Angewandte
Zuschriften

Nanocrystals

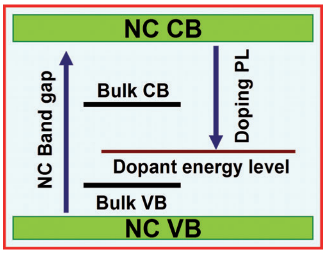
DOI: 10.1002/ange.201210080

Insights into the Energy Levels of Semiconductor Nanocrystals by a Dopant Approach**

Zhuolei Zhang, Dongze Li, Renguo Xie, and Wensheng Yang*

The energy levels of semiconductor nanocrystals (NCs) are among the key factors controlling the performance of solar cells[1–6] and optoelectronics devices.[7–9] Therefore, an accurate determination of the conduction band (CB) and valence band (VB) of the NCs is important and a prerequisite in rational design of the building blocks using the NCs. The energy levels of the NCs are acquirable by X-ray absorption,[10] photoelectron,[11–14] or scanning tunneling spectroscopy.[15] Theoretical predictions on band structures of the NCs have also been reported.[16–20] Recently, cyclic voltammetry (CV)[21–23] has been employed to estimate the CB and VB positions of the NCs. These techniques for determining the energy levels of the NCs generally involve sophisticated instruments and tedious sample preparation and/or complicated operation procedures. For example, the CV method requires that the samples are stable during the measurements. Furthermore, these methods depend on charging the NCs during the measurements, which may lead to a shift in their CB and/or VB positions. Thus, determination of the energy band positions of the NCs still remains a challenge.

Herein, we developed an approach to determine the energy levels of the NCs by introduction of certain transition-metal ions (dopants) into the NCs. It is well-known that the energy level of a dopant is independent on size of the host semiconductor.[24–29] If the energy level of the doped transition metal ions located in the energy gap of the host semiconductor NCs, band-gap photoluminescence (PL) of the NCs will usually be quenched.[24,26,29] Instead, a PL peak associated with the doped metal ions (Doping PL) appears. As shown in Scheme 1, bottom of the CB (or LUMO) of the NCs can thus be determined based on the doping PL, given the known position of the energy level of the dopant. The band gap (or HOMO–LUMO energy gap) of the NCs can be readily measured by using UV/Vis spectroscopy. Subsequently, the top of the VB (or HOMO) of the NCs is deducible by subtracting the band gap (or HOMO–LUMO energy gap) of the NCs from the energy level of the CB (or LUMO) of the NCs (see Supporting Information for the detailed procedure to calculate the energy levels of a typical sample).



Scheme 1. Representation of the approach used to determine the energy levels of semiconductor NCs. Green bands: the conduction band (CB) and valence band (VB) of the NCs. Black lines: the bottom of the conduction band (Bulk CB) and the top of the valence band of the corresponding bulk semiconductor (Bulk VB). Red line: the energy level of the dopant ions.

InP NCs and Cu doped InP NCs were used as a model system for determination of the energy levels of the NCs. InP NCs with various sizes and a relatively narrow size distribution[30] and Cu-doped InP NCs possessing an efficient doping PL[26,31,32] were synthesized according to reported methods (see the Supporting Information for the detailed synthetic procedures of all of the NCs concerned in this work, and Figure S1 a for the absorption and doping PL spectra of the as-prepared InP and Cu-doped InP NCs). Figure 1 a shows the variation in HOMO–LUMO energy gap of the InP NCs calculated from the first exciton absorption peak with the size of the NCs. Following the approach as shown in Scheme 1,

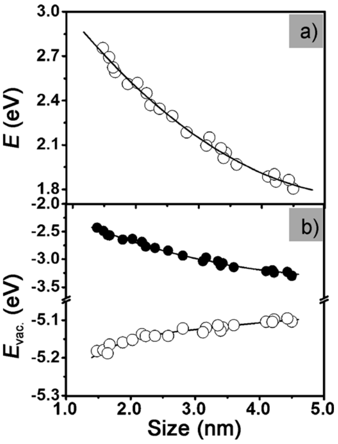


Figure 1. Variations in a) the HOMO–LUMO energy gap and b) energy levels of the CB (●) and VB (○) of the InP NCs versus vacuum (E_{vac}) with their sizes.

---

[*] Z. L. Zhang, D. Z. Li, Prof. R. G. Xie, Prof. W. S. Yang
College of Chemistry, Jilin University
Changchun, 130012 (P.R. China)
E-mail: renguoxie@jlu.edu.cn

[**] This work was supported by the National Basic Research Program of China (No. 2011CB935800), NSF of China (51072067, 50825202), and the Program for NCET in University of Chinese Ministry of Education.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201210080.

variation in energy levels of the CB and VB with the size of the InP NCs were deduced (Figure 1 b). The energy level of the CB decreased from −2.48 to −3.25 eV and that of the VB increased from −5.18 to −5.10 eV as the size of the NCs increased from 1.4 to 4.5 nm; these values are in a good agreement with theoretical values (Supporting Information, Figure S1 b) calculated using the classic Brus's equation,[34,35] indicating the reasonability of this dopant approach.

Obviously, the determination of the doping PL peak position and energy gap of the NCs is one of the crucial factors in the current method. In this study, all of the PL spectra were calibrated using a standard light source (Supporting Information, Figure S2). Instead of the band edge, the exciton band gap derived from the first exciton absorption peak was used to determine the energy gap of the NCs as mentioned above (Supporting Information, Figure S3 and Table S1). Credibility of the energy levels of the InP NCs determined by this method was inspected by the following control experiments. After being mixed with 1,3,5-tris(N-phenylbenzimidazol-2,yl)benzene (TPBI), the emission intensity of 1.5 nm InP NCs decreased slightly, whereas that of 3.2 nm InP NCs increased slightly, attributed to the formation of type II and type I structures,[36] respectively, between the two different-sized NCs with TPBI (Supporting Information, Figure S4).

The energy level of the dopants depends on both the type of the host semiconductors and the kind of the transition metal ions used. For example, the energy levels of Cu and Ag dopants vary dramatically with the type of the host semiconductors (Supporting Information, Table S2).[31–35,37–39] According to Scheme 1, energy levels of the NCs can also be determined by employing other transition-metal ions with a dopant energy level located in the band gap. Ag-doped InP quantum dots were synthesized and their UV-visible and doping PL spectra absorption were recorded to determine the energy levels of the InP NCs (Supporting Information, Figure S5). The energy levels of the InP NCs with different sizes determined by the Ag dopant were found to be the same as those calculated by using Cu ions as the dopant, which further indicates the reliability of such dopant approach.

The simplicity of such a dopant approach allows the band offset determination of the NCs with different shapes. Cu-doped InP quantum shells (QSs) were synthesized by using ZnSe NCs as the templates.[40] Because of the formation of a reverse type I structure between ZnSe and InP, optical properties of the InP QSs should only depend on thickness of the InP shell (Supporting Information, Figure S6). Figure 2 a,b show variations in the HOMO–LUMO energy gap and energy levels with thickness of two series of the InP QSs prepared by using 2.7 and 3.7 nm ZnSe NCs as templates. The InP QSs bearing the 2.7 nm template presented larger energy gap than those with the 3.7 nm template. Given the same thickness, both the CB and VB of the InP QSs with 2.7 nm inner cores exhibited a larger shift toward the vacuum energy level than those with 3.7 nm inner cores.

Cu doped InP QSs were further synthesized by using 2.7 nm ZnS NCs as templates and characterized to check the effect of the type of the templates on energy levels of the InP QSs (Supporting Information, Figure S7). The InP QSs with 2.7 nm ZnS cores presented the same energy levels as those with 2.7 nm ZnSe cores (Figure 2 c). When the original ligands (oleylamine) on the InP QSs were replaced by tri-*n*-octylphosphine (Supporting Information, Figure S8),[41] there were no changes in their absorption and PL spectra (Supporting Information, Figure S9). These results suggested that both the types of ligands and templates had negligible effects on the energy levels of the InP QSs.

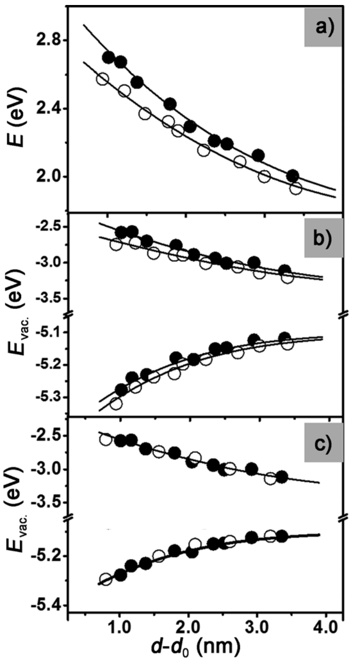


Figure 2. Variations in a) the HOMO–LUMO energy gaps and b) energy levels of the InP QSs versus vacuum (E_{vac}) with thickness of the QSs with 2.7 (●) and 3.7 nm (○) ZnSe core templates. c) Variations in the energy levels of the InP QSs with thickness of the QSs on 2.7 nm ZnS (○) and ZnSe (●) core templates; d is the outer diameter of the core–shell NCs and d_0 is the size of the templates.

This dopant approach was extended to determine the energy levels of typical II–VI NCs, such as ZnSe and CdSe. Cu-doped ZnSe NCs[24] were synthesized and their absorption and doping PL spectra were recorded (Supporting Information, Figure S10). Consequently, energy levels of the ZnSe NCs were determined (Figure 3 a). The energy level of the CB decreased from −2.32 to −2.62 eV and that of the VB increased from −5.64 to −5.55 eV as the size of the ZnSe NCs increased from 2.6 to 4.6 nm. In the case of CdSe NCs, instead of Cu ions, Ag ions were employed to determine the energy levels of the CdSe NCs (Supporting Information, Figure S11 a). The energy levels of the CdSe NCs determined by such a dopant approach are in good agreement with these by the CV method (Supporting Information, Figure S11 b), further indicating the credibility of this present approach. Importantly, the advantage of this approach is that the NCs do not need to go through tedious and harsh treatments.

This dopant approach was further extended to reveal the differences in energy levels of the different types NCs with the same energy gap. For example, 2.0 nm InP and 2.4 nm CdSe dots showed the same energy gap (505 nm, $E_g = 2.45$ eV) as derived from their absorption spectra. However, the differ-

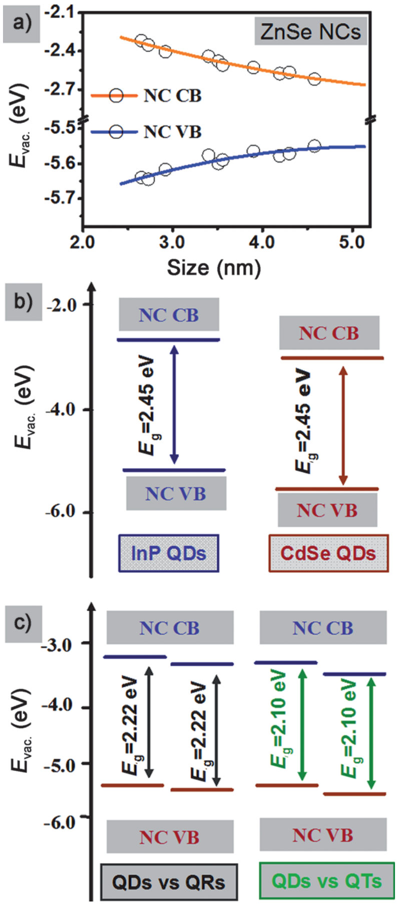


Figure 3. a) Variations in the energy levels of the ZnSe NCs with size. b) Energy levels of the InP (2.0 nm) and CdSe (2.4 nm) dots with the same energy gap (505 nm, $E_g = 2.45$ eV). c) Energy levels of the CdSe dots (3.2 nm) versus CdSe rods (diameter × length: 3.2 × 7.5 nm) with the same energy gap (558 nm, $E_g = 2.22$ eV) (left), and CdSe dots (4.0 nm) versus CdSe tetrapods (diameter × arm length: 4.0 × 28 nm) with the same energy gap (583 nm, $E_g = 2.10$ eV) (right).

ence in their energy levels could be readily revealed by recording the Doping PL spectra of the Cu doped InP and Ag doped CdSe NCs (Supporting Information, Figure S12). As shown in Figure 3b, the CB and VB positions of the InP dots were 0.33 eV higher than these of the CdSe dots. Such an approach is also powerful to reveal the difference in energy levels of different-shaped NCs with the same energy gap. Taking CdSe NCs for example (Supporting Information, Figure S13), 3.2 nm CdSe dots[42] presented the same exciton band gap of $E_g = 2.22$ eV as 3.2 × 7.5 nm CdSe rods;[43] however, the CB and VB positions of the dots were 0.12 eV higher than these of the rods. 4.0 nm CdSe dots had the same energy gap of 2.10 eV as 4.0 × 28 nm CdSe tetrapods,[44] and the CB and VB positions of the dots were 0.21 eV higher than those of the tetrapods (Figure 3c).

In conclusion, we developed a dopant approach to determine HOMO and LUMO levels of the semiconductor NCs based on electronic spectroscopy methods. Energy levels of the NCs with different compositions, sizes, and shapes were investigated by measuring the absorption and doping PL spectra of the NCs. The experimental results were found to be in good agreement with those obtained by the conventional CV method and theoretical calculations. Such an approach provides an alternative way for facile determination of the HOMO and LUMO levels of the semiconductor NCs, which is of great technical and fundamental importance in rational design of the devices with the NCs as building blocks.

Received: December 18, 2012
Revised: February 21, 2013

Keywords: band gap · dopants · energy levels · nanocrystals · photoluminescence

---

[1] S. G. Bailey, D. J. Flood, *Prog. Photovolt. Res. Appl.* **1998**, *6*, 1.
[2] R. P. Raffaelle, S. L. Castro, A. F. Hepp, S. G. Bailey, *Prog. Photovoltaics* **2002**, *10*, 433.
[3] B. Carlson, K. Leschkies, E. S. Aydil, X. Y. Zhu, *J. Phys. Chem. C* **2008**, *112*, 8419.
[4] A. Kongkanand, K. Tvrdy, K. Takechi, M. Kuno, P. V. Kamat, *J. Am. Chem. Soc.* **2008**, *130*, 4007.
[5] P. V. Kamat, *J. Phys. Chem. C* **2008**, *112*, 18737.
[6] A. Salant, M. Shalom, Z. Tachan, S. Buhbut, A. Zaban, U. Banin, *Nano Lett.* **2012**, *12*, 2095.
[7] H. L. Peng, C. Xie, D. T. Schoen, K. Mcllwrath, X. F. Zhang, Y. Cui, *Nano Lett.* **2007**, *7*, 3734.
[8] M. G. Panthani, V. Akhavan, B. Goodfellow, J. P. Schmidtke, L. Dunn, A. Dodabalapur, P. F. Barbara, B. A. Korgel, *J. Am. Chem. Soc.* **2008**, *130*, 16770.
[9] L. Sun, J. J. Choi, D. Stachnik, A. C. Bartnik, B. R. Hyun, G. G. Malliaras, T. Hanrath, F. W. Wise, *Nat. Nanotechnol.* **2011**, *7*, 369.
[10] J. R. I. Lee, R. W. Meulenberg, K. M. Hanif, H. Mattoussi, J. E. Klepeis, L. J. Terminello, T. van Buuren, *Phys. Rev. Lett.* **2007**, *98*, 146803.
[11] V. L. Colvin, A. P. Alivisatos, J. G. Tobin, *Phys. Rev. Lett.* **1991**, *66*, 2786.
[12] T. Van Buuren, L. N. Dinh, L. L. Chase, W. J. Siekhaus, L. J. Terminello, *Phys. Rev. Lett.* **1998**, *80*, 3803.
[13] J. Nanda, B. A. Kuruvilla, D. D. Sarma, *Phys. Rev. B* **1999**, *59*, 7473.
[14] P. K. Santra, R. Viswanatha, S. M. Daniels, N. L. Pickett, J. M. Smith, P. O'Brien, D. D. Sarma, *J. Am. Chem. Soc.* **2008**, *131*, 470.
[15] B. Alperson, I. Rubinstein, G. Hodes, D. Porath, O. Millo, *Appl. Phys. Lett.* **1999**, *75*, 1751.
[16] A. Franceschetti, H. Fu, L. W. Wang, A. Wang, *Phys. Rev. B* **1999**, *60*, 1819.
[17] J. Hu, L. Wang, L. Li, W. Yang, A. P. Alivisatos, *J. Phys. Chem. B* **2002**, *106*, 2447.
[18] R. Viswanatha, S. Sapra, T. Saha-Dasgupta, D. D. Sarma, *Phys. Rev. B* **2005**, *72*, 045333.
[19] J. Jasieniak, L. Smith, J. V. Embden, P. Mulvaney, M. Califano, *J. Phys. Chem. C* **2009**, *113*, 19468.
[20] J. Jasieniak, M. Califano, S. Watkins, *ACS Nano* **2011**, *5*, 5888.
[21] E. Kucur, J. Riegler, G. A. Urban, T. Nann, *J. Chem. Phys.* **2003**, *119*, 2333.
[22] S. K. Poznyak, N. P. Osipovich, A. Shavel, D. V. Talapin, M. Gao, A. Eychmueller, N. Gaponik, *J. Phys. Chem. B* **2005**, *109*, 1094.
[23] S. K. Haram, A. Kshirsagar, Y. D. Gujarathi, P. P. Ingole, O. A. Nene, G. B. Markad, S. P. Nanavati, *J. Phys. Chem. C* **2011**, *115*, 6243.
[24] N. Pradhan, D. Goorskey, J. Thessing, X. Peng, *J. Am. Chem. Soc.* **2005**, *127*, 17586.
[25] D. J. Norris, A. L. Efros, S. Erwin, *Science* **2008**, *319*, 1776.
[26] R. G. Xie, X. Peng, *J. Am. Chem. Soc.* **2009**, *131*, 10645.

[27] N. S. Karan, D. D. Sarma, R. M. Kadam, N. Pradhan, *J. Phys. Chem. Lett.* **2010**, *1*, 2863.

[28] R. Viswanatha, S. Brovelli, A. Pandey, S. A. Crooker, V. I. Klimov, *Nano Lett.* **2011**, *11*, 4753.

[29] B. B. Srivastava, S. Jana, N. Pradhan, *J. Am. Chem. Soc.* **2011**, *133*, 1007.

[30] R. G. Xie, D. Battaglia, X. G. Peng, *J. Am. Chem. Soc.* **2007**, *129*, 15432.

[31] N. Kullendorff, L. Jansson, L. A. Ledebo, *J. Appl. Phys.* **1983**, *54*, 3203.

[32] D. Pal, D. N. Bose, *J. Electron. Mater.* **1996**, *25*, 677.

[33] P. Reiss, M. Protiere, L. Li, *Small* **2009**, *5*, 154.

[34] M. L. Steigerwald, L. E. Brus, *Acc. Chem. Res.* **1990**, *23*, 183.

[35] A. P. Alivisatos, *Science* **1996**, *271*, 933.

[36] P. T. Jing, X. Yuan, W. Y. Ji, M. Ikezawa, Y. A. Wang, X. Y. Liu, L. G. Zhang, J. L. Zhao, Y. Masumoto, *J. Phys. Chem. C* **2010**, *114*, 19256.

[37] A. L. Robinson, R. H. Bube, *J. Appl. Phys.* **1971**, *42*, 5280.

[38] I. M. Vitomirov, C. M. Aldao, G. D. Waddill, C. Capasso, J. H. Weaver, *Phys. Rev. B* **1990**, *41*, 12.

[39] S. Gul, J. K. Cooper, C. Corrado, B. Vollbrecht, F. Bridges, J. Guo, J. Z. Zhang, *J. Phys. Chem. C* **2011**, *115*, 20864.

[40] S. Kim, J. Park, T. Kim, E. Jang, S. Jun, H. Jang, B. Kim, S. W. Kim, *Small* **2011**, *7*, 70.

[41] X. Ji, D. Copenhaver, C. Sichmeller, X. Peng, *J. Am. Chem. Soc.* **2008**, *130*, 5626.

[42] L. Liu, Z. Zhuang, T. Xie, Y. Wang, J. Li, Q. Peng, Y. Li, *J. Am. Chem. Soc.* **2009**, *131*, 16423.

[43] Z. Peng, X. G. Peng, *J. Am. Chem. Soc.* **2002**, *124*, 3343.

[44] R. G. Xie, U. Kolb, T. Basche, *Small* **2006**, *2*, 1454.