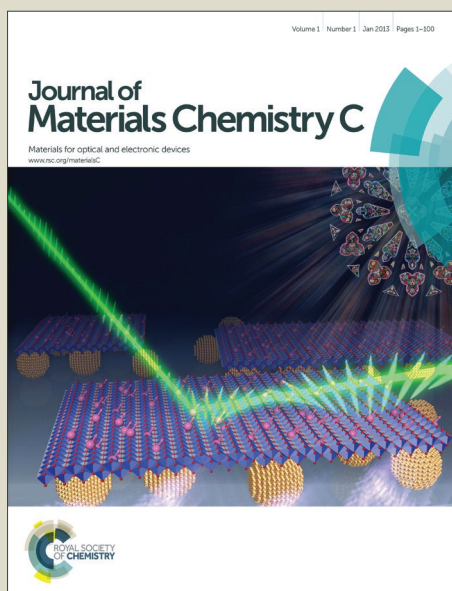


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COMMUNICATION

The effect of surface structures and compositions on the quantum yields of highly effective Zn_{0.8}Cd_{0.2}S Nanocrystals

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We have synthesized white light emitting ternary Zn_{0.8}Cd_{0.2}S nanocrystals with high quantum yields about 99 %. Through detailed surface and structures characterizations with the investigation of Cd and Zn coordination numbers, it can be found that besides surface state emission, the highly effective white light emission is strongly related to the surface chemical states of Zn and Zn-O/Cd-O bondings.

II-VI semiconductor nanocrystals (NCs, also called quantum dots, QDs) have exhibited great potential applications in the fabrication of solid state white-light emitting devices, owing to their novel optical properties such as tunable emission wavelengths and high quantum yields (QYs).¹⁻⁴ Because of the quantum confinement effect and the wide band gap of these NCs, the narrow band emission can be tuned in the visible light range by controlling not only the particle sizes but also the compositions of the NCs.⁵⁻⁹

Phosphor-based white light-emitting diodes (WLEDs) have two main drawbacks which are scattering and low conversion efficiency, lowering the WLED performance. In our previous work, mixing commercial phosphors with yellow NCs can improve both color rendering index (CRI) and luminous efficacy of WLED.¹⁰ Although the use of NCs with narrow band emission can improve the CRI of WLEDs,³ mixing several kinds of NCs to get white light still suffers from self-quenching effect and self-absorption problem, which result in the decay of luminous efficacy in WLEDs when compared with traditional phosphors. Therefore, the white-light emitting NCs have been synthesized successfully in “magic-sized” CdSe system with the QY of 2~3 %¹¹ and the doped ZnS and ZnSe systems.¹²⁻¹⁷ The mechanism of white-light emission from NCs is proposed to be surface-state and dopant emissions dependent, although the former one is regarded as “emission by chance” in trap-rich CdS NCs.¹⁸ Conversely, the white-light emission of the onion-like CdSe/ZnS/CdSe/ZnS NCs can be tuned by changing the diameter of the core and the thickness of the shell, which is called “emission by design.”¹⁸ These core-shell structure not only controls the optical properties but also enhances the QYs of semiconductor NCs because of the effective surface passivation from inorganic capping such as a ZnS overlayer.¹⁹⁻²⁰ On the other hand, Schreuder et al. have reported the correlation between surface ligands and the shift of emission energies in ultrasmall CdSe system.²² They have found that the

broad emission comes from surface trap states, which can be tuned by changing the ligands on the surface of NCs and affects the overall optical properties and the QYs.²²

Basically, the colloidal NCs are stabilized by a layer of surface ligands which contain metal coordinating groups as well as solvophilic groups.²³ The common organic surface ligands include alkyl phosphine, amines, phosphine oxide, and so on. These molecules not only prevent the further growth and aggregation of colloidal NCs but also provide good solubility in solvents.²³ In order to explore the influence of the surface ligands on the semiconductor NCs, Peng et al. has reported the surface ligand dynamics of NCs, which have found to be strongly related to the growth temperature, the concentration and the chain length of ligands.²⁴⁻²⁵ The formation of high-quality semiconductor NCs should maintain the balanced rate of nucleation and growth during synthesis.²⁴ In addition, the surface ligands coverages influence not only the emission but also the QY, which relies on the boiling points and the reaction rates of the ligands.²⁴ Therefore, the ligand-ligand interaction on the surface of the NCs plays an important role for surface ligand dynamics in the synthesis of high-quality colloidal NCs.²⁴

Previously, the correlation of QYs and the surface state of white-light NCs has been reported, suggesting that the oxidation of the NCs surface may cause the decrease of the QYs.²¹ We have also investigated that the surface-state emission is related to the Zn-rich shell, especially in Zn_{0.8}Cd_{0.2}S system, thus enhancing the white emission and QYs.²⁶ In this communication, we have shown through changing the carbon chain length of alkenes as surface ligands and the reaction time, the QYs of as prepared Zn_{0.8}Cd_{0.2}S NCs can reach up to 99.0%, which is much higher than those of other white-light emitting semiconductor NCs reported previously.^{11-17,26} By this facile one-pot synthetic route, the particle size and emission wavelength of NCs can be controlled easily. In order to go insight into the origin of high QYs, X-ray absorption spectroscopy (XAS) and X-ray photoelectron spectroscopy (XPS) analysis have been used to illustrate the surface structures and compositions of Zn_{0.8}Cd_{0.2}S NCs. We have found that the coordination number of Zn-O and surface metallic Zn content may be the dominate factors that affect the QY of Zn_{0.8}Cd_{0.2}S system. Besides, the optical properties, morphologies, size distributions, crystal structures and

functional groups of capping ligands on NCs surface are investigated by fluorescence luminescence (FL), high resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD) and Fourier-transform infrared spectrometer (FTIR), respectively.

The colloidal ternary semiconductor $Zn_{0.8}Cd_{0.2}S$ named as $Zn_{0.8}$ NCs were prepared by thermal pyrolyzed organometallic route. Decene (DE), tetradecene (TDE) or octadecene (ODE) with different carbon chain lengths were used as surface ligands and named as DE-time (10, 30 or 60), TDE-10, and ODE-10, respectively.

The normalized FL emission spectrum of various $Zn_{0.8}$ NCs is shown in Fig. 1 and the quantitative FL emission spectrum is shown in Fig. S1 in supporting information (ESI†). It can be noted that $Zn_{0.8}$ NCs possess wide emission range with two obvious peaks in which the sharper one is band edge and the broader one is surface state emissions. Table S1† lists their wavelengths of emission peaks and quantum yields (QYs). It has been reported that in the InP system, if the surface states are removed, NCs show only band-edge emission with very high QY, suggesting that the high QY is related to band-edge emission.²⁷ In Fig. 1, an obvious red shift of the emission peaks toward longer wavelength and the change of QY on NCs can be easily observed with longer reaction time and using alkenes with shorter carbon chain length as surface ligands from ODE, TDE to DE. This red shift may be attributed to the larger particle size and faster growth during these two conditions. In addition, in order to investigate the effect of surface states on the QYs, the calculation results of area ratio between band edge and surface state emissions are listed in Table S1. It seems that the relative intensity of surface state emission of NCs, R_A , increases as using alkenes with longer carbon chain length as surface ligands. When DE with shorter carbon chain length is used as the surface ligands, faster reaction rate of NCs takes place, resulting in the stronger band edge emission than TDE and ODE as shown in Fig S1†. It has been reported that in the CdS system, alkylamines with different chain lengths were used to perform the capping exchange procedures. The enhancement of band edge emission was obtained for short chain octylamine-capped CdS NCs, indicating an increase of QY.²³ In this study, the QYs of $Zn_{0.8}$ NCs prepared by DE for 10 minutes (DE-10) can reach up to 99.0 % which is much higher than those of $Zn_{0.8}$ NCs prepared by TDE and ODE because of the different passivation effect on the NCs surface caused by surface ligands.²⁸ In order to investigate the functional groups of capping ligands on the $Zn_{0.8}$ NCs surface, FTIR spectra are shown in Fig. S2†. The strong absorption bands at 2850-2950 and 1156 cm^{-1} are attributed to the C-H and P=O stretches of the TOPO, respectively.²⁹ The presence of the broad bands in 3250-3550 cm^{-1} was obtained from the O-H and N-H vibrations of solvent and HDA.³⁰ The characteristic absorption bands of C-H and C=C are observed at 1465 and 1640 cm^{-1} respectively, which provides the evidence of the TOPO, HDA and the alkenes capping on the $Zn_{0.8}$ NCs surface. To the best of our knowledge, the QYs of these $Zn_{0.8}$ NCs are also higher than those of CdS, CdSe, or ternary white light emitting NCs reported in the literatures.^{11,31} On the other hand, although a decay of QY can be noted for DE samples with longer reacting time, the R_A does not follow the same trend, suggesting that besides surface state, there is another QY-determining factor. Moreover, in order to explore the morphology and size distribution of NCs, the TEM images are shown in Fig. S3† and lattice fringes of crystalline NCs can be seen in the insets of Fig. S3†. The average particle size of $Zn_{0.8}$ NCs prepared by DE,

TDE and ODE at various reaction time is 2.4 ± 0.3 nm (DE-10), 2.9 ± 0.4 nm (DE-30), 3.1 ± 0.3 nm (DE-60), 2.3 ± 0.2 nm (TDE-10) and 2.1 ± 0.2 nm (ODE-10), in which all have spherical shape and narrow size distribution with the relationship between emission wavelength and particle size.

Fig. S4† shows the XRD patterns of $Zn_{0.8}$ NCs and zinc blende CdS and ZnS references. The broad peaks can be found in all XRD patterns, due to the small particle sizes and lack of long-range order in the NCs. Each diffraction peak of $Zn_{0.8}$ NCs is between the corresponding phases of reference zinc blende CdS and ZnS, demonstrating that the ternary $Zn_{0.8}$ NCs with zinc blende structure have been obtained. As the reaction time increases, the diffraction peaks shift toward lower angles, suggesting that the $Zn_{0.8}$ NCs tend to form the ZnS phase under rapid reaction rate, which may influence the optical properties of the NCs.

XPS measurements are used to determine the surface chemical states of NCs and the XPS spectra of Zn 2p, Cd 3d and S 2p are shown in Fig. 2 and the fitting results of Zn 2p spectra are shown in Fig. S5†. The peaks of Zn spectrum appear around 1022 eV for Zn 2p $3/2$ with the peak shift toward higher energy of $Zn_{0.8}$ NCs, illustrating the oxidation of Zn on the $Zn_{0.8}$ NCs surface. The presence of peak shift toward higher energy can be also found in both Cd and S spectra, indicating that the oxidation of Zn, Cd and S on the $Zn_{0.8}$ NCs surface may affect the optical properties. Asami et al. have reported that the oxidation of Se might be the factor that contributes to the enhancement of QY in CdSe system.²¹ Contrarily, the oxidation of Cd and S in our ZnCdS system may result in the decrease of the QY. The fitting results show that the DE-10 has the highest Zn/ Zn^{2+} ratio, suggesting that the high QYs of $Zn_{0.8}$ NCs are related to the metallic state of Zn and the formation of the oxide may reduce the QYs.²⁶ Table S2† lists the surface compositions and binding energies of $Zn_{0.8}$ NCs. The surface Zn: Zn^{2+} :Cd composition of DE-10, DE-30, DE-60, TDE-10 and ODE-10 is 42:21:38, 21:28:51, 14:25:61, 33:24:43 and 28:32:40, respectively. The decrease of surface Zn content with longer reaction time can be found, revealing that the higher QYs have a relationship with the higher surface Zn metallic composition. Furthermore, compared with DE-10 and ODE-10, these two samples have very similar surface Zn content but the former one has much higher QYs than the latter one, suggesting that the oxidation of Zn may deteriorate the QYs, as the fitting results shown in Fig. S5†. Through the above discussion, it seems that the high QYs may be attributed to the high surface Zn content and the metallic state of surface Zn.

Adersh et al. have shown that the comparison of the ZnO QDs from an oxygen rich and oxygen deficient environment.²⁰ It has revealed that the synthesis of ZnO QDs under an oxygen deficient environment are rich in oxygen vacancies which can enhance the PL intensity.²⁰ Therefore, the bonding of oxygen with Zn and Cd may be the reason that affects the QYs. Although the XPS can provide the information of surface chemical states, XAS is an alternative powerful tool to investigate the bonding and coordination number in the view point of the bulk. The X-ray absorption near edge structure (XANES) spectra of Zn and Cd K-edge of $Zn_{0.8}$ NCs are shown in Fig. 3 and Fig. S6†, respectively. In the Zn K-edge, the white line energies are close to that of ZnS, indicating the formation of Zn-S bond in these NCs. Furthermore, the white line intensities increase with the longer reaction time, implying that the oxidation on the surface of $Zn_{0.8}$ NCs takes place, which results in the decrease in QYs. For the Cd K-edge, the white line energies and intensities of $Zn_{0.8}$ NCs are all nearby those of CdS, suggesting that there are S ligands around

Cd species. In addition, the higher white line intensity of DE-60 proves that the oxidation increases with longer reaction time. Therefore, the oxide-rich surface structure of Zn_{0.8} NCs may be the reason that degrades the QYs. Fig. S7[†] shows the corresponding Fourier transformed radial structure function of Zn and Cd K-edge, and the fitting results and the detailed parameters are listed in Tables 1 and S3, respectively. In the Zn K-edge, it can be observed that the coordination number of Zn-O bond increases and that of Zn-S bond decreases with the longer reaction time, which is consistent with the results of XANES and XPS. Furthermore, the CN ratio of Zn-O bond (CN_{Zn} ratio) increases as the QYs decreases with not only longer reaction time but also using longer carbon chain length of alkenes as surface ligands, indicating that the oxidation states of Zn is the major factor that influences QYs. For the Cd K-edge of DE-samples, the CN of Cd-S is about 2 and the relationship between QY and CN is not as obvious as that in Zn, indicating a Zn shell/Cd core structure. It seems that the decrease of QY is strongly related to the increase of the coordination number for Zn-O and Cd-O. Based on the above results, we suggest that the optical properties of Zn_{0.8} NCs are truly affected by the surface composition and the oxidation of Cd and Zn.

In summary, ternary alloyed Zn_{0.8}Cd_{0.2}S NCs with very high QYs about 99.0 % and white light emission have been successfully synthesized by a facile one-pot synthetic route. The QYs of the Zn_{0.8}Cd_{0.2}S NCs are affected by the different reaction time and the passivation effects of surface ligands on the NCs surface. Both of the band edge and surface state emission which is regarded as “emission by chance” can be tuned by using different carbon chain length of alkenes as surface ligands in this study. The key factor that influences the optical properties of these ternary Zn_{0.8}Cd_{0.2}S NCs has been investigated by the XAS and XPS characterizations, suggesting that the formation of metallic Zn-rich surface and Zn-O bondings of the Zn_{0.8}Cd_{0.2}S NCs may be the major reason of high QYs and white light emission, implying the great potential as nanophosphors for applications in WLEDs.

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Notes and references

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[†] Electronic Supplementary Information (ESI) available: Experimental procedure, TEM, XRD, XPS, FL, FTIR and XAS results. See DOI: 10.1039/c000000x/

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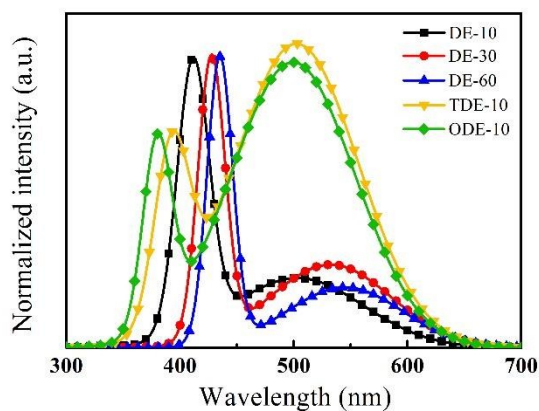


Fig. 1 FL emission spectrum of $Zn_{0.8}$ NCs prepared by DE, TDE and ODE.

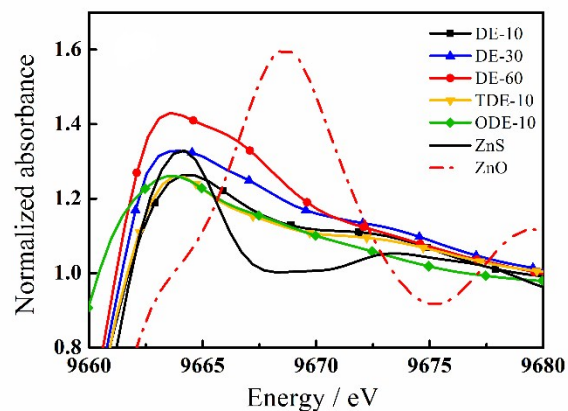


Fig. 3 The XANES patterns of $Zn_{0.8}$ NCs at Zn K-edge.

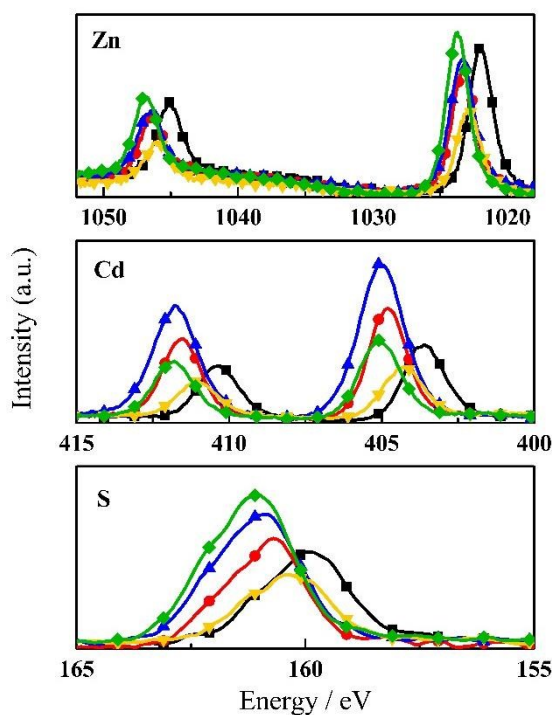
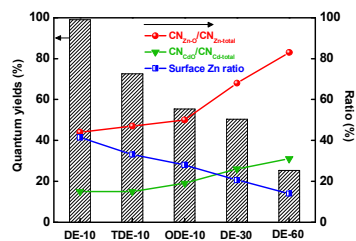


Fig. 2 XPS spectra of various $Zn_{0.8}$ NCs. ■: DE-10, ●: DE-30, ▲: DE-60, ▼: TDE-10 and ◆: ODE-10.

Table 1 EXAFS fitting results of the Zn K-edge and Cd K-edge for the $Zn_{0.8}$ NCs.

Sample	Zn path	CN _{Zn}	CN _{Zn} ratio	Cd path	CN _{Cd}	CN _{Cd} ratio	QY (%)
$Zn_{0.8}$ -DE-10	Zn-O	1.2	0.44	Cd-O	0.4	0.15	99.0
	Zn-S	1.5		Cd-S	2.3		
$Zn_{0.8}$ -DE-30	Zn-O	1.9	0.68	Cd-O	0.8	0.26	50.4
	Zn-S	0.9		Cd-S	2.3		
$Zn_{0.8}$ -DE-60	Zn-O	2.0	0.83	Cd-O	0.9	0.31	25.3
	Zn-S	0.4		Cd-S	2.0		
$Zn_{0.8}$ -TDE-10	Zn-O	1.5	0.47	Cd-O	0.4	0.15	72.6
	Zn-S	1.7		Cd-S	2.2		
$Zn_{0.8}$ -ODE-10	Zn-O	1.2	0.50	Cd-O	0.6	0.19	55.4
	Zn-S	1.2		Cd-S	2.5		

$CN_{Zn} \text{ ratio} = N_{Zn-O} / (N_{Zn-O} + N_{Zn-S})$
 $CN_{Cd} \text{ ratio} = N_{Cd-O} / (N_{Cd-O} + N_{Cd-S})$



The white light emission of ZnCdS is strongly related to the surface chemical states of Zn, and Zn-O/Cd-O bondings.