousi, M. G. Bawendi, J. J. Macklin, J. K. Trautman, T. D. Harris, and L. E. Brus; *Nature* (London) 383, p. 802 (1996).

[7] Al. L. Efros, and M. Rosen; *Phys. Rev. Lett.* 78, p. 1110 (1997).

[8] J. Martin, U. Staudinger, E. Demir, C. Spudat, P. Pötschke, B. Voit, T. Otto, and T. Gessner; SPIE Photonics West 2012, San Francisco, USA, Proc. SPIE, p. 8264 (2012).

[9] Y. Shirasaki, G. J. Supran, M. G. Bawendi, and V. Bulović; *Nature Photon.* 7, pp. 13–23 (2013).

[10] H.-J.Eisler, V. C. Sundar, M. G. Bawendi, M. Walsh, H. I. Smith and V. Klimov; *Appl. Phys. Lett.* 80 (24), pp. 4614-4616 (2002).

[11] H.-Y. Park, D. Lim, S.-H. Oh, P.-H. Kang, G. Kwak and S.-Y. Jang, "Inverted-structure polymer solar cells fabricated by sequential spraying of electron-transport and photoactive layers", *Organic Electronics* 15(10), pp. 2337–2345, (2014); doi: 10.1016/j.orgel.2014.06.036

[12] S.-C. Shei, P.-Y. Lee, S.-J. Chang, „Effect of temperature on the deposition of ZnO thin films by successive ionic layer adsorption and reaction", *Appl. Surf. Sci.* 258, p. 8109-8110, (2012); doi: 10.1016/j.apsusc.2012.05.004

[13] T. Kuwabara, T. Nakashima, T. Yamaguchi, K. Takahashi, „Flexible inverted polymer solar cells on polyethylene terephthalate substrate containing zinc oxide electron-collection-layer prepared by novel sol-gel method and low-temperature treatments", *Organic Electronics* 13, p. 1137 (2012); doi: 10.1016/j.orgel.2012.03.015

[14] Mao, J. K. Kim, K. Shin, D. H. Wang, P. J. Yoo, G. Y. Han, J. H. Park, "Hematite modified tungsten trioxide nanoparticle photoanode for solar water oxidation", Journal of Power Sources 210, p. 32 (2012); doi:10.1016/j.jpowsour.2012.02.112

[15] Yasuhiro Shirasaki, Geoffrey J. Supran, Moungi G. Bawendi & Vladimir Bulović, Emergence of colloidal quantum-dot light-emitting technologies, *Nature Photonics* 7, 13–23 (2013).

[16] J. Zhang, H. Yang, G. Shen, P. Cheng, J. Zhang, and S. Guo, "Reduction of graphene oxide via L-ascorbic acid.", *Chemical communications* (Cambridge, England) 46, 1112–4 (2010).

[17] X. Yang, Y. Ma, E. Mutlugun, Y. Zhao, K. S. Leck, S. T. Tan, H. V. Demir, Q. Zhang, H. Du, and X. W. Sun, "Stable, efficient, and all-solution-processed quantum dot light-emitting diodes with double-sided metal oxide nanoparticle charge

transport layers.", *ACS applied materials & interfaces* 6, 495–9 (2014).

[18] V. Wood, M. J. Panzer, J. E. Halpert, J.-M. Caruge, M. G. Bawendi, and V. Bulovic, "Selection of metal oxide charge transport layers for colloidal quantum dot LEDs.", *ACS nano* 3, 3581–6 (2009).

[19] A. Reindl, Semiconducting Nanoparticles for Application in Printable Electronics: Dispergieren und Stabilisieren Von Halbleitenden Nanopartikeln Zur Anwendung in. PhD thesis, Universität Erlangen-Nürnberg, (2009).

[20] S. Bubel, N. Mechau, and R. Schmechel, "Electronic properties of polyvinylpyrrolidone at the zinc oxide nanoparticle surface", *Journal of Materials Science* 46, 7776–7783, (2011).

[21] D.-Y. Wang, I.-S. Wang, I.-S. Huang, Y.-C. Yeh, S.-S. Li, K.-H. Tu, C.-C. Chen, and C.-W. Chen, "Quantum Dot Light-Emitting Diode Using Solution-Processable Graphene Oxide as the Anode Interfacial Layer", *The Journal of Physical Chemistry C* 116, 10181–10185 (2012).

[22] H. Mattoussi, L. H. Radzilowski, B. O. Dabbousi, E. L. Thomas, M. G. Bawendi, and M. F. Rubner, "Electroluminescence from heterostructures of poly(phenylene vinylene) and inorganic CdSe nanocrystals", *Journal of Applied Physics* 83(12), 7965 (1998).