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Quantum Dots OPEN ACCESS

On Carbon "Replacing" the Core in Classical Semiconductor Core/ZnS Quantum Dots

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Abstract Among best known semiconductor quantum dots (QDs) are CdSe/ZnS core/shell nanostructures, whose much enhanced photoexcited state properties over those of uncapped CdSe nanoparticles are rationalized in the literature such that "the ZnS capping with a higher bandgap than CdSe passivates the core crystallite removing the surface traps". In this work, the method commonly employed in the ZnS capping of CdSe for CdSe/ZnS QDs was applied to the same capping of small carbon nanoparticles (CNPs) for CNP/ZnS core/shell nanostructures, which are conceptually and configuration-wise equivalent to the replacement of the semiconductor (CdSe) core with CNP in the classical core/shell QDs. The fluorescence emission properties of CNP/ZnS core/shell nanostructures were found to be similar to those of organic functionalized CNPs in classically defined carbon dots (CDots), both dramatically enhanced from those of "naked" CNPs in solvent dispersions. Mechanistic implications of the findings are discussed.

Keywords quantum dots, carbon dots, core/shell nanostructures, surface passivation, fluorescence properties, mechanism

Introduction

Among classical semiconductor quantum dots (QDs), CdSe/ZnS core/shell nanostructures (Figure 1) are most famous and popular in terms of technological applications.[1,2] In early investigations of CdSe nanoparticles for quantum confinement effects and the associated tuning in optical spectroscopic properties, the surface capping of CdSe nanoparticles was found to be necessary to protect the photoexcited states of the nanoparticles for high fluorescence emission quantum yields. The selection of wide bandgap semiconductors like ZnS for the surface capping purpose was rationalized such that with the wide bandgap of ZnS it could effectively stop the leaking of the photoexcitation energy through the CdSe nanoparticle surface,[1-5] which resulted in the invention of CdSe/ZnS QDs and their increasing popularity even since.[1,2]

The popularity of CdSe/ZnS QDs has also benefitted from successful development of the relatively facile synthesis methods.[1-5] Typically, dimethylcadmium and trioctylphosphine selenide dissolved in hot coordinating solvent trioctylphosphine oxide (TOPO) or trioctylphosphine (TOP) are decomposed at a high temperature (*e.g.*, 350 °C) into the formation of CdSe nanoparticles, followed by the separation of the nanoparticles from the reaction mixture for subsequent capping with ZnS,[4] or without the separation at all to proceed with the capping in "one-pot".[3] Either way, the capping step is generally at a lower temperature (140—220 °C) sufficient for the decomposition of organo zinc and sulfur compounds such as diethylzinc and hexamethyldisilathiane, respectively, for the formation of ZnS on the CdSe nanoparticle surface.[3-5]

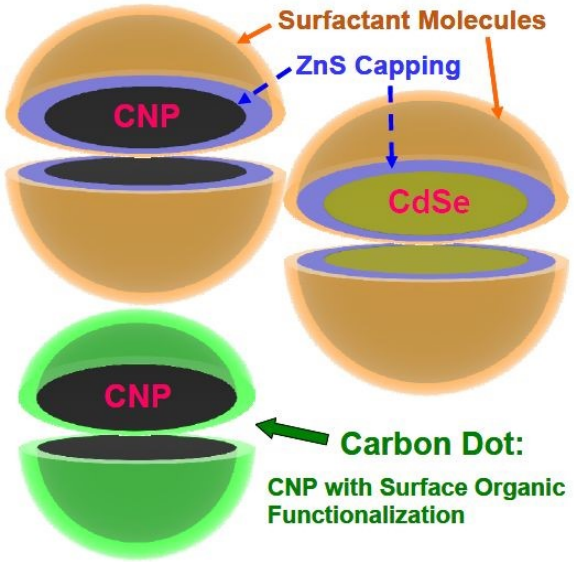

Figure 1 Cartoon illustration on the structural similarity of the CNP/ZnS core/shell nanostructure (upper-left) with CdSe/ZnS QD (right) and classical carbon dot (lower-left).

Over the years, there have been many variations with different organometallic precursors and processing conditions, but a common feature has been the use of solvents like TOPO and TOP for their surfactant-like characteristics to control the nucleation and growth of the targeted nanoparticles and to avoid Ostwald ripening.[1,2,5]

The surface capping might be considered as equivalent

to highly effective surface passivation of the CdSe nanoparticles by the wide bandgap semiconductor like ZnS, resulting in substantial improvements in the desired optical spectroscopic properties. Similarly strong surface passivation effect has been found in the organic functionalization of small carbon nanoparticles (CNPs), and the resulting surface functionalized CNPs are dubbed carbon "quantum" dots or carbon dots (CDots, Figure 1).[6-8] On the electronic transitions reflected by the observed optical spectroscopic properties of CNPs and their derived CDots, the optical absorptions of CNPs and CDots are similar,[9-11] but upon photoexcitation their excited state characteristics are very different, because in CDots the organic functionalization of the core CNPs (Figure 1) provides effective surface passivation that prevents the leaking of the excitation energy, analogous to the surface capping effect in CdSe/ZnS QDs. For example, CDots are brightly fluorescent,[6-10] in sharp contrast to the very weakly emissive nature of "naked" CNPs in various solvent dispersions.[11] The photoexcited CDots are also capable of many functions for which classical semiconductor QDs are famous, such as photoinduced redox characteristics and highly potent antimicrobial activities.[12,13]

In the work reported here, the popular synthesis protocol for the capping of CdSe nanoparticles with ZnS for CdSe/ZnS QDs was employed for the similar capping of CNPs by ZnS for the targeted CNP/ZnS core/shell nanostructure. Conceptually and configuration-wise, the CNP/ZnS nanostructure is equivalent to "replacing" the CdSe core with CNP in the classical core/shell QDs (Figure 1), even though the "replacement" seems mostly phenomenological because of the fact that CNP is hardly recognized as a semiconductor in any classical and/or quantum mechanical definitions. Nevertheless, the same ZnS capping of CNPs as that of CdSe nanoparticles resulting in similarly substantial property enhancements/changes may have major implications to the understanding of the role and significance with the surface passivation effects, not only in CDots but also in more established core/shell semiconductor QDs.

Experimental

Materials

The carbon nanopowder sample was purchased from US Research Nanomaterials, Inc. Trioctylphosphine (TOP, > 97%) and trioctylphosphine oxide (TOPO, > 90%) were obtained from Strem Chemicals, Inc., hexadecylamine (HDA, > 90%) from Thermal Science, zinc nitrate hexahydrate (reagent grade) from Ward's Science, dodecanethiol (DDT, > 95%) from TCI America, methanol (ACS grade) from Mallinckrodt Chemicals, nitric acid (68%—70%, ACS grade) from VWR, and toluene (HPLC grade) and hexane (HPLC grade) from Fisher Scientific.

Measurement

Optical absorption spectra were recorded on Shimadzu UV-1280 and UV-2501 spectrophotometers. Fluorescence spectra were acquired on a Jobin-Yvon emission spectrometer equipped with a 450 W xenon source, Gemini-180 excitation and Triax-550 emission monochromators, and a photon counting detector (Hamamatsu R928P PMT at 950 V). 9,10-Bis(phenylethynyl)-anthracene in cyclohexane was used as a standard in the determination of fluorescence quantum yields by the relative method (matching the absorbance at the excitation wavelength between the sample and standard solutions and comparing their corresponding integrated total fluorescence intensities). Transmission electron microscopy (TEM) images were obtained on a Hitachi H-9500 high-resolution TEM system, and the energy dispersive X-ray (EDX) analysis was conducted on a Hitachi SU-9000 CFE ultrahigh-resolution STEM system equipped with an Oxford AztecEnergy with X-MaxN 100 LE-100 nm^2 windowless ultra large solid angle SSD detector.

Carbon nanoparticles

The commercially supplied carbon nanopowder sample (4 g) was reflux in concentrated nitric acid (8 M, 200 mL) for 48 h. The reaction mixture was cooled to room temperature, and centrifuged at 1,000 g for 10 min to collect the supernatant as an aqueous dispersion. The dispersion was concentrated by rotary evaporation, and the acid in the concentrated aqueous dispersion was removed by 4 cycles of the dilution with water and then rotary evaporation. In each cycle, water (300 mL) was added to the concentrated dispersion, followed by rotary evaporation. After the dilution - rotary evaporation cycles, the aqueous sample was dialyzed in a membrane tubing (MWCO ~500) against fresh water for 48 h, followed by centrifuging at 20,000 g for 10 min to collect the supernatant as aqueous dispersed small carbon nanoparticles (CNPs). The removal of water yielded a solid sample of the nanoparticles.

ZnS capping of CNPs for CNP/ZnS core/shell nanostructure

The small carbon nanoparticles (CNPs, 50 mg) in an ethanol (1 mL) dispersion were mixed with TOPO (1.54 g) and hexadecylamine (2.9 g) in a three-neck round bottom flask at around 60 °C with vigorous stirring and nitrogen protection. To the resulting dispersion was added an ethanol solution of $Zn(NO_3)_2$ (0.27 M, 1 mL), followed by the removal of ethanol via evaporation at 90 °C and purging with nitrogen gas. The mixture was heated to 180 °C under nitrogen protection, and then to the mixture was injected very slowly (in small drops over about 10 min) with dodecanethiol (1 mL) in a syringe for the formation of ZnS to cap CNPs. The reaction mixture was allowed to cool down to 60 °C, followed by its mixing with methanol (100 mL). The resulting liquid mixture was centrifuged at 3,070 g for 10 min to collect the supernatant as a homogenous dispersion in methanol. To the dispersion was added hexane for extraction, and the hexane layer was kept and then washed with methanol 3 times. A colloidally stable hexane dispersion of the CNP/ZnS core/shell nanostructures with the surface decoration by a small amount of surfactant molecules was obtained.

Results and Discussion

Experimentally, CNPs were harvested from commercially acquired carbon nanopowder sample by using the established processing protocol.[14] For the ZnS capping, CNPs were dispersed in a mixture of TOPO and hexadecylamine, followed by the mixing with zinc nitrate. The mixture was heated to 180 °C in an oil bath with vigorously stirring under nitrogen protection, and to the mixture was added drop-wise dodecanethiol to form ZnS for the capping of CNPs. The resulting CNP/ZnS core/shell nanostructure with the surface decorated by some surfactant molecules could be separated from the reaction mixture and dispersed in organic solvents for stable dispersions appearing no different from a typical solution (Figure 2).

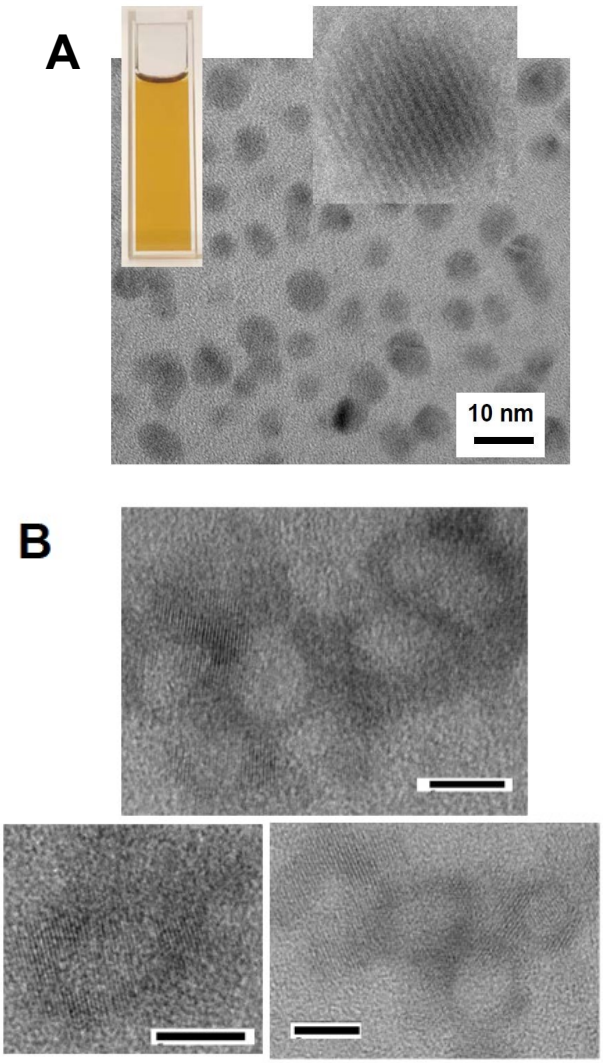

Figure 2 (A) TEM images of CNP/ZnS nanostructures, with the insets on the right for a high-resolution image showing the lattice fringes of the ZnS shell and on the left for a photo of CNP/ZnS solution in toluene. (B) More TEM imaging results (each of the size bars representing 5 nm), obtained from exploiting the contrast due to CNPs being mostly amorphous to emphasize the crystalline ZnS capping.

The CNP/ZnS nanostructures on silicon oxide-coated copper grids were imaged by using transmission electron microscopy (TEM). The TEM images show mostly individually dispersed nanoscale entities (Figure 2A). The individual dots were examined more closely at a higher TEM resolution, in which the lattice fringe spacing of the capping ZnS (0.23 nm for the 102 plane) could be clearly identified (Figure 2A), which matches the spacing in the known hexagonal (wurtzite) ZnS nanoparticles,[15,16] as also confirmed by the TEM imaging results of the neat ZnS nanoparticles prepared without CNPs.

As requested by the reviewers, more TEM imaging of the CNP/ZnS sample was performed to exploit the contrast between the mostly amorphous CNP core and the more crystalline ZnS domains. Some of the high-resolution TEM images thus acquired are shown in Figure 2B. These images seem consistent with the targeted nanostructure of the CNP core coated with ZnS, though realistically the desired unambiguous demonstration on the expected core/shell

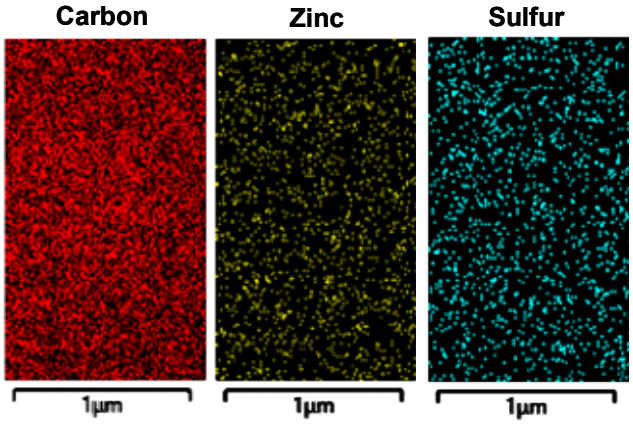

Figure 3 Energy dispersive X-ray (EDX) images of carbon, zinc, and sulfur acquired on a Hitachi SU-9000 CFE ultra-high-resolution STEM system for a CNP/ZnS specimen on a silicon oxide-coated copper grid.

configuration is still beyond the capability of the extremely high-end TEM instrument (Hitachi H-9500) used in the imaging experiments. Besides, even if one or a few such core/shell nanostructures were captured by a global search over the entire specimen for the imaging, it would hardly be sufficient to justify any conclusion that the sample specimen is indeed dominated by the targeted CNP/ZnS core/shell nanostructures. In fact, the same issue or challenge also confronts the much more mature research field of semiconductor core/shell QDs in terms of the ability to extrapolate what might be found in some high-resolution microscopy images to the bulk sample level. For the other reviewer concern on the existence of ZnS at all in the sample, one may take comfort in its known extremely large formation constant that should ensure the ZnS formation in the processing. Nevertheless, more direct evidence for the presence of ZnS in the carefully cleaned sample was found in the EDX analysis (Figure 3), considering the fact that free zinc cations and soluble sulfur-containing compounds were removed post-synthesis in the sample cleaning process.

In the development and investigation of semiconductor core/shell QDs, the capping with ZnS or the like has been understood (or "proven") mostly in terms of the property enhancements and changes due to the presumed capping. The same philosophy and practice may be applicable to the study of CNP/ZnS nanostructures in this work. "Naked" CNPs in solvent dispersions are absorptive in the visible spectrum (Figure 3), with the absorptivities at 400—420 nm of 75 ± 25 M_C^{-1} cm^{-1}, where M_C is the molar concentration of carbon atoms in the dispersed CNPs (about 7,000 carbon atoms in a CNP of 5 nm in diameter).[8] However, the solvent dispersed CNPs are generally very weakly emissive, with observed fluorescence emission quantum yields mostly less or much less than 0.5%.[11] Upon the ZnS capping of CNPs for CNP/ZnS core/shell nanostructure, the optical absorptions remain largely similar (Figure 4), but in sharp contrast are the significant spectral changes in fluorescence emissions (Figure 4) and the dramatically higher fluorescence emission intensities. The magnitude of increase in the fluorescence quantum yields due to the ZnS capping of CNPs, from the less than 0.1% for the selected solvent dispersion of CNPs[11] (which are "naked" CNPs without the benefit of surface passivation by organic functionalization in classically defined CDots) to higher than 20% for the same solvent dispersed CNP/ZnS nanostructure (Figure 4), is more than the magnitude of enhancement resulted from the ZnS

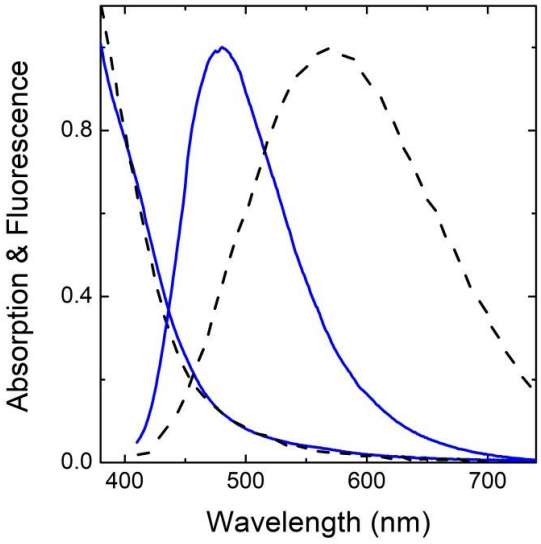

Figure 4 Optical absorption (ABS) and fluorescence emission (FLSC, 400 nm excitation) spectra of the CNP/ZnS in toluene solution (solid line) and aqueous dispersed CNPs (dashed line). The FLSC spectra were corrected for non-linear instrument responses of the emission spectrometer using separately determined correction factors, and then normalized at the peaks of both spectra (though in fact the absolute emission intensities of CNP/ZnS are higher than those of CNPs by more than two orders of magnitude).[11]

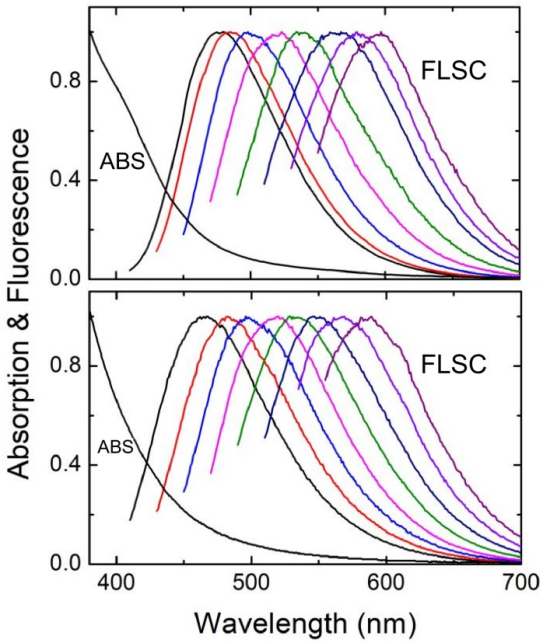

Figure 5 The optical absorption spectra (ABS) and the characteristic excitation wavelength dependence of fluorescence spectra (FLSC, from left to right corresponding to excitation wavelengths of 400 nm to 540 nm in 20 nm increment) for CNP/ZnS (upper) and the EDA-CDots [lower, EDA = 2,2'-(ethylenedioxy)bis(ethylamine)].[14]

capping of CdSe to yield CdSe/ZnS QDs.[1-5] As controls, the same experiments with CNPs without $Zn(NO_3)_2$ (the Zn source) and/or dodecanethiol (the S source), thus no ZnS formation possible, under otherwise the same processing conditions did not result in any major enhancements in the observed fluorescence quantum yields.

Also, interesting and striking is that the effects associated with the ZnS capping of CNPs on their optical spectroscopic properties are rather similar to those due to the surface organic functionalization of CNPs for CDots.[6,9,17] The effects are both characterized by the same dramatic enhancement in fluorescence emission brightness or quantum yields and the substantial narrowing of the emission spectra, yet without any major changes in optical absorptions (Figures 4 & 5). Also, shared between the CNP/ZnS core/shell nanostructure and the classical CDots are the rather characteristic excitation wavelength dependencies of fluorescence emissions (Figure 5, which in classical CDots are established as being due to a distribution of emissive excited states in individual dots[14,17]), again indicative of their very similar photoexcited state properties and processes and by extension largely the same surface passivation effects on CNPs due to either the organic surface functionalization or the surface capping with a nanoscale semiconductor like ZnS.

CNPs are generally not considered as conventional semiconductors, lack of the classical quantum confinement behavior found in CdSe nanoparticles or the like, despite the fact that some of the observed properties of CNPs-derived CDots may justify the consideration of CNPs as being equivalent or analogous to nanoscale semiconductors.[8,18,19] In the mechanistic framework for the photoexcitation and the excited state properties and processes of CDots,[8,17,19] in which the core CNPs are solely responsible for the observed optical absorptions due to the common use of only colorless organic molecules for the CNP surface functionalization, the initial processes following photoexcitation are likely rapid charge transfers and separation to result in the separated electrons and holes. Such transient processes and species are conceptually and phenomenologically analogous to those found in photoexcited CdSe and other semiconductor nanoparticles.[1-5,20-22] The relationship between "naked" CNPs and the effectively surface passivated CNPs in the classical CDots or the CNP/ZnS core/shell nanostructure (Figure 1) may also be comparable (conceptually and phenomenologically at least) to the relationship between CdSe nanoparticles and CdSe/ZnS QDs, such that both CNPs and CdSe nanoparticles experience dramatic property enhancements upon modifications of their particle surfaces. Mechanistically, in CdSe/ZnS QDs "the ZnS capping with a higher bandgap than CdSe passivates the core crystallite removing the surface traps",[3,22] while in CDots the organic functionalization of the core CNPs is thought to stabilize the CNP surface defect sites where the separated electrons and holes are trapped, which therefore enables more radiative recombinations of the separated redox pairs for the dramatic enhancement in fluorescence emission quantum yields.[8,10] It may be argued that the function of ZnS in the CNP/ZnS core/shell nanostructure must be similar to that of the organic functionalization in CDots, all for stabilizing the surface traps of the core CNPs. In this regard, the same mechanistic framework for the photoexcited state properties and processes shared, conceptually and phenomenologically at least, by CdSe/ZnS QDs and the CNP/ZnS core/shell nanostructure is also shared by classical CDots.

Conclusion and Perspective

The reported results show that the capping of CNPs with ZnS for the CNP/ZnS core/shell nanostructure can provide largely the same effective surface passivation as that by the surface organic functionalization of CNPs in classical CDots,

not only making the CNP/ZnS nanostructure a special configuration of CDots but also demonstrating its rather striking comparable relationship with CdSe/ZnS QDs. Obviously, one may argue that CNP/ZnS core/shell nanostructures are still not QDs in the classical sense, lack of the kind of quantum confinement behavior found in CdSe/ZnS QDs and the associated dot size-dependent optical absorptions and fluorescence emissions. Because of such an argument the word replacing is placed in quotation marks in the title to highlight the special meanings of "replacing" the CdSe core with CNP, which include the understanding that CdSe nanoparticles and CNPs are very different nanomaterials but at the same time the recognition that the comparable property enhancements of these clearly different nanomaterials upon the surface capping with ZnS for their shared nanoscale core/shell configurations are more than just coincidence. Here the linkage is the comparable effective surface passivations of the two different kinds of nanoparticles with the same ZnS capping, namely the surface passivation effect is not so sensitive to the identities of the nanomaterials being passivated.

A major implication to the development of CDots and their derived technologies is a significant expansion in the schemes for the required effective surface passivation of CNPs for high-performance CDots, beyond the deliberate surface organic functionalization of CNPs or the comparable passivation effects due to nano-carbon domains immersed in organic materials in the appropriately carbonization produced dot samples.[23]

To the more mature research field of semiconductor QDs, a significant implication of the reported findings might be with the commonly accepted mechanistic rationale for the surface capping of semiconductor nanoparticles with wider bandgap semiconductors. While one may argue that the wider bandgap is necessary to eliminate any potential photoexcited state energy transfers from the core to the shell, a counterargument could be that the overemphasis on bandgap would mask the true mechanistic origins of the capping effects in core/shell QDs. For the capping of CNPs for core/shell nanostructures, there is experimental evidence suggesting that the shell material for the capping effect may not be limited to nanoscale semiconductors, with other candidates including some simple inorganic solids.[8,24] In this regard, the striking comparability in core/ZnS nanostructures with classical semiconductor nanoparticle *versus* CNP as the core does serve to remind and encourage the research community to think outside the box in theoretical and technological development of QDs.

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Author Contributions

Weixiong Liang: Investigation, Writing. Kirkland Sheriff: Investigation. Buta Singh: Investigation. Haijun Qian: Investigation. Simran Dumra: Investigation. Jordan Collins: Investigation. Subhadra Yerra: Investigation. Liju Yang: Conceptualization, Supervision. Ya-Ping Sun: Conceptualization, Supervision, Writing.

Conflict of Interest

The authors declare no conflict of interest.

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