

Photochemical Electronic Doping of Colloidal CdSe Nanocrystals

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Supporting Information

ABSTRACT: A method for electronic doping of colloidal CdSe nanocrystals (NCs) is reported. Anaerobic photoexcitation of CdSe NCs in the presence of a borohydride hole quencher, $\text{Li}[\text{Et}_3\text{BH}]$, yields colloidal *n*-type CdSe NCs possessing extra conduction-band electrons compensated by cations deposited by the hydride hole quencher. The photodoped NCs possess excellent optical quality and display the key spectroscopic signatures associated with NC *n*-doping, including a bleach at the absorption edge, appearance of a new IR absorption band, and Auger quenching of the excitonic photoluminescence. Although stable under anaerobic conditions, these spectroscopic changes are all reversed completely upon exposure of the *n*-doped NCs to air. Chemical titration of the added electrons confirms previous correlations between absorption bleach and electron accumulation and provides a means of quantifying the extent of electron trapping in some NCs. The generality of this photodoping method is demonstrated by initial results on colloidal CdE ($\text{E} = \text{S}, \text{Te}$) NCs as well as on CdSe quantum dot films.

The generation and manipulation of charge carriers in semiconductor nanostructures is central to emerging solar,^{1–5} battery,^{6,7} nanoelectronics,⁸ and nanospintronics^{9–11} technologies, as well as to nanocrystal (NC) blinking and multicarrier Auger processes that impact the use of such nanostructures as phosphors in display, lasing, or imaging technologies.^{12–14} To study the physical properties of semiconductor nanostructures possessing “extra” charge carriers, chemical reduction of colloidal NCs,¹⁵ electrochemical reduction of quantum dot (QD) solids,¹⁶ and low-temperature charge separation¹⁷ have been used to introduce the carriers. Many of these processes involve harsh reductants, require precipitation and ligand exchange, or only occur at cryogenic temperatures. A general method for introducing additional charge carriers to free-standing colloidal NCs would enable a wide variety of experiments and applications involving electronically doped semiconductor NCs.

Photochemistry offers a convenient in situ method for modulating carrier densities in colloidal NCs. For photochemical *n*-doping, capture of photogenerated holes by suitable hole quenchers strands extra electrons inside the NCs, compensated by cations deposited upon quencher oxidation. This method has been applied successfully with several oxide semiconductor NCs.^{18–21} Although chalcogenide semiconductor NCs are frequently used as sensitizers in solar photochemistry, photovoltaic, and photoelectrochemical devices because of their strong visible absorption and ability to separate photogenerated

charges,^{1–5} photochemical electronic doping of this class of nanomaterials has not been explored. In contrast with oxides, chalcogenides such as CdE ($\text{E} = \text{S}, \text{Se}, \text{Te}$) possess shallow valence bands and are consequently not as reactive toward many hole quenchers commonly used with oxides. For generality, more reactive hole quenchers are thus required. Here, we report facile and reversible photodoping of colloidal CdSe NCs using a reactive borohydride, $\text{Li}[\text{Et}_3\text{BH}]$, as the hole quencher (Figure 1). This photodoping allows formation of kinetically stable

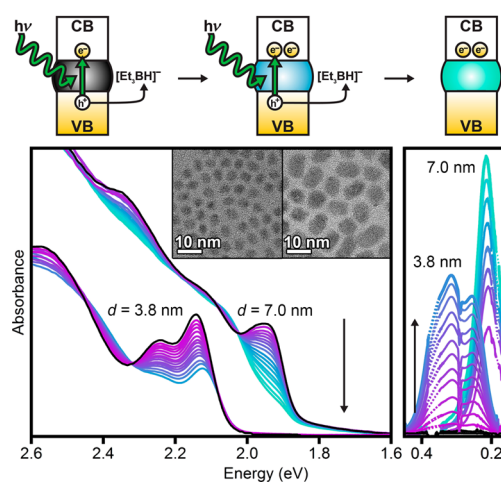


Figure 1. Top: Nanocrystal photodoping using $\text{Li}[\text{Et}_3\text{BH}]$. The photogenerated hole (h^+) is quenched by $\text{Li}[\text{Et}_3\text{BH}]$, leaving an electron (e^-) in the conduction band. Further photoexcitation can add more electrons. Bottom: Absorption spectra of $d = 3.8$ nm and $d = 7.0$ nm CdSe NCs at various stages of photodoping starting from no prior photoexcitation (black) to maximum photodoping (teal). The data show exciton bleach and growth of IR absorption with photodoping. Inset: TEM images of these NCs.

colloidal *n*-type CdSe NCs without the surface degradation caused by chemical reductants examined previously. Moreover, this approach allows CdSe NC photodoping even in the presence of ZnSe shells that impede direct electron injection. Although the present work is focused on colloidal CdSe QDs, it is expected to be broadly applicable for preparing *n*-type NCs in various forms. Proof-of-concept results confirm successful CdE ($\text{E} = \text{S}, \text{Te}$) QD photodoping, as well as photodoping of CdSe QD solids.

Colloidal trioctylphosphine-oxide-ligated CdSe NCs with average diameters (d) of 3.8 and 7.0 nm, as determined by excitonic absorption and transmission electron microscopy

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(Figure 1), were prepared by established synthetic procedures.²² These NCs were transferred to dry, deoxygenated toluene and stored in the presence of excess trioctylphosphine oxide under inert atmosphere. Under these conditions, exposure to visible or UV radiation does not alter the NC spectra or cause sample degradation. After addition of $\text{Li}[\text{Et}_3\text{BH}]$ to these suspensions, exposure to light exceeding the band gap energy causes a bleach of the first excitonic absorption feature (Figure 1). This bleach occurs even with excitation solely by ambient room light, but no absorption changes are detected without photoexcitation (Figure S3). The absorption bleach approaches an asymptotic limit with extended photoexcitation. When the absorption spectrum is unchanged over ~ 30 s of photoexcitation, the samples are considered to have reached their maximum photodoping. Photodoping can be halted at any intermediate stage, the partially photodoped CdSe NCs used for spectroscopic measurements, and the photoexcitation then resumed to increase photodoping up the asymptotic limit. After spectroscopic or other measurements are complete, exposure of these n -doped NCs to an oxidant such as O_2 (air) completely reverses the absorption bleach (*vide infra*).

The absorption bleach is a signature of the presence of one or more delocalized electrons in the quantum-confined CdSe NC conduction band.¹⁵ This bleach is accompanied by a concurrent redshift of the first two excitonic absorption bands (e.g., ~ -15 meV for the $d = 3.8$ nm CdSe NCs at maximum photodoping in Figure 1, see Figure S4). This redshift is comparable to that of trion luminescence relative to neutral exciton luminescence in other CdSe QDs^{23,24} and is thus tentatively attributed to the reduced energy required for trion formation by photoexcitation of n -doped CdSe NCs. Electrostatic exciton stabilization by localized charges may also contribute to the redshift. Infrared absorption spectroscopy verifies the presence of extra quantum-confined electrons, showing intense new absorption corresponding to intraband excitations of the newly introduced conduction electrons (Figure 1), with an energy that increases with decreasing NC diameter. A per-electron molar extinction coefficient of $(8.9 \pm 0.6) \times 10^4 \text{ M}_e^{-1} \cdot \text{cm}^{-1}$ is estimated at the IR absorption maximum (0.32 eV) of $d = 3.8$ nm CdSe NCs (Figure S10). This IR absorption verifies that the added electrons do not simply reside in localized trap states. Interestingly, the IR absorption of the smaller NCs shows distinct structure. Similar structure has been seen previously in chemically reduced CdSe NCs¹⁵ and may reflect a low-symmetry splitting of the 1P_e degeneracy. The IR absorption grows with photodoping (Figure 1), and in some cases blueshifts slightly. These blueshifts are small compared to those observed in ZnO NCs heavily photodoped (average electron density, $\langle n_{\text{max}} \rangle \approx 6 \times 10^{20} \text{ cm}^{-3}$) using the same hole quencher,²¹ suggesting smaller carrier densities in the photodoped CdSe NCs. The IR spectroscopic changes are also fully reversed upon NC reoxidation by exposure to air.

To quantify the maximum (average) number of excess electrons per NC ($\langle n_{\text{max}} \rangle$) achievable by these methods, the magnitude of the absorption bleach was analyzed. Previous studies have established a linear correlation between the number of CdSe conduction-band electrons and the fractional bleach at the first excitonic absorption maximum, where a 100% bleach corresponds to 2 conduction-band electrons.^{19,25} By Gaussian deconvolution of the data in Figure 1 (Figure S4), we find a maximum bleach of 41% for the $d = 3.8$ nm CdSe NCs and 98% for the $d = 7.0$ nm CdSe NCs. The data in Figure 1 thus suggest

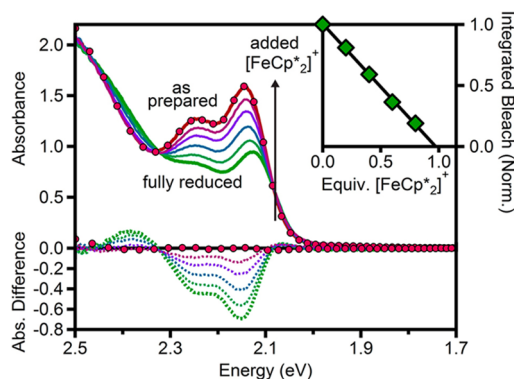


Figure 2. Absorption spectra of $d = 3.8$ nm (43 μM) CdSe NCs collected during redox titration in 1:1 toluene/THF. The red spectrum shows data collected before introduction of $\text{Li}[\text{Et}_3\text{BH}]$. The solid green spectrum is of the maximally photodoped NCs, and the red circles represent the reoxidized NCs. The intermediate spectra were collected following incremental oxidation by addition of $[\text{FeCp}^*_2]^+$ aliquots. The corresponding difference spectra ($A - A_{\text{as prepared}}$) are plotted as dotted lines. Inset: Integrated absorption bleach of the first excitonic feature as a function of $[\text{FeCp}^*_2]^+$ equivalents, with a solid line showing the best linear fit to the data. The crossing of this line with zero indicates 0.97 electron per NC.

$\langle n_{\text{max}} \rangle \approx 0.8$ ($\langle N_{\text{max}} \rangle \approx 2.8 \times 10^{19} \text{ cm}^{-3}$) and 2 ($\langle N_{\text{max}} \rangle \approx 1.1 \times 10^{19} \text{ cm}^{-3}$), respectively.

An attractive aspect of the photodoping method described here is that the resulting n -type NCs are amenable to direct chemical titration of the added electrons, something not possible with chemically reduced NCs because of the excess reductant present under equilibrium conditions. Chemical titration of excess electrons in chalcogenide NCs has not been described previously. Figure 2 shows electronic absorption spectra of the 3.8 nm CdSe NCs from Figure 1 before photodoping, at maximum photodoping, and at various stages of reoxidation by $[\text{FeCp}^*_2][\text{BAR}_\text{F}]$ ($[\text{FeCp}^*_2]^+$ = decamethylferrocenium, $[\text{BAR}_\text{F}]^-$ = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate). Titration of these 3.8 nm NCs yields an $\langle n_{\text{max}} \rangle$ of 0.97, consistent with the spectroscopic estimation. Titrations were also performed on $d = 4.6$ and 7.0 nm CdSe samples (Supporting Information (SI)). Titration of the 4.6 nm NCs yields $\langle n_{\text{max}} \rangle = 1.1$, similar to the 1.4 estimated using absorption spectroscopy. By contrast, although the absorption bleach of the 7.0 nm CdSe suggests ~ 2.0 conduction-band electrons per NC, titration requires nearly 30 equiv of $[\text{FeCp}^*_2][\text{BAR}_\text{F}]$. This divergence suggests substantial electron trapping in these NCs, e.g., by surface diselenide bonds.²⁶ Many previous experiments have suggested the existence of near-band-edge electron traps in CdSe NCs. Such traps have been proposed to play major roles in blinking and other physical processes,^{5,13,27} but little is known about their potentials, densities, or redox reactivities. These results emphasize that titration is also sensitive to other electrons accessible at the potential defined by the titrant, such as trapped electrons that do not contribute to the band-edge absorption bleach, and titration therefore complements the spectroscopic evaluation described above.

A second attractive feature of this photodoping methodology is that the resulting colloidal n -type NCs are of high spectroscopic quality, making them well suited for advanced characterization by various spectroscopic techniques. For illustration, Figure 3 summarizes the changes in room-temperature photoluminescence of $d = 4.6$ nm CdSe NCs upon

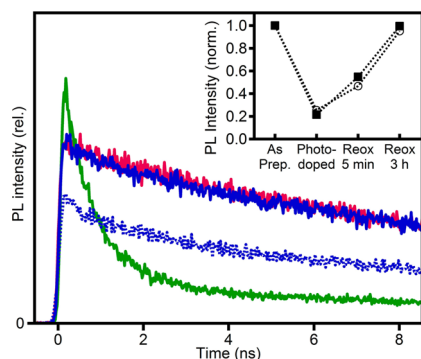


Figure 3. Time-resolved photoluminescence decay of $d = 4.6$ nm CdSe/ZnSe NCs measured before photodoping (red), after photodoping (green), after 5 min reoxidation in air (dotted blue), and after 3 h in air (solid blue). Inset: Normalized steady-state (squares) and time-resolved (at 7.5 ns, circles) photoluminescence intensities showing slow reoxidation in air.

photodoping. For these measurements, thin ZnSe shells were grown around the NCs to passivate surface traps and hence suppress nonradiative decay. Prior to photodoping, these NCs show single-exponential excitonic photoluminescence decay with a time constant of $\tau = 16$ ns. After photodoping to $\langle n \rangle \approx 0.5$ (estimated by absorption spectroscopy), their steady-state photoluminescence is quenched by $\sim 80\%$ (Figure 3, inset), and the two characteristic signatures of trion decay are observed in their photoluminescence decay curves: (1) an increase in luminescence intensity at short times (< 500 ps) relative to the neutral NCs, and (2) appearance of a fast decay component attributable to Auger recombination. The persistence of a slow decay component in the photodoped sample reflects the presence of some undoped CdSe NCs, as expected for $\langle n \rangle \approx 0.5$. Analysis of these data yields a trion decay time of $\tau_{x-} = 750$ ps that agrees well with those reported previously for electrochemically reduced CdSe/CdS core/shell NCs in films,²⁸ but here has been collected on a high-optical-quality colloidal suspension with minimal sample perturbation.

Like absorption, the luminescence also recovers completely upon introduction of air, but this recovery is markedly slower than the absorption recovery. Whereas absorption recovers within seconds of exposure to air, both the time-resolved and steady-state luminescence intensities have not fully recovered even after 5 min in air (Figure 3, inset). This discrepancy indicates that the NC photoluminescence is sensitive not only to the presence of conduction-band electrons but also to other changes induced upon photodoping, which we tentatively associate with electron trapping. These results suggest that deeply trapped electrons react more slowly with air than conduction electrons do, as might be anticipated from Marcus-theory considerations. The reactivities and reaction dynamics of redox-active traps in semiconductor NCs have been of central interest to many aspects of NC photophysics and electronics,^{3,5,13,27} and the present results illustrate a promising new avenue for deliberate investigation of such trap chemistries.

A final important feature of this photodoping methodology that distinguishes it from all other chalcogenide NC reduction strategies reported to date is that electrons are placed in the conduction band by photoexcitation, not by equilibrium electron injection. Photodoping is fundamentally governed by the reactivities of the quenchers toward the photogenerated holes.²¹ For some applications, n -type nanostructures encapsu-

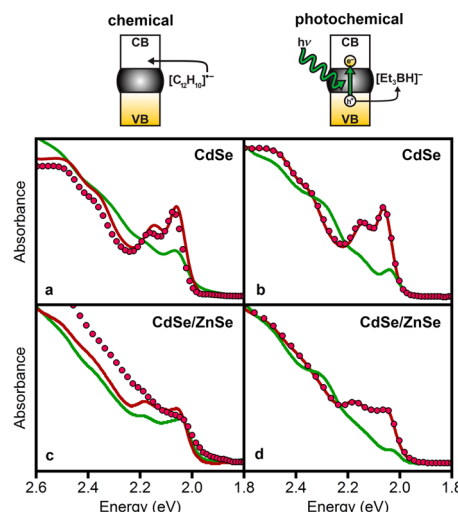


Figure 4. Top: Scheme outlining chemical and photochemical doping methods. Absorption spectra of $d = 4.6$ nm CdSe NCs with and without a ~ 1 nm ZnSe shell, measured before reduction (red lines), after maximum reduction (green lines), and after reoxidation by air (red circles). Panels a and c show reduction of core and core/shell NCs using 10^3 and 10^4 equiv of Na[biphen], respectively. Panels b and d show photodoping of the same core and core/shell NCs, respectively, using ~ 50 equiv of Li[Et₃BH].

lated within barrier heterostructures may be desired. In other cases, competing redox reactions may interfere with direct NC reduction. To illustrate, Figure 4 summarizes the results obtained when the $d = 4.6$ nm CdSe NCs of Figure 3 and the same NCs with ~ 1 nm thick (~ 4 monolayers) ZnSe shells were reduced by either chemical or photochemical methods. For chemical reduction, Na[biphen] ([biphen] $^{\bullet-}$ = biphenyl radical anion) was used, as reported previously.¹⁵

Figure 4a shows that addition of 10^3 equiv of Na[biphen] reduces the core $d = 4.6$ nm CdSe NCs, consistent with literature results.¹⁵ The absorption bleach is similar to that achieved photochemically with the same NCs (Figure 4b, both $\sim 60\%$), albeit with the appearance of a small sub-bandgap tail and less complete reversibility in the case of chemical reduction. The core/shell NCs show markedly different results: Incremental addition of up to 10^4 equiv of Na[biphen] causes only a small ($\sim 20\%$) bleach of the first excitonic absorption (Figure 4c). A large sub-bandgap absorption tail and an offset at higher energy are observed, suggestive of scattering due to NC clustering or absorption due to trapped electrons. Furthermore, the spectral changes are only partially reversed upon exposure to air, suggesting substantial NC degradation. These irreversible changes are attributed to deleterious side reactions of the chemical reductant, Na[biphen]. In contrast, photodoping the same core/shell NCs (Figure 4d) yields a clean $\sim 85\%$ bleach of the first exciton that is rapidly and completely reversed upon exposure to air. These data demonstrate superior results with photodoping compared to chemical reduction. The high optical quality of the photodoped NC samples and the excellent reversibility of the photodoping will facilitate future spectroscopic and electronic structure studies of these and related n -type nanostructures.

Although this study has focused on colloidal CdSe QDs, preliminary results have also been obtained for colloidal CdE (E = S, Te) NCs and CdSe QD films (SI). CdE (E = S, Te) NCs of $d = 6.0$ and 4.1 nm were prepared by established methods.^{29,30} Anaerobic photoexcitation of these NCs in the presence of

Li[Et₃BH] leads to successful photodoping as evidenced by a band-edge absorption bleach or new IR absorption similar to that obtained for photodoped CdSe NCs. Perhaps more intriguingly, anaerobic photoexcitation of CdSe QD solids prepared by co-deposition of $d = 7.0$ colloidal CdSe NCs with Li[Et₃BH] onto fluorine-doped tin oxide electrodes also yields comparable n -doping to that found in solution. In all cases, these changes are fully reversed upon reoxidation in air. These results, in conjunction with our recent demonstration of enhanced ZnO NC photodoping using Li[Et₃BH],²¹ demonstrate this as a general and versatile approach for preparing n -type semiconductor NCs, both in colloidal suspensions and in solids. The precise roles played by the charge-compensating cations (Li⁺, H⁺) in this chemistry remain an open topic for future research. In ZnO NCs, bulky cations slow and decrease the extent of photodoping,²¹ but it is not yet known whether small cations associate with the surfaces or can intercalate into the internal volumes of such photodoped NCs.

In summary, a new method for preparation of colloidal n -type CdSe nanocrystals has been demonstrated that involves photodoping using Li[Et₃BH] as a hole quencher. This hydride is commercially available, shelf-stable, and compatible with the solvents and ligands commonly used for colloidal semiconductor NCs. The n -type CdSe NCs prepared by this method are kinetically stable, show excellent optical quality, and are readily returned to their original oxidation state upon exposure to air. Photodoping is successful even for CdSe/ZnSe core/shell heterostructures that are significantly more difficult to reduce directly with Na[biphen]. This photodoping methodology is also applicable to other colloidal chalcogenide and oxide NCs, offering a facile general approach to in situ NC electronic doping. As such, this methodology will enable a broad range of fundamental science experiments to address n -type doped NC electronic structures, electron spin dynamics, QD plasmonics, and inter-NC electron-transfer processes, among other intriguing topics. It is equally attractive for in situ, nondestructive, tunable carrier doping of QD solids currently of interest in more applied areas of QD photovoltaics, photodetectors, and transistors.

■ ASSOCIATED CONTENT

■ Supporting Information

Additional spectroscopic and TEM data, photodoping results for CdS and CdTe NCs and CdSe NC solids, and experimental procedures for NC photodoping, absorption spectroscopy, and photoluminescence. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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