Synthesis of ligand-selective ZnS nanocrystals exhibiting ligand-tunable fluorescence

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Received 23 May 2007; accepted 16 August 2007
Available online 28 August 2007

Abstract
High-quality ZnS nanocrystals (NCs) of nearly identical size are synthesized using isomeric ligands, o-, m-, p-phenylenediamines (PDAs) that bind to the NC cores. The fluorescence emission from the NC is tunable according to the structure of the isomer. The measured fluorescence quantum yields (QYs) are 2–3 times higher for NCs that are passivated with isomeric PDA ligands than the fluorescence QY of NCs prepared at the absence of PDAs. The NC morphologies were studied by low-angle and wide-angle X-ray diffraction (XRD), and by transmission electron microscopy (TEM). The average correlating sizes were found to be 3.0 ± 0.3, 3.7 ± 0.30, and 3.0 ± 0.5 nm for the NCs that were passivated with o-PDA, m-PDA, and p-PDA, respectively. The Fourier-transform infra-red (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS) studies were carried out to investigate the shell structure and the interaction between the core and the shell. The adsorbed ligands were quantitatively analyzed by TGA. The structure, morphology, and optical properties of these PDA passivated NCs were compared with the NCs prepared in the absence of PDA.

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Keywords: Isomeric ligands; Phenylenediamine; ZnS nanocrystals; Fluorescence tuning

1. Introduction

Colloid-based ‘soft-solution’ methods are suitable for the synthesis of encapsulated nanocrystals (NCs) because the particle size can be controlled readily upon changing the concentration and the type of organic molecular ligand [1]. Functional ligands may be used to coat the surfaces of the particles to allow them to become free standing in solution and prevent their direct aggregation. Such NCs often become soluble in organic solvents or in aqueous solutions when the ligands bind strongly to their surfaces [2]. Water-soluble nanocrystals are used widely for studies in biological systems [2a,3]. NCs that are soluble in common organic solvents are suitable for preparing polymer/inorganic composite materials, which may find applications in high-refractive-index films, tunable light-emitting diodes, optical waveguides, photovoltaic solar cells, and nonlinear optical devices [4].

Small, uncapped semiconductor NCs usually form with defective states on their surfaces because of their large surface-to-volume ratios. The state of their surface dramatically affects their degree of luminescence quenching at the crystal surface. Surface defects are also often prominent in capped NCs when the ligands are not anchored suitably onto the surfaces. When the core semiconductor NCs are passivated effectively with appropriate ligands, however, their luminescence and fluorescence intensities can be increased substantially [5]. Such enhanced fluorescence emission results from suppression of nonradiative recombination because of the reduced concentration of surface states that feature dangling bonds and/or unstable surface atoms [1a,6].

The choice of capping ligand for the NCs is critical because it determines the stability, solubility, reactivity, size, and shape of the NCs during their synthesis [2a,7]. Size-dependent shifts in the absorption onsets and emission maxima to higher ener-
gies with decreasing size have been studied widely [3a,3d,4e, 8,9]. Recently, we reported that PDAs are excellent capping ligands for silver nanoparticles, where the ligand-to-metal interaction is extremely strong, and the size, shape and the phase of the colloidal nanoparticles are determined by the isomers of PDA [10]. In the present study, we report a simple novel approach for the synthesis of high-quality ZnS NCs capped with either of three isomeric ligands: ortho (o-), meta (m-) and para (p-) phenylenediamines (PDAs). The NCs are of nearly identical size, but the fluorescence emission of the NC was tunable according to the structure of the isomer, i.e. fluorescence emission can be sharply tuned by the same structure molecules with different positioning amine functional groups.

2. Experimental

2.1. Materials

All of the chemical reagents used in this study are analytical grade and used without further purification. The reagents, o-, m-, and p-PDAs, zinc acetate dihydrate [Zn(CH3COO)2·2H2O], thiacetamide, 2-(4-biphenyl)-5-phenyl-1,3,4-oxadiazole (PBD), anhydrous N,N-dimethylacetamide (DMAc) and dimethylsulfoxide (DMSO) were purchased from Sigma–Aldrich.

2.2. Synthesis

The following procedure was used to synthesize the o-, m-, and p-PDA-passivated ZnS NCs. Typically, the PDA (2.77 mmol) was dissolved in dimethylacetamide (DMAc) (10 mL) at ca. 45 °C. In a separate vial, Zn(CH3COO)2·2H2O (1.15 mmol) was dissolved in DMAc (10 mL) under sonication (ca. 2 min) and was then added into the PDA solution to allow the Zn2+ ions to adsorb onto the amino groups of the PDA. Thioacetamide (1.15 mmol) was dissolved in DMAc (20 mL) in a two-channel flask under magnetic stirring near room temperature; N2 gas was purged for a few minutes. The temperature of the solution was increased to 110 °C (the melting point of thioacetamide) at a rate of 3 °C/min. Under vigorous magnetic stirring, the Zn2+–PDA solution was injected into the thioacetamide solution and then the temperature of the mixed solution was raised to 165 °C (the boiling point of DMAc); the mixture was heated under reflux for ca. 25 min. The reaction mixture containing the ZnS NC was then cooled to room temperature. Transparent clear solutions of ZnS NCs were obtained when o-PDA and m-PDA were used as the capping ligands, but a colloidal solution ZnS NC was obtained when p-PDA was the capping ligand. Each of the NC solutions was, however, precipitated in ethanol and washed several times until colorless ethanol was obtained. The NC products were collected through careful decantation. A ZnS NC sample was also synthesized in the absence of PDA, while maintaining all of the other parameters identical to those described above.

2.3. Characterization

The low- and wide-angle X-ray diffraction (XRD) data were collected on a Rigaku Miniflex X-ray diffractometer, operated at 40 kV and 30 mA, using CuKα (λ = 1.5401 Å) radiation. The NC aliquots were cast on a glass substrate and dried at 50 °C for 12 h. Transmission electron microscopy (TEM) images were obtained using a JEOL JEM 2010 electron microscope operated at 200 kV. A drop of diluted suspension of each NC aliquot was placed on a copper TEM grid, covered completely with carbon, and then the solvent was left to evaporate. The FTIR spectra were recorded at room temperature on a JASCO FTIR 460 Plus operated at a resolution 4 cm⁻¹. Specimens for analysis were prepared as KBr pellets of the dried NCs (50 °C for 12 h). X-ray photoelectron spectroscopy (XPS) was performed using a VG-Scientific ESCA lab 250 spectrometer and AlKα radiation (1486.6 eV); the peak positions were referenced internally to the C 1s peak at 284.6 eV. For XPS, samples were prepared in a manner similar to those for XRD analysis, except that a silicon substrate was employed. Thermogravimetric analysis (TGA) data with their derivative signals were recorded on a TGA Q50 in nitrogen atmosphere at a ramp 10 °C min⁻¹ from 40 to 750 °C. The samples for TGA measurements were prepared by vacuum drying at room temperature. UV–vis spectra were measured using a Hitachi U-2910 spectrometer. Fluorescence emission and excitation spectra were measured using a Hitachi F-4500 spectrometer. Time correlated single photon counting (TCSPC) technique was used for the time-resolved fluorescence (TRF) measurements. The fluorescence was dispersed by a monochromator and detected with a thermoelectrically cooled microchannel plate photomultiplier tube (Hamamatsu R3809U-51). Outputs of the photomultiplier tube (start pulse) and a fast photodiode (stop pulse) were analyzed by a picosecond time analyzer (EG&G Ortec, 9308). The width of the instrument response function was 40 ps to provide better than 10 ps time resolution after deconvolution. The femtosecond light source was based on a home-built cavity-dumped infrared optical parametric oscillator which has been described in detail elsewhere [11]. The cavity-dumped fundamental output at 1240 nm was frequency quadruled by successive second harmonic generations using a 3 mm LBO and 500 µm BBO crystals to generate the pump pulse at 310 nm. For UV–vis and FL spectroscopic measurements DMAc was used as solvent. For quantum yield measurements, samples as well as standard, 2-(4-biphenyl)-5-phenyl-1,3,4-oxadiazole (PBD), were dispersed in DMAc by sonication (5–10 min). PBD has an emission maximum at 380 nm, when excitation wavelength, 315 nm, and quantum yield, 83% [12].

3. Results and discussion

Our synthetic approach was quite simple (Scheme 1). First, Zn2+ ions were adsorbed onto the amine of the PDAs. The Zn2+–PDA complex ions were reacted with the S2– ions (in DMAc) that arose from thermal decomposition of thioacetamide. The reacting solutions were then heated under reflux to provide well-passivated, high-quality ZnS NCs. The role of
vinylideneamine (CH$_2$CNH), a by-product of the thermal decomposition of thioacetamide, in this process is not presented in Scheme 1 because of the negligible interactions of this amine with the NC surface in the presence of the PDAs. The purified (washed) ZnS NCs that were passivated with PDA were readily soluble in dimethylsulfoxide (DMSO) and DMAc. In contrast, the NC synthesized in the same manner, but in the absence of the passivating PDA, was insoluble in DMAc, DMSO, and other common solvents. The views (a–c) in the image (Fig. 1) indicate that the NCs passivated with o-, m-, and p-PDA, respectively, were completely soluble in DMSO; view d (Fig. 1) provides an image of the NCs (that are not passivated with the PDA) in DMSO. The complete solubility of PDA encapsulated NCs is the physical evidence that PDAs are strongly bonded to the core (ZnS). For convenience, however, we name the NC products passivated with o-, m-, and p-PDA as PNC1, PNC2, and PNC3, respectively, and the bare NC (passivated only with CH$_2$CNH) as BNC.

To characterize the NCs morphologically, we studied their low- and wide-angle X-ray diffraction (XRD) patterns. The low-angle XRD peaks (Fig. 2a) of PNC1, PNC2, PNC3, and BNC occurred at 2$\theta$ values of 2.5°, 2.1°, 2.4°, and 3.0°, respectively. Such characteristic low-angle peaks have been reported previously by Nanda et al. [9e] in the case of ZnS NCs and by Murray et al. [9g] in the case of CdS NCs. Using the Bragg
equation \((2d \sin \theta = \lambda)\) allows the correlation length \(d\) between crystallites to be obtained from these low-angle diffraction peaks. Since each NC is separated from its nearest neighbors by an organic encapsulation layer, the average separation distance between the NCs is the mean particle size including the ligand shell [9e,9g]. If the separation distances are highly regular, well-defined diffraction peaks should be observed. The average NC sizes for PNC1, PNC2, PNC3, and BNC, which we determined from the diffraction peak data in the low-angle region, are 3.5, 4.1, 3.6, and 2.8 nm, respectively. Although the diffraction peaks for the first three crystalline samples were well defined, the latter one was broadened. The broad nature of the BNC peak suggests a lower degree of order in terms of the separation distance (i.e., a wide size distribution). This may be the cause of weak adsorption of \(\text{CH}_2\text{CNH}\) onto the surfaces of the NCs. In contrast, the well-defined peaks for PNC1, PNC2, and PNC3 indicate that their well-separated NCs were strongly encapsulated with PDA molecules leading to their narrow size distributions. The slightly larger, but better oriented, PNC1, PNC2, and PNC3 systems, relative to BNC, may have arisen as a result of molecular rearrangement of \(\text{CH}_2\text{CNH}\) and PDA molecules under the synthesis conditions (i.e., under reflux).

Fig. 2b presents the wide-angle (WA) diffraction patterns of PNC1, PNC2, PNC3, and BNC. Although the diffraction peaks were broadened significantly because of their small crystallite sizes, the peak positions at 28.6°, 47.7°, and 56.7° correspond to the (111), (220), and (311) planes of cubic sphalerite \(\text{ZnS}\). To obtain further information from the WAXRD data of the crystallites, we applied the Debye–Scherrer formula [9e,13] expressed as \(L = 0.9\lambda/B\cos \theta\), where \(L\) is the coherence length, \(B\) is the full width at half maximum of the peak, \(\lambda\) is the wavelength of the X-ray radiation, and \(\theta\) is the diffraction angle. If the NCs are considered to have spherical morphologies, where \(D\) is the diameter of the NC, the relation between \(L\) and \(D\) is expressed as \(D = 4/3L\) [9e]. To determine the values of \(L\) with minimum error, we used the (111) peak along with a solid fitted line. The values of \(L\) that we obtained for PNC1, PNC2, PNC3, and BNC were 2.4, 2.9, 2.5, and 2.3 nm, respectively, giving values of \(D\) of 3.2, 3.9, 3.3, and 3.0 nm, respectively. The values of \(D\) for PNC1, PNC2, and PNC3 are lower than the corresponding particle sizes determined from the low-angle diffraction peaks, presumably because wide-angle diffraction is dominated by the higher electron density of the core crystals, i.e., it disregards the lower-electron-density organic shell. The wide-angle crystallite size \((D)\) for BNC was a little larger, however, than the size measured from the low-angle peak. This small size difference (0.2 nm) in between the systems is expected because the low-angle diffraction peak for BNC was wider enough to clearly mark the corresponding \(\theta\) value.

To verify the morphologies suggested by the low- and wide-angle XRD patterns, we obtained transmission electron microscopy (TEM) images (Fig. 3) of PNC1, PNC2, PNC3, and BNC. We used Gatan software to draw the size-histogram from the images of the samples. The average sizes for PNC1, PNC2, and PNC3, which we estimated from the size-histograms, were 3.0 ± 0.3, 3.7 ± 0.30, and 3.0 ± 0.5 nm, respectively. Thus, the NC sizes measured by TEM are consistent with the sizes obtained by XRD. The size histogram for BNC was too broad, and thus its standard deviation was large. The average size-range, however, we estimated to be 2.0–3.5 nm. This broad size distribution reveals that the NCs are unstable in the absence of PDA molecules.

The Fourier transform infrared (FTIR) absorption spectroscopic data of PNC1, PNC2, and PNC3 confirmed that their shell structures consisted dominantly of \(o\text{-}, m\text{-},\) and \(p\text{-PDA}\) molecules, respectively, while that of BNC indicated that its NCs contained \(\text{CH}_2\text{CNH}\) molecules (Fig. 4). Although the PDA-passivated NCs (PNC1, PNC2, and PNC3) may have possibility to adsorb a little amount of \(\text{CH}_2\text{CNH}\) moieties, however, it is difficult to resolve them from PDA in the FTIR spectra of NCs that are dominantly passivated by PDAs.

We used X-ray photoelectron spectroscopy (XPS) to reveal the nature of the interfaces between the cores and ligands. Because the amino functional groups coordinated to the surface Zn atoms of the NCs, the N 1s and Zn 2p states provided important information regarding the ligand-to-core interaction. The high-resolution XPS data (Fig. 5, top) for the Zn 2p states indicated binding energy shifts of ca. 2 eV to lower energy for each of PNC1, PNC2, and PNC3, relative to that of BNC, indicating that the PDA amino groups were attached strongly to Zn atoms compared to the amino group of \(\text{CH}_2\text{CNH}\). The N 1s data corroborated this finding. The high-resolution N 1s spectra (Fig. 6) for PNC1, PNC2, and PNC3 each display two bands (at ca. 396 and 399 eV), whereas that for BNC presents only one (at 399 eV). The bands at ca. 399 eV represent nitrogen atoms in amino environments [10,14]. The lower-energy band probably arose from charge transfer from the core to the ligand. Similar charge interaction band was previously observed for N 1s in the case of phenylenediamine encapsulated Ag [10b]. The center band positions for the S 2p levels were almost the same for each NC (Fig. 5, bottom), because the S atoms did not have interaction directly with the nitrogen atoms of any of the amino groups.
To quantify the amounts of the adsorbed ligands on the NC surfaces, we also performed thermogravimetric analysis (TGA) with their derivative thermogravimetric (DTG) analysis data of PNC1, PNC2, PNC3, and BNC (Fig. 7). The weight loss up to 180 °C is due to the removal of the adsorbed DMAc and ethanol/moisture on the NC surfaces as suggested by the DTG curves. After removing DMAc from the NC surfaces, weight loss takes place via following steps: organic ligands are desorbed from the core NCs, followed by the decomposition of the organic ligands (both PDA and aliphatic vinylideneamine) and then the recrystallization of the core NCs. In particular, a DTG peak centered at 175 °C obtained for PNC1 is not observed for PNC2, PNC3, and BNC. This may indicate that DMAc makes weak complexation with the NC surfaces and the solvent is not completely removed until 220 °C. The shoulder-like broad peak from 220 to 600 °C for the PNC1 is due to the weight loss caused by the decomposition of ligands, where the amounts of adsorbed ligands are estimated as 18% of total weight of NCs. The DTG peak around 680 °C for the PNC1 is due to the recrystallization of the NCs (by subsequent aggregation after decomposition of ligands). The loss of weight due to the recrystallization is 0.9%. In this way, the amounts of adsorbed ligands are estimated as 12.3% and 16.4%, respectively, for PNC2 and PNC3. For BNC, however, the recrystallization peak was not observed around 680 °C, since the recrystallization peak may be overlapped with the decomposition of aliphatic vinylideneamine at lower temperature. The weight loss due to the combined decomposition and recrystallization was estimated as around 11.6%.

Fig. 8a presents the UV–vis absorption spectra of the NCs. The spectra compares the absorption of PDA functionalized NCs and bare NCs. Each NC displays an absorption band at 302 ± 3 nm, which is a finding consistent with the results reported by Yanagida et al. [15a] and Inoue et al. [15b]; such a wavelength fits the curve (absorbance vs diameter) simulated by Nakaoka and Nosaka [15c] for ZnS particles of diameter 2–5 nm. Whereas the absorbances of PNC1, PNC2, and PNC3 in the visible region were near to zero and remained parallel to the baseline, for BNC we observed a monotonic absorbance curve from the visible to the UV region. This finding indicates that the absorbance of BNC in the visible region was due to scattering [16a], possibly because of the agglomerated particles that were improperly dispersed in the solvent. The absorption bands at 302 ± 3 nm, which are blue-shifted from the bulk band-gap wavelength of ca. 340 nm, are due to quantum confinement effects in the ZnS nanoparticles [16]. The negligible differences (maximum ∼6 nm) between the positions of the absorption bands in the spectra of PNC1, PNC2, and PNC3 suggest that their particle size distributions were nearly similar (maximum deviation 0.7 nm from PNC1 and PNC3 to PNC2, as observed by TEM and XRD). Fig. 8b shows the absorbance nature of the free ligands (α-PDA, m-PDA, and p-PDA) in the same solvent into which the absorbance of NCs were measured. Upon comparison of absorbance spectral profiles of free ligands and NCs functionalized with the corresponding ligands, one can see that unreacted free ligands were completely removed from the nanocrystallite samples.

Fig. 9 displays the fluorescence emission (FL) and fluorescence excitation (FLE) spectra of the NCs. The FL band positions did not shift at different excitation wavelengths indicating
that the FL originates from a single emitting state of the NCs [17]. The maximum emissions were observed at 360, 343, and 397 nm with the excitation wavelengths at 305, 310, and 335 nm for PNC1, PNC2, and PNC3, respectively (Figs. 9a–9c). The FL of BNC displays a sharp peak at 329 nm and a broad band centered at 440 nm (Fig. 9d). The 329 nm band may be due to the Raman peak or artifact. The broad band should be surface defect-related emission as reported previously [18]. Such a defect-related emission band was not present in the FL spectra of PNC1, PNC2, and PNC3. Fig. 10 shows the FL and FLE spectra of the free ligands for comparison. The FL band positions and lineshapes of the free ligands are practically the same as those of the NCs to denote that the emission bands at 360, 343, and 397 nm in NCs arise from the ligands. The FLE spectra are slightly different from those of the free ligands and the excitation maxima are shifted to lower wavelengths by 18, 8, and 12 nm for PNC1, PNC2, and PNC3, respectively, compared to those of the free ligands. We have investigated the possibility of the energy transfer from the core ZnS nanocrystals to the ligands by time resolved fluorescence (TRF). The time profiles at the emission maxima, however, do not show any sign of the energy transfer; no rise component was observed at the emission maxima, although the excitation light predominantly excites the
Fluorescence emission and excitation spectra of (a) PNC1, (b) PNC2, (c) PNC3, and (d) BNC.

ZnS core. The time profiles of the NCs are also similar to those of the free ligands to confirm that the emissions arise from the ligands. Thus, we conclude that the emissions in the NCs are due to the direct excitation of the ligands and that the slight shifts of the excitation maxima in the NCs are due to the adsorption of the ligands to the ZnS surface.

Fig. 10. Fluorescence emission and excitation spectra of (a) o-PDA, (b) m-PDA, (c) p-PDA.

Fluorescence quantum yields ($\phi_{em}$) were measured using 2-(4-biphenylyl)-5-phenyl-1,3,4-oxadiazole (PBD) as a standard [16a] in DMAc for PNC1, PNC2, PNC3, and BNC, and the quantum yields were calculated using the following equation [12],

$$\phi_{em} = \phi_{em}'(I/I')(A'/A)(n/n'),$$

where $I$ (sample) and $I'$ (standard) are the integrated emission peak areas, $A$ (sample) and $A'$ (standard) are the absorbances at the excitation wavelength, $n$ (sample) and $n'$ (standard) are the refractive indices of the solvents, and $\phi_{em}'$ is the quantum yield of the standard. As we used DMAc as a solvent for the standard as well as for the samples, refractive index part was unity. The measured quantum yields of PNC1, PNC2, PNC3, and BNC were 4.65, 5.80, 6.15, and 1.96%, respectively. The measured quantum yields are 2–3 times higher for the NCs that are passivated with isomeric PDA ligands than the vinylideneamine (CH$_2$CNH) passivated NCs. The enhanced quantum yields of
PDA-capped ZnS NCs are the direct results of more effective surface passivation, by which nonradiative recombination paths are reduced significantly.

4. Conclusions
In summary, we have demonstrated a simple approach to synthesize high-quality ZnS NCs of nearly identical size using isomers of PDAs that bind strongly to the core surface. The NCs are characterized microscopically and spectroscopically to reveal the roles of isomeric ligands of PDAs to core crystals. The ligands, PDAs, perform three roles: (1) due to the strong interactions between the PDAs and the NC cores the agglomeration is avoided and the NCs are obtained in narrow size distributions; (2) PDAs effectively suppress the formation of surface defects and prohibit fluorescence quenching and defect-related emissions; (3) finally, PDAs tune the FL because emissions in the NCs are due to the direct excitation of the ligands.

Acknowledgments
This study was financially supported by the Korea Science and Engineering Foundation (KOSEF) through the National Research Laboratory Program funded by the Ministry of Science and Technology (MOST; M10300000369-06J0000-0980), the SRC/ERC program of MOST/KOSEF (Grant # R11-2000-070-80020) and the Brain Korea 21 project.

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