

Nanoscale Interaction Between CdSe or CdTe Nanocrystals and Molecular Dyes Fostering or Hindering Directional Charge Separation**

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Nanoscale materials will play an important role in the development of future devices and applications. Among these materials, semiconductor nanocrystals (NCs) are attracting increasing interest due to their relatively easy preparation and the striking properties determined by quantum confinement.^[1] There are several examples of the use of NCs in biological applications, spintronics, and electronic or optoelectronic devices as transistors, light-emitting diodes, lasers, or solar cells.^[1–3] In most of these devices and applications, charge- or energy-transfer processes play an important role. For example, energy transfer could allow for the design of single-molecule

optoelectronic switches, providing building blocks for more-complex nanophotonic circuitry.^[4] From the point of view of photovoltaic devices, the high extinction coefficient of NCs^[5] and their bandgap tunability, via control of their size, offer a wide range of possibilities in the development of photovoltaic devices in which charge transfer plays a determinant role. However, the successful application of the potentialities of semiconductor NCs for hot-carrier collection^[6] or multiple carrier generation^[7,8] has been very limited so far because the problems of internal recombination and low charge extraction could not be overcome. The use of NCs, in combination with molecular dyes as supracollector nanocomposites could offer an additional degree of control over their charge recombination and/or transfer properties, thus opening new routes in the development of photovoltaic and optoelectronic devices based on nanoscale interactions. Combined with the increase of the light-absorption-wavelength range due to the added absorption of both absorbers,^[9] this strategy of material design could allow for the successful design of novel, efficient supracollector nanocomposites.

A number of previous studies have explored the interaction between semiconductor NCs and dyes in energy^[4,10] and charge transfer.^[11–13] We have systematically studied the interaction between CdSe or CdTe NCs and four different dyes, namely three Ru dyes, N3, N719, and black dye (BD), the most commonly used materials in dye-sensitized solar cells,^[14] and a novel metal-free organic dye, FL6.^[15] The molecular structures of these dyes and their absorption spectra in solution are shown in Supporting Information Figures S1 and S2a, respectively. Nanocomposites of CdTe or CdSe NCs and different dyes have been evaluated in terms of their charge-separation properties in an external wide-bandgap semiconductor, TiO₂ (Figure 1a). The analysis of several combinations of colloidal CdSe and CdTe NCs and four different molecular dyes by electro-optical techniques shows a dramatic change in the NC–dye interaction depending on the NC semiconductor material used. The combined use of CdSe NCs and dyes increases the effect of injection from NCs towards external acceptors by nearly two orders of magnitude in a process dominated by charge transfer. In contrast, the interaction of CdTe NCs with the same dyes shows no significant effect.

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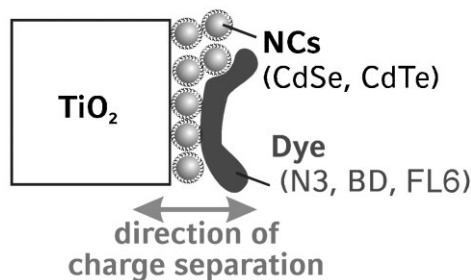
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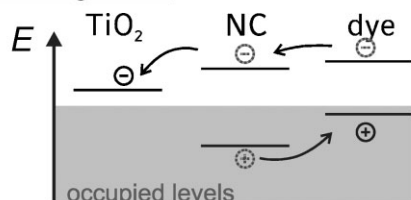
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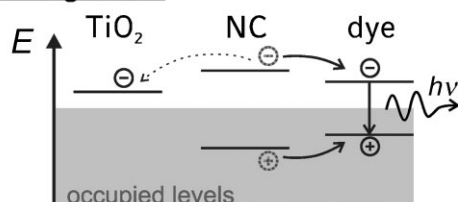
a) investigated system



b) type II alignment



c) type I alignment



d) new recombination channels

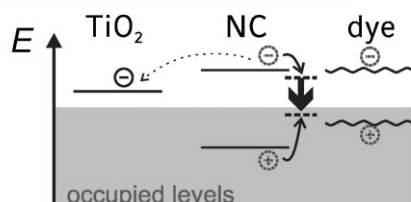


Figure 1. a) Scheme of the investigated nanocomposite system: CdSe or CdTe NCs combined with dyes and deposited on a compact TiO₂ layer as a substrate. b–d) Schematic illustration of possible energy-level alignments and related photogenerated-charge-carrier dynamics. b) Type II alignment between NCs and dye leads to charge separation. c) Type I alignment with a dye of a smaller bandgap hinders charge separation and energy transfer to the dye competes with the charge separation from the NCs. d) Changes in the local electronic environment may lead to the appearance of new recombination channels so that processes like dark recombination^[16] can take place.

Different alignments of the energetic levels of the single components may lead to different efficiencies of charge separation of the TiO₂–NC–dye system. Three different basic arrangements of the energetic levels are generally possible, as illustrated in Figure 1b–d. The only working alignment in terms of charge separation is a type II alignment, where the occupied and unoccupied electronic states descend from the dye via the NC to the TiO₂ (Figure 1b). Under the condition that charge transfer takes place both for holes and electrons, different energy gaps of the single materials do not play an important role; energy-transfer-like Förster resonant energy transfer (FRET) should not hinder charge separation as long as the

energetic steps are high enough to foster separation of excitons. In a type-I-aligned dye that has its lowest unoccupied molecular orbital (LUMO) below the conduction band (CB) of the NCs, electrons will have the choice of being transferred to TiO₂ or to the dye (Figure 1c). Directional charge separation will be weakened; the dye can only act as a hole scavenger and no longer inject electrons for the charge separation. Furthermore, FRET may be fostered, leading to an increased photoluminescence (PL) emission of the dye. Besides the most commonly discussed positions of the highest occupied molecular orbital (HOMO) and LUMO levels of the single nanomaterials, one has to consider that interactions between the components of the nanocomposite may result in the appearance of intraband states (Figure 1d). It is known that changes in the surroundings of the dyes may change their electronic conformations and optical properties. Blaudeck et al. discussed surface-trap states of the NCs induced due to interactions with the dye,^[16] which may lead to non-FRET exciton quenching. These effects compete strongly with charge separation and may hinder or even prevent it.

Figure 2 presents surface photovoltage (SPV) measurements for direct investigation of charge separation on TiO₂–NC–dye nanocomposites. The graphs show only the SPV amplitude, as the SPV phase was constant for each spectrum at values between –60° and –30°. The SPV spectra were not

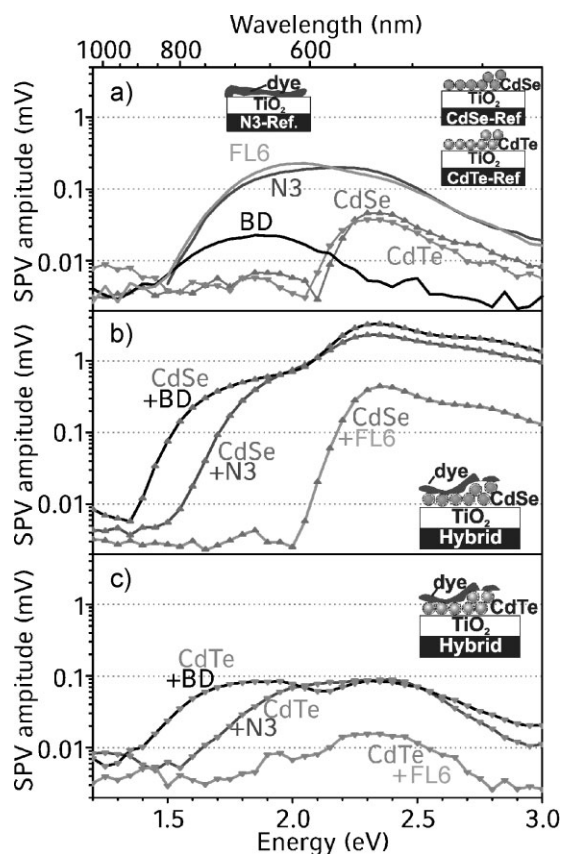


Figure 2. SPV amplitude spectra of a) individual dyes and individual NCs, b) CdSe520 NCs coated with N3, BD, and FL6 dyes, and c) CdTe520 NCs coated with N3, BD, and FL6 dyes. All samples were deposited on compact TiO₂ layers. The factors of the linear superposition are given in Table 1.

normalized to the photon flux since the SPV signal may no longer depend linearly on the intensity in the saturation regime and since thickness interference patterns from the substrate varied the exposure to the exciting light. Reference spectra are displayed in Figure 2a: dyes absorb from 1.5 eV upwards, leading to a transfer of only the electrons to the TiO₂. The NCs, with their larger bandgap, start to absorb from ≈2.1 eV, having a maximum at around 2.35 eV corresponding to the first absorption maximum at around 520 nm. The maximum amplitudes for a single absorbing material are below 0.2 mV. Henceforth, the NCs are denoted by giving the material with the absorption-peak maximum in nanometers, that is, CdSe510, CdSe520, CdTe520, and CdTe535.

Figure 2b and c presents SPV spectra of TiO₂-CdSe520-dye and TiO₂-CdTe520-dye systems, respectively. Contributions from the electron injection of both absorbers into the TiO₂ can be generally observed. The SPV spectra of the hybrid samples (Figure 2b and c) can be fitted using a linear superposition of the SPV spectra of the single absorbers (Figure 2a). Table 1 shows the coefficient factors of the linear superposition of TiO₂-NCs and TiO₂-dye structures that provide a close fit of the SPV amplitude for TiO₂-NC-dye structures (see Supporting Information Figure S3 for further details).

For all the CdSe520-dye samples (Figure 2b), the SPV amplitudes are significantly higher than 0.2 mV, indicating that CdSe NCs in combination with dye enhance the charge-separation efficiency. The TiO₂-CdSe-dye nanocomposites show a CdSe NC signal enhanced by more than one order of magnitude over the highest enhancements for the Ru dyes (by a factor of 70 for BD in particular). The SPV enhancement cannot be caused by a varying concentration of NCs as the reference spectra are taken from the same sample before the deposition of dye. It can be explained by an increase in the amount of electrons injected from the NCs into TiO₂ and an increased charge-separation distance when holes are transferred to the dye. Dyes are known to act as efficient hole scavengers,^[13,17] promoting the separation of electron-hole pairs in CdSe NCs, which significantly increases the net amount of electrons injected into the TiO₂ as internal recombination in the NCs is reduced by the hole scavenging. This effect is universal for all investigated dyes, indicating that the HOMO level of the dyes lies above the valence band (VB) of CdSe NCs.

Regarding the behavior of different dyes in CdSe520-dye samples, a qualitative difference is observed for Ru dyes and FL6. When only the dye is excited in the region from 1.5 to 2.0 eV, there is no signal for TiO₂-CdSe-FL6, while the signal

Table 1. Factors of the linear superposition of TiO₂-NCs and TiO₂-dye nanocomposite samples providing a close fit of the SPV amplitude in TiO₂-NC-dye structures.

TiO ₂ -CdSe520-Dye	CdSe520	Dye
N3	40	3
BD	70	22
FL6	13	0
TiO ₂ -CdTe520-Dye	CdTe520	Dye
N3	0.4	0.4
BD	2	4
FL6	0.4	0

of N3- or BD-containing hybrid nanocomposites is higher than the reference samples without CdSe NCs (Table 1). Several different effects play a part in the enhanced signal from Ru dyes in hybrid samples: (i) the NCs between the TiO₂ and the dye increase the separation distance, leading to a higher SPV potential; (ii) the separation efficiency can be increased by fast extraction of the electron by the CdSe NCs; (iii) the amount of dye adsorbed can be higher, leading to a higher number of separated charges. That there was no SPV signal below 2.0 eV in the TiO₂-CdSe-FL6 system indicates suppressed charge separation. The electrons are not injected into the NCs and no charge separation takes place. The reason may be a type I structure for CdSe-FL6 (Figure 1c), where the exciton binding energy in the dye hinders the charge separation, while, in the case of Ru dyes, electron injection from dyes into the TiO₂ occurs through the NCs, suggesting a type II structure (Figure 1b). Figure 3 shows a tentative scheme of the band-level positions of the different materials used in this study, with values obtained from the literature and from electrochemical measurements, as discussed in Supporting Information Figure S4. The absolute positions of the energy levels displayed in Figure 3 are in good correlation with the relative band positions extracted from the previous discussion based on SPV measurements.

Figure 2c presents SPV spectra of TiO₂-CdTe-dye systems. The significant difference compared to CdSe-based nanocomposites (Figure 2b) is obvious: the SPV signal of CdTe-based systems is always below 0.1 mV, thus being on the order of (or lower than) the reference samples (Figure 2a). The SPV signal of TiO₂-CdTe-FL6 became negligible and hardly rose from the noise background, indicating that FL6 was no longer able to act as a hole scavenger for positive charges from CdTe NCs. As seen in Table 1, there is only a minor enhancement for BD, while N3 or FL6 coatings result in a reduced SPV signal. Thus, all the dyes apparently no longer act as hole scavengers in combination with CdTe NCs and even the electron transfer from NCs to TiO₂ is partially hindered by the presence of these dyes. This situation corresponds to the arrangement of energy levels as shown in Figure 1c and d.

Taken together, Figure 2 presents significant differences between the charge-separation behavior of CdTe and CdSe

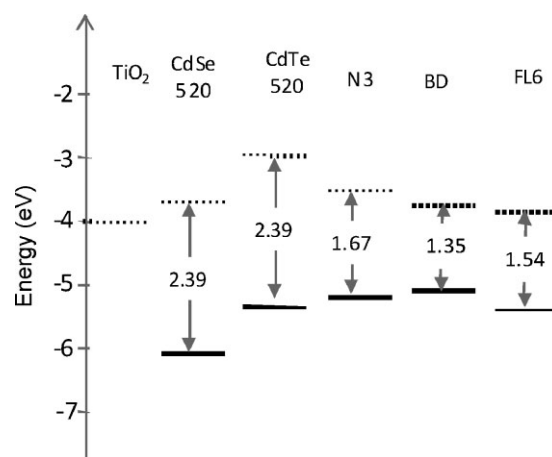


Figure 3. Scheme of the absolute energy-band position of the materials used in this study.

NCs in combination with dyes N3, BD, and FL6. The relative energy-level alignments proposed from the SPV results are in agreement with a type II junction between CdSe and CdTe NCs, with the CB and VB of CdSe lying below those of CdTe (Figure 3).^[18–20]

Results of optical studies on the hybrid nanocomposites and corresponding NCs are presented in Figure 4 for CdTe535 and CdSe510 with N3 dye. The plot of the optical densities is shown in Figure 4a and b for CdTe and CdSe, respectively. No absorption is measurable at 600 nm for the NCs, where the N3 dye still absorbs. It is thus possible to excite either the NCs and dye together (at 400 nm) or to separately excite the dye (at 600 nm). The PL spectrum of a CdTe535–N3 hybrid nanocomposite is shown in Figure 4c and that of the CdSe–N3 nanocomposite in Figure 4d, together with the corresponding reference PL spectra of single NC and dye components. The CdTe535 reference sample (Figure 4c) shows an emission at 565 nm (2.2 eV) originating from the radiative recombination of excitons in the CdTe core. This peak becomes strongly quenched in the hybrid sample with N3 dye. Due to background PL, we can no longer resolve the quenched CdTe535 peak in the hybrid nanocomposite but the quenching is significantly stronger than one order of magnitude. Additionally, in the hybrid sample, a new broad peak appears around 755 nm (1.64 eV), which may be attributed to N3 dye despite of a blueshift of 30 nm (60 meV). This infrared peak is strongly enhanced, most probably due to the energy transfer from CdTe

to the N3 dye, in agreement with the decrease in the SPV signal observed in these samples (Figure 2c). PL measurements at the excitation wavelength of 600 nm (2.07 eV), where only the dye is excited, revealed that the N3 dye in contact with the NCs also shows both the blueshift in emission and the PL enhancement. This is valid for N3 dye on both CdTe NCs (Figure 4c) and CdSe NCs (Figure 4d), indicating that contact with the NCs changes the optical properties of the N3 dye significantly. In Figure 4c and d, the set of PL spectra excited at 600 nm was rescaled so that the spectrum of the dye reference sample taken at 600 nm overlays the one taken at 400 nm in order to be able to directly compare the PL emission of the dye in the hybrid sample. We observe a similar shape of the spectra of the hybrid nanocomposite in the red and near-infrared parts of Figure 4c independently of the excitation energy. When the NCs in the nanocomposites are also excited using 400-nm light, this part of the spectra is further enhanced by about 45%, most probably due to energy transfer from the CdTe NCs to the dyes, as previously commented.

The CdSe510 reference sample (Figure 4d) shows two PL peaks when excited at 400 nm, one at around 535 nm (2.32 eV) originating from excitonic core emission and one peak of trap emission at about 730 nm (1.7 eV), which is a typical spectrum for CdSe NCs capped with thiol ligands.^[22] In the hybrid CdSe510–N3 sample, both peaks were strongly quenched but, since the trap emission is still pronounced, we cannot extract information about the spectrum of the dye. A reduced trap emission of CdSe NCs (Figure 4d) indicates that either the charge separation (proven by the SPV measurements discussed previously) takes place on a comparable time scale to the exciton trapping in the CdSe NCs or that the trapped charge carriers still can contribute to charge separation through the recycling of trapped excitons.^[21]

In summary, an additional degree of control over the electron charge-transfer process from CdSe NCs into TiO₂ is obtained when dye is coabsorbed with the CdSe NCs, strongly increasing the amount of charge injected into TiO₂ from CdSe NCs. Additionally, a type II junction between Ru dyes and CdSe NCs promote injection from the dye into the TiO₂. This could have important implications in the development of supracollectors with enhanced absorption and charge-separation properties for photovoltaic devices, which may be superior to the individual dye or NC components. When CdTe NCs are used instead of CdSe, the type I junction promotes energy transfer between the CdTe NCs and the dye. This effect should not necessarily be considered parasitic and could be explored in the development of optoelectronic devices as well.

Experimental Section

CdSe and CdTe NCs capped with thioglycolic acid (TGA) were synthesized in water by the methods previously described.^[22,23] The two CdSe NC samples had absorption-peak maxima (corresponding to the first excitonic transition) at 510 nm and 520 nm (Figure 4a and b and Supporting Information Figure S2b). Comparing the position of the peak maximum with sizing curves reported by Peng et al.,^[5] sizes of 2.4 and 2.5 nm were determined for CdSe NCs. The two CdTe NC samples had absorption peaks at 520 and 535 nm (Figure S2b), thus having sizes of 2.3 and 2.5 nm,

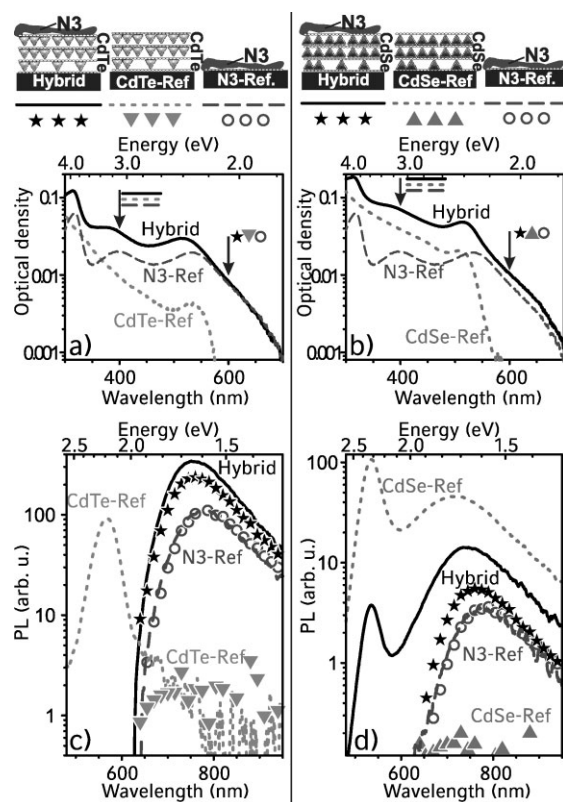


Figure 4. a,b) Absorption spectra and c,d) PL spectra of CdTe535–N3 and CdSe510–N3 hybrid nanocomposites and corresponding reference samples of single NC and dye components on glass substrates. Arrows indicate excitation wavelengths for PL spectra.

respectively.^[5,23] As mentioned above, the NCs are denoted by giving the material with the absorption-peak maximum in nanometers, that is, CdSe510, CdSe520, CdTe520, and CdTe535.

Two complementary techniques have been employed to distinguish between energy and charge transfer. The quenching of the PL signal from the NCs may indicate either energy or charge transfer, while SPV spectroscopy^[24] is an excellent technique to characterize charge transfer. To obtain a SPV signal, two consecutive processes are needed. First, light absorption inducing excess charge carriers in the analyzed sample and, second, charge separation producing a net electric field and, consequently, an induced photovoltage.^[25] We have previously used this method to study charge transfer from dyes^[26–28] and NCs^[17,29] into TiO₂, where the SPV signal (proportional to the amount of charge multiplied by the charge separation) is the fingerprint of electron injection from absorbing materials into a wide-bandgap semiconductor.^[29] The combination of both techniques allows us to distinguish between energy and charge transfer in the nanocomposite systems studied.

For SPV measurements, compact ultrathin TiO₂ layers (≈15-nm thickness) were deposited on FTO substrates by the ion-layer gas reaction (ILGAR) technique. NCs were deposited on TiO₂ layers by dipping the substrates into colloidal solution for 1 h and then drying in air. This process provided samples with 1–2 monolayers of NCs.^[29] After a SPV reference measurement of the NC-only-sensitized sample, the dye was deposited on top of the NC layer by drop casting. The dye concentration used in this process was 0.3 mM for Ru dyes in ethanol and 0.3 mM for FL6 dye in CH₂Cl₂. The SPV measurements were carried out in the arrangement of a parallel-plate capacitor.^[30] SPV spectra were measured in vacuum (≈10⁻¹ mbar) by using a halogen lamp with a quartz-prism monochromator for the excitation and a chopper for modulation (modulation frequency 2.5 Hz, signal detected with a lock-in amplifier).

PL measurements were carried out with Fluorolog-4 spectrofluorimeter (Horiba Jobin Yvon) on multilayer samples of NCs deposited by the layer-by-layer (LbL) technique^[18] and dye spin coated on top. Glass served as a substrate to analyze the interaction between NCs and dye only while avoiding the effect of charge injection into the substrate. The samples were made through alternating deposition of the positively charged polyelectrolyte poly(diallyldimethylammonium chloride) (PDDA, 1 g L⁻¹ in a 0.5 M NaCl solution) and negatively charged CdTe535 NCs (concentration 20 μM) or CdSe510 NCs (1100 μM). A thoroughly cleaned microscopy glass slide, activated by 5 min of N₂-plasma cleaning and precovered with a PDDA film, served as substrate. Three NC–PDDA bilayers were deposited. Dipping times of 15 min in each solution were used. The N3 dye was spin coated using 100 μL of 0.3 mM solution in ethanol at 3000 rpm over 30 s. The NC-only reference samples were spin coated with pure ethanol for comparability reasons. Absorption spectra measured before and after the N3 spin coating indicated that the same amount of dye was deposited on samples with 3–20 NC layers, indicating that interpenetration of the dye into the NC layers is insignificant.

Keywords:

charge separation · dyes · nanocrystals · quantum dots · solar cells

- [1] A. P. Alivisatos, *Science* **1996**, *271*, 933.
- [2] P. V. Kamat, *J. Phys. Chem. C* **2008**, *112*, 18737.
- [3] V. I. Klimov, *J. Phys. Chem. B* **2006**, *110*, 16827.
- [4] K. Becker, J. M. Lupton, J. Müller, A. L. Rogach, D. V. Tapalin, H. Weller, *J. Feldmann, Nat. Mater.* **2006**, *5*, 777.
- [5] W. Yu, L. H. Qu, W. Z. Guo, X. G. Peng, *Chem. Mater.* **2003**, *15*, 2854.
- [6] A. J. Nozik, *Physica E* **2002**, *14*, 115.
- [7] J. A. McGuire, J. Joo, J. M. Pietryga, R. D. Schaller, V. I. Klimov, *Acc. Chem. Res.* **2009**, *41*, 1810.
- [8] M. T. Trinh, A. J. Houtepen, J. M. Schins, T. Hanrath, J. Piris, W. Knulst, A. P. L. M. Goossens, L. D. A. Siebbeles, *Nano Lett.* **2008**, *8*, 1713.
- [9] H. Lee, H. C. Leventis, S.-J. Moon, P. Chen, S. Ito, S. A. Haque, T. Torres, F. Nüesch, T. Geiger, S. M. Zakeeruddin, M. Grätzel, M. K. Nazeeruddin, *Adv. Funct. Mater.* **2009**, *19*, 2735.
- [10] A. M. Funston, J. J. Jasieniak, P. Mulvaney, *Adv. Mater.* **2008**, *20*, 4274.
- [11] J. Huang, D. Stockwell, Z. Huang, D. L. Mohler, T. Lian, *J. Am. Chem. Soc.* **2008**, *130*, 5632.
- [12] S. N. Sharma, Z. S. Pillai, P. V. Kamat, *J. Phys. Chem. B* **2003**, *107*, 10088.
- [13] M. Sykora, M. A. Petruska, J. Alstrum-Acevedo, I. Bezel, T. J. Meyer, V. I. Klimov, *J. Am. Chem. Soc.* **2006**, *128*, 9984.
- [14] B. O'Regan, M. Grätzel, *Nature* **1991**, *353*, 737.
- [15] E. M. Barea, R. Caballero, F. Fabregat-Santiago, P. de la Cruz, F. Langa, J. Bisquert, *Chem. Phys. Chem.* **2009**, in press.
- [16] T. Blaudeck, E. I. Zenkevich, F. Cichos, C. von Borczyskowski, *J. Phys. Chem. C* **2008**, *112*, 20251.
- [17] I. Mora-Seró, T. Dittrich, A. S. Sussha, A. L. Rogach, J. Bisquert, *Thin Solid Films* **2008**, *516*, 6994.
- [18] D. Gross, A. S. Sussha, T. A. Klar, E. Da Como, A. L. Rogach, J. Feldmann, *Nano Lett.* **2008**, *8*, 1482.
- [19] I. Gur, N. A. Fromer, N. L. Geier, A. P. Alivisatos, *Science* **2005**, *310*, 462.
- [20] S.-H. Wei, S. B. Zhang, A. Zunger, *J. Appl. Phys.* **2000**, *87*, 1304.
- [21] T. Franzl, T. A. Klar, S. Schietinger, A. L. Rogach, J. Feldmann, *Nano Lett.* **2004**, *4*, 1599.
- [22] A. L. Rogach, A. Kornowski, M. Gao, A. Eychmüller, H. J. Weller, *J. Phys. Chem. B* **1999**, *103*, 3065.
- [23] A. L. Rogach, T. Franzl, T. A. Klar, J. Feldmann, N. Gaponik, V. Lesnyak, A. Shavel, A. Eychmüller, Y. P. Rakovich, J. F. Donegan, *J. Phys. Chem. C* **2007**, *111*, 14628.
- [24] L. Kronik, Y. Shapira, *Surf. Sci. Rep.* **1999**, *37*, 1.
- [25] I. Mora-Seró, T. Dittrich, G. Garcia-Belmonte, J. Bisquert, *J. Appl. Phys.* **2006**, *100*, 103705.
- [26] T. Dittrich, I. Mora-Seró, G. Garcia-Belmonte, J. Bisquert, *Phys. Rev. B* **2006**, *73*, 045407.
- [27] I. Mora-Seró, J. A. Anta, T. Dittrich, G. Garcia-Belmonte, J. Bisquert, *J. Photochem. Photobiol. A* **2006**, *182*, 280.
- [28] I. Mora-Seró, T. Dittrich, A. Belaidi, G. Garcia-Belmonte, J. Bisquert, *J. Phys. Chem. B* **2005**, *109*, 14932.
- [29] I. Mora-Seró, J. Bisquert, T. Dittrich, A. Belaidi, A. S. Sussha, A. L. Rogach, *J. Phys. Chem. C* **2007**, *111*, 14889.
- [30] V. Duzhko, V. Y. Timoshenko, F. Koch, T. Dittrich, *Phys. Rev. B* **2001**, *64*, 75204.

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