

Research Article

Chemiluminescence of Mn-Doped ZnS Nanocrystals Induced by Direct Chemical Oxidation and Ionic Liquid-Sensitized Effect as an Efficient and Green Catalyst

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A novel chemiluminescence (CL) method was proposed for doping water-soluble Mn in ZnS quantum dots (QDs) as CL emitter. Water-soluble Mn-doped ZnS QDs were synthesized by using L-cysteine as stabilizer in aqueous solution. These nanoparticles were structurally and optically characterized by X-ray powder diffraction (XRD), dynamic light scattering (DLS), Fourier transform infrared spectroscopy (FTIR), UV-Vis absorption spectroscopy, and photoluminescence (PL) emission spectroscopy. The CL of ZnS QDs was induced directly by chemical oxidation and its ionic liquid-sensitized effect in aqueous solution was then investigated. It was found that oxidants, especially hydrogen peroxide, could directly oxidize ZnS QDs to produce weak CL emission in basic solutions. In the presence of 1,3-dipropylimidazolium bromide/copper, a drastic light emission enhancement was observed which is related to a strong interaction between Cu^{2+} and the imidazolium ring. In these conditions, an efficient CL light was produced at low pH which is suggested to be beneficial to the biological analysis. The CL properties of QDs not only will be helpful to study physical chemistry properties of semiconductor nanocrystals but also they are expected to find use in many fields such as luminescence devices, bioanalysis, and multicolor labeling probes.

1. Introduction

Colloidal semiconductor nanocrystals, better known as quantum dots (QDs), are prospective materials for a wide variety of applications. QDs are characterized by a unique set of optical properties that primarily arise from quantum confinement effects [1, 2]. Luminescent properties of semiconductor nanocrystals are usually investigated by photoluminescence (PL) produced using photoexcitation [3], electrochemiluminescence (ECL) generated by electron injection [4, 5], and cathodoluminescence given from electron impact [6]. In recent years, CL and related analysis techniques have been utilized in different fields such as biology, bioimaging, biotechnology, and analytical technology because of their

widespread liner range, simple instrument, and lack of background scattering light interference [7]. With development and recent advance of nanotechnology, the CL study has been extended to nanoparticle systems from traditional molecular systems. Today, the CL systems that involved nanoparticles have attracted an increased consideration because of the unique physical and chemical properties of nanoparticles [8].

Recently Zhou et al. described that ZnS QDs could enhance CL signals emitted from interaction of NaClO with H_2O_2 in basic medium [9]. Xiao's group prepared different types of ZnS QDs and has reported their effects on H_2O_2 - NaIO_4 CL system [10]. Wang et al. found that CdTe could enhance the CL emission of luminol- KMnO_4 [11]. Sun et al. found that QDs could sensitize the CL of Ce(IV)-sulfite [12].

Chen et al. and Frigerio et al. discussed the mechanism of QDs in CL reactions and summarize the applications of QDs-based CRET in detection of small biological molecules, DNA and protein analysis, cell imaging, and immunoassays [13,14]. Our group also reported the effect of CdS QDs on the CL of hydrogen peroxide-sodium hydrogen carbonate system [15].

However, the CL property of QDs as emitting species of the CL reactions is rarely studied. Talapin et al. [16] firstly observed the CL emission of QDs when adding H_2O_2 to CdSe/CdS (core/shell) nanocrystals in solution and in nanoparticulate layers; following Talapin's observation, Wang et al. [17], Liu et al. [18], and Li et al. [19] reported the CL of CdTe and CdS QDs directly oxidized by H_2O_2 in basic media, respectively. At the present stage, the efficiency of the nanoparticle CL system is much lower than that of the traditional luminol or bis(2,4,6-trichlorophenyl) oxalate system [16].

On the other hand, in the reported QDs CL system, high concentration H_2O_2 (1 mol L^{-1} [17] or 0.8 mol L^{-1} [19]) was used as the CL oxidant, and high concentration H_2O_2 is very easy to decompose, which would thus result in unstable CL signal. These disadvantages of the QDs CL system will limit its application. Therefore, it is necessary to improve the CL properties of QDs by using appropriate catalyst. But the catalyzed chemiluminescence (CL) reaction of QDs as emitting species is rarely reported. Recently Wang et al. reported catalyzed effect of sodium hexametaphosphate on CdTe QDs- $KMnO_4$ CL system [20]. Kang et al. investigated the influence of various surfactants on the CdTe QDs- H_2O_2 system [21]. Enhancement of CL emission for the purpose of higher sensitivity is necessary for application in trace analysis. Zhang et al. have reported many prominent works about noble metal nanoparticles-catalyzed CL systems. It has been demonstrated that gold, silver, and platinum nanoparticles could greatly enhance a series of CL reactions including luminol- H_2O_2 [22], luminol- $AgNO_3$ [23], lucigenin-KI [24], and tris(2,2'-bipyridyl)ruthenium-cerium(IV) [25]. Recently Santafé et al. firstly reported the catalyzed chemiluminescence of luminol in the presence of 1-ethyl-3-methylimidazolium ethylsulfate/copper as catalyst, have provided new avenues to enhance the inherent sensitivity, and expand new applications of this mode of detection [26]. So in the present study, we introduce a new ionic liquid/copper catalyst on the CL reaction of QDs. Mn-doped ZnS QDs which is one of the classic semiconductor nanocrystals was synthesized in aqueous solution and used as a model to investigate CL properties of QDs as light emitter.

The aim is to introduce the beneficial effect of imidazolium ring-based ionic liquids (Figure 1) on signal amplification for the catalyzer of the CL system and to improve the efficiency of nanoparticle CL, which is lower than that of luminol- or bis(2,4,6-trichlorophenyl)oxalate-based systems. It will be helpful to promote the step of QDs' application in various fields such as bioassay and trace detection of analyte. Organic compounds containing reducing groups of OH, NH_2 , or SH can react with oxygen-containing intermediate radicals [27, 28]. In this proposed Mn-doped ZnS QDs- H_2O_2 CL system, some intermediate radicals such as $O_2^{\cdot-}$ and OH^{\cdot} were formed during the CL reaction. Therefore, some

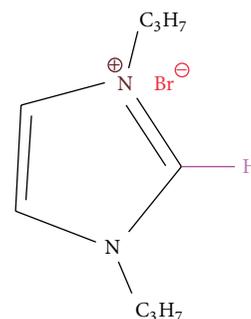


FIGURE 1: Structure of the 1,3-dipropylimidazolium bromide ionic liquid (IL) [(1,3-Pr₂im)Br].

biologically small molecules containing OH, NH_2 , or SH groups are expected to compete with Mn-doped ZnS QDs for active oxygen intermediates, and a decrease in CL intensity may be found. So the Mn-doped ZnS QDs- H_2O_2 CL system is applicable for the determination of such compounds.

2. Experimental Section

2.1. Reagents and Chemicals. All the reagents or solvents were of analytical grade and used without further purification. Ultrapure water (deionized and doubly distilled) was used throughout. $ZnSO_4 \cdot 7H_2O$ and L-cysteine hydrochloride anhydrous were from Fluka (Buchs, Switzerland). $MnCl_2 \cdot 4H_2O$, $CuCl_2$ and hydrogen peroxide (H_2O_2 , %) were purchased from Merck (Darmstadt, Germany). $Na_2S \cdot 9H_2O$ was from Acros (Geel, Belgium). 0.1M phosphate buffer solutions (PBS) with various pH values were prepared by dissolving an appropriate amount of Na_2HPO_4 in water and adjusting the pH values with 0.1M HCl or NaOH solutions. Fresh working solutions of H_2O_2 were prepared daily from 30% (v/v) H_2O_2 and were standardized by titration with a standard solution of $KMnO_4$.

2.2. Characterization Techniques. X-ray diffraction (XRD) patterns were recorded on a Bruker AXS D8 Advance X-ray diffractometer (Bruker, Germany) with $Cu K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Size distribution of Mn-doped ZnS QDs was performed on Hydrosol Nanoparticle size analyzer and Zeta Potential Analyzer (Malvern, UK) which is based on a dynamic light scattering (DLS) technique. The FT-IR spectra ($4000-400 \text{ cm}^{-1}$) in KBr were recorded using FT-IR spectrometer (Tensor 27-Bruker). UV-Vis absorbance spectra of Mn-doped ZnS nanocrystals were obtained from aqueous Mn-doped ZnS QDs solutions using a Cecil CE5501 spectrophotometer (Cambridge, UK). Photoluminescence (PL) measurements were recorded on a Perkin Elmer LS-3B Luminescence Spectrometer (Waltham, USA) using 10 mm quartz cuvettes. The CL light intensity time curve was obtained on Berthold detection systems, Sirius-tube luminometer (Pforzheim, Germany). PL quantum yields of QDs were calculated by comparing their integrated emission to that of the standard dye solutions. Optical density of all solutions was adjusted to values below 0.1 at the excitation wavelength

to avoid reabsorption effects [29]. All optical measurements were carried out at room temperature.

2.3. Synthesis of Aqueous Mn-Doped ZnS Quantum Dots. Colloidal water-soluble Mn-doped ZnS QDs were synthesized via arrested precipitation in water as described previously with slight modifications [30]. Briefly, 50 mL of 0.02 M L-cysteine, 5 mL of 0.1 M ZnSO₄, and 1.5 mL of 0.01 M MnCl₂ were added into a three-necked flask. The mixed solution was adjusted to pH 11 with 1 M NaOH and stirred under dry nitrogen at room temperature for 30 min. Then, 5 mL of 0.1 M Na₂S was quickly injected into the solution. The mixture was stirred for another 20 min, and then the solution was aged at 50°C under air for 2 h to form L-cysteine capped Mn-doped ZnS QDs. Purification of the QDs was carried out by precipitation of the nanoparticles with ethanol in a centrifuge at 5000 rpm for 5 min (the procedure was repeated for 3 times). The obtained QDs were dried under vacuum and stored as a water soluble brown solid powder. Finally, the purified QDs were redissolved in water for further experiments.

2.4. Procedure for the Preparation of 1,3-Dipropylimidazolium Bromide Ionic Liquid (IL). 1,3-Dipropylimidazolium bromide ionic liquid was synthesized according to the procedure reported previously [31]. Briefly, N-trimethylsilylimidazole (12.6 mL, 0.0858 mol), 1-bromopropane (21.7 mL, 0.239 mol), and toluene (28 mL) were refluxed for 10 h and the crystalline product was isolated by the filtration. 1,3-Dipropylimidazolium bromide was dissolved in dry acetonitrile and admixtures were removed by hexane extraction. After acetonitrile removal the product was dried in vacuo for 5 h; yield was 14.2 g (71%), mp 135. ¹H NMR (acetone-d₆): δ = 0:89 (t, 6H, CH₃, J(HH) = 7.6 Hz), 1.95 (m, 4H, CH₂CH₂CH₃, J(HH) = 7.2 Hz), 4.49 (t, 4H, NCH₂, J(HH) = 7.2 Hz), 8.15 (s, 2H, H4, 5 (Imidazole)), 10.27 (s, 1H, H2 (Imidazole)). Anal. Calcd for C₉H₁₇N₂Br (232.9): C, 46.37%; H, 7.29%; Br, 34.30%; N, 12.02%. Found: C, 44.09%; H, 7.25%; Br, 30.29%; N, 11.90% [32].

2.5. Analytical Procedure for CL Detection. Assays were performed in a 0.1 M phosphate buffer with a 330 μL final volume. Briefly, cells were filled with solution A that was made by 230 μL of an aqueous solution of IL, copper, phosphate buffer, and Mn-doped ZnS QDs (appropriate concentrations in water). The mixture was shaken thoroughly and equilibrated at room temperature for 5 min. Then 100 μL of a solution of complementary reagents (various concentration of hydrogen peroxide) were injected to initiate the light emission and the chemiluminescence spectrum was recorded. The CL signal kinetics is identical in the presence and in the absence of IL.

3. Results and Discussion

3.1. Characterization of Mn-Doped ZnS QDs. The XRD pattern of Mn-doped ZnS QDs exhibited a cubic structure with some peaks for (111), (220), and (311) planes (Figure 2). No diffraction peaks from manganese impurities were detected.

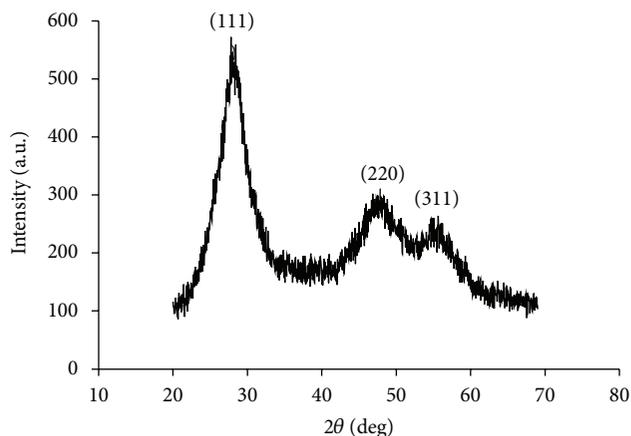


FIGURE 2: XRD patterns of Mn-doped ZnS QDs aged at 50°C for 2 h.

The average size (D) of ZnS nanoparticles can be calculated according to Scherrer's equation [33]:

$$D = k \left(\frac{\lambda}{\beta \cos \theta} \right), \quad (1)$$

where k is a constant (shape factor, about 0.89), λ is the X-ray wavelength (0.15418 nm), β is the full width at half maximum, and θ is the diffraction angle. Based on the full width at half-maximum of (111) reflection, the averaged crystallite sizes of Mn-doped ZnS QDs was estimated to be 4 nm approximately.

The size and distribution of Mn-doped ZnS QDs particles were examined by DLS. Figure 3 shows the scattering intensity distribution of nanocrystals dispersed in water at room temperature. It was found to be aggregate free. The average hydrodynamic size was determined from the DLS data and was 11 nm, thus suggesting that the nanoparticles dispersed well in water. The hydrodynamic diameters were larger than those of the cores due to the solvation layer around the QDs in aqueous solution [34, 35].

In addition, Fourier transform infrared spectroscopy was carried out in order to confirm the bonding of L-cysteine to the nanoparticle surface. Figure 4 shows the FT-IR spectra of free L-cysteine and L-cysteine-capped Mn-doped ZnS nanoparticles. The IR absorption band around 1550–1600 cm⁻¹ (*sv* COO⁻), 1400 cm⁻¹ (*mv* COO⁻), and 3000–3500 cm⁻¹ (*mv* OH, COOH) indicate the –COO⁻ group. The peak at 2900–3420 cm⁻¹ (*mv* N–H) is indicated –NH₂ group, at 600–800 cm⁻¹ (*wv* C–S) is represented the C–S group and at 2550–2750 cm⁻¹ (*wv* S–H) is belong to the –S–H group. Results showed that the stretching band of the S–H thiol group (2550–2670 cm⁻¹ *wv* S–H) is not observed when the nanoparticles are evaluated. The reason for disappearance of S–H group vibration on the surface of ZnS nanoparticles is due to the formation of covalent bonds between thiols and the surface of ZnS.

3.2. Spectral Characteristics of Mn-Doped ZnS QDs. Water-soluble L-cysteine-capped Mn-doped ZnS QDs are optically characterized by UV-vis absorption spectroscopy and fluorometry. The characteristic absorption peak of L-cysteine-capped Mn-doped ZnS QDs occurs at 290 nm as shown in

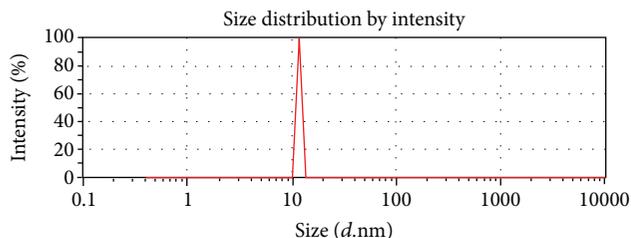


FIGURE 3: Particle size distribution of Mn-doped ZnS QDs measured by DLS.

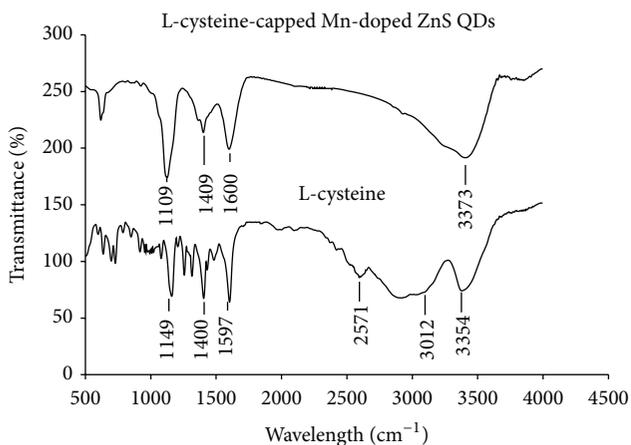


FIGURE 4: FT-IR spectra of free L-cysteine and L-cysteine-capped Mn-doped ZnS QDs.

Figure 5(a). For all the doped samples, two different emission bands dominated the fluorescence spectra (Figure 5(b)). The first emission band at about 460 nm also existed in the PL spectrum of the undoped ZnS nanocrystals; this emission band should indeed originate from the host ZnS but not from Mn^{2+} ions. Upon Mn^{2+} doping, a second characteristic emission band centered at around 582 nm is developed for the well-known ${}^4T_1 \rightarrow {}^6A_1$ d-d transition of Mn^{2+} ions on Zn^{2+} sites, where Mn^{2+} is tetrahedrally coordinated by S^{2-} [36, 37].

Sooklal et al. [38] found that Mn^{2+} incorporated into the ZnS lattice led to the Mn^{2+} -based orange emission while ZnS with surface-bound Mn^{2+} yielded the ultraviolet emission. Thus, it could be concluded that the Mn^{2+} ions in our samples were indeed incorporated into the host ZnS nanocrystals.

Photoluminescence quantum yields (QY) were estimated by comparison of the fluorescence intensity with standard dye solutions with the same optical density at the excitation wavelength and similar fluorescence wavelength [39].

The QY values were calculated by the following equation:

$$\text{QY}_{(\text{sample})} = \left(\frac{F_{\text{sample}}}{F_{\text{ref}}} \right) \left(\frac{A_{\text{ref}}}{A_{\text{sample}}} \right) \left(\frac{n_{\text{sample}}^2}{n_{\text{ref}}^2} \right) \text{QY}_{(\text{ref})}, \quad (2)$$

where F , A , and n are the measured fluorescence value (area under the emission peak), the absorbance at the excitation wavelength, and the refractive index of solvent, respectively. PL spectra were spectrally corrected and quantum yields were determined relative to Rhodamine 6 G in water (QY = 95%)

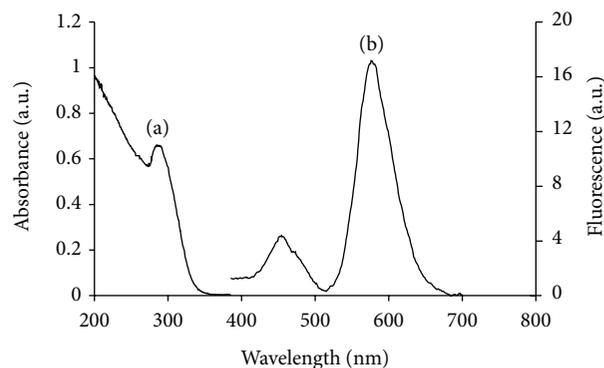


FIGURE 5: Absorption (a) and fluorescence (b) spectra of L-cysteine-capped Mn-doped ZnS QDs. $\lambda_{\text{ex}} = 290$ nm.

[40]. The PL quantum yield of 13.0% was calculated for Mn-doped ZnS QDs.

3.3. Sensitized Effect of [(1,3-Pr₂im)Br]/Copper on Mn-Doped ZnS QDs CL. The effect of [(1,3-Pr₂im)Br]/copper on the Mn-doped ZnS QDs- H_2O_2 chemiluminescent system was investigated. In previous experiments, it was found that in alkaline media QDs could be directly oxidized by KMnO_4 or H_2O_2 to generate CL radiation [16–19]. Aiming to improve the CL properties of QDs and further enhance the QDs induced CL intensity, ionic liquid was introduced into Mn-doped ZnS QDs induced CL system. The presence of ionic liquids (IL) in oxidation reaction catalyzed by transition metals is well known to provide significant advantages in terms of improvement of catalyst stability and activity [41]. Moreover, as most IL currently in use are stable to oxidation, they provide ideal solvents for oxidation processes [42]. In the presence of H_2O_2 the CL response of Mn-doped ZnS QDs system was investigated firstly. As shown in Figure 6(a), the kinetic curve shows that the oxidation of Mn-doped ZnS QDs by H_2O_2 generates weak CL in alkaline media. In presence of [(1,3-Pr₂im)Br]/copper, the CL signal intensity could be greatly enhanced (Figure 6(c)). As a control experiment, the same measurements were performed in the absence of Cu^{2+} . It could be seen from Figure 6 that the CL intensity of ionic liquid/copper-ZnS QDs- H_2O_2 system (Figure 6(c)) is far stronger than that of ionic liquid-ZnS QDs- H_2O_2 system (Figure 6(b)), indicating the great sensitized effect of ionic liquid/copper on ZnS QDs- H_2O_2 CL reaction. Parameters influencing the CL signals of ionic liquid/copper-ZnS QDs- H_2O_2 system were then investigated to establish the optimal conditions for the CL reaction. This optimization was carried out in the following experiment.

3.4. Optimization of the Experimental Conditions. A series of experimental parameters were investigated and optimized for obtaining the maximum sensitivity of the CL system. In order to perform optimization analysis, four factors were evaluated, including pH, stoichiometry of [(1,3-Pr₂im)Br]/ Cu^{2+} complex, H_2O_2 concentration, and ZnS QDs concentration. The CL emission intensity of QDs (peak height) was considered as the experimental response.

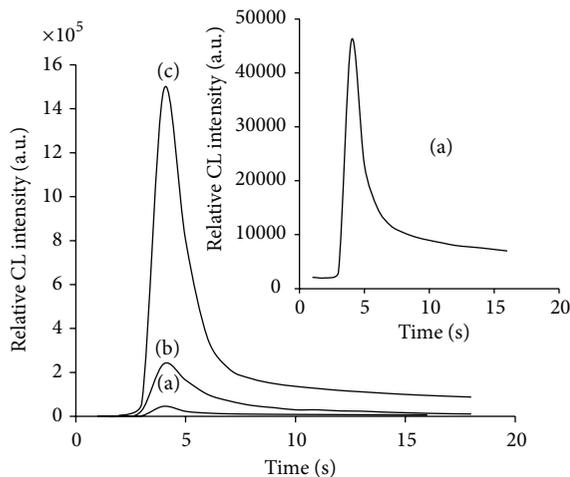


FIGURE 6: CL kinetic curves of ZnS QDs- H_2O_2 system (a), 1,3-dipropylimidazolium bromide IL-ZnS QDs- H_2O_2 system (b), and [(1,3-Pr₂im)Br]/copper-ZnS QDs- H_2O_2 system (c). Conditions: pH 8.0, ZnS QDs, 20 mg L⁻¹; H_2O_2 , 0.5 M.

3.4.1. Effect of Buffer and pH. The reaction media plays an important role in the ionic liquid/copper-ZnS QDs- H_2O_2 CL reaction and the effect of reaction media was investigated. In order to explore the influence of different buffers on the CL intensity of the ionic liquid/copper-ZnS QDs- H_2O_2 system, three buffer solutions, borax, carbonate, and phosphate, were studied at the same pH (pH = 8). It was found that the CL intensity was the strongest when phosphate buffer solution was used. Therefore, phosphate buffer solution was chosen to control acidity in all of experiments. The effect of buffer pH on the CL intensity was examined over the pH range of 6 to 11 using 0.1 mol L⁻¹ PBS solution. Figure 7 presents the CL signals obtained for different pH values in the presence and in the absence of IL. As a matter of fact, the pH seems to have a drastic effect on the CL enhancement. The maximum light intensity value and amplification factor ($\text{Intensity}^{+\text{IL}}/\text{Intensity}^{-\text{IL}}$) was obtained at pH 8 in the presence of IL. This pH dependency of the CL enhancement is assumed to be related to an interaction taking place between Cu^{2+} and 1,3-dipropylimidazolium bromide.

So an organized [(1,3-Pr₂im)Br]/ Cu^{2+} complex can be suggested in the presence of phosphate buffer, which might be reliant to the presence of the labile proton in the C₂ position of the imidazolium ring [43–45].

3.4.2. Effect of Stoichiometry of [(1,3-Pr₂im)Br]/ Cu^{2+} Complex. Since the CL enhancement was observed to be dependent on the presence of [(1,3-Pr₂im)Br]/ Cu^{2+} complex, a study of the stoichiometry of this complex formation has been performed. For that purpose, various concentrations of copper and IL were mixed and used to catalyze the ZnS QDs- H_2O_2 CL reaction at pH 8.0. As shown in Figure 8 the most favorable stoichiometry of 1000/1 ([1,3-Pr₂im)Br]/ Cu^{2+}) between the two reagents can be calculated. The observed intensity enhancement can be indicative of the catalytic effect of the formed [(1,3-Pr₂im) Br]/ Cu^{2+} complex in the presence of

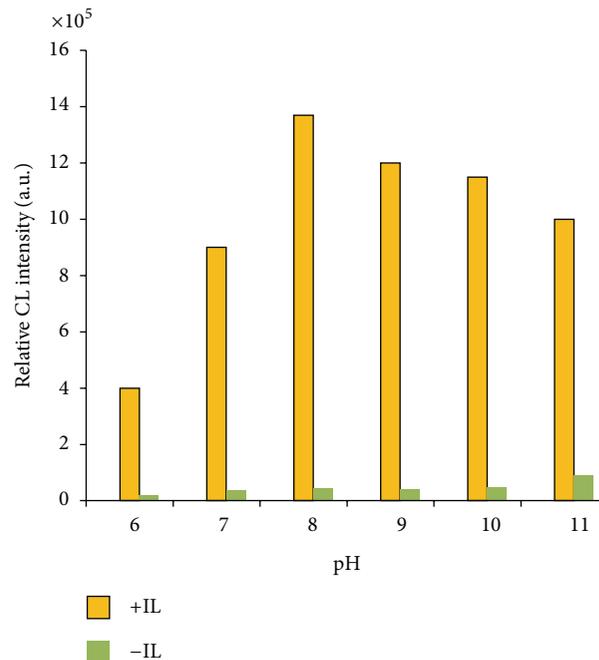


FIGURE 7: Maximum light intensity at pH 6.0–11.0 in the presence and in the absence of 2 M of [(1,3-Pr₂im)Br]. Conditions: pH 8.0, ZnS QDs, 20 mg L⁻¹, H_2O_2 , 0.5 M.

phosphate buffer [28]. However, further addition of Cu^{2+} revealed a gradual decrease of the CL intensity. This is most probably due to formation of insoluble copper(II) hydroxide at higher concentration, which can decrease efficiency of CL emission.

3.4.3. Effect of H_2O_2 Concentration. The effect of H_2O_2 concentration on the CL intensity was examined in the range of 0.005–1.5 mol L⁻¹ (Figure 9). The results showed that the CL intensity increased along with the increased concentration of H_2O_2 in the range of 0.005–0.5 mol L⁻¹. However, if the concentration of H_2O_2 was more than 0.5 mol L⁻¹, the CL system would be quite instable. Since high concentration H_2O_2 can cause rapid decomposition producing air bubbles in the reaction which will affect the system light emitting and stability [46]. So H_2O_2 concentration where then selected 0.5 mol L⁻¹ H_2O_2 as an optimum concentration.

3.4.4. Effect of ZnS QDs Concentration. The response of different concentrations of ZnS QDs to the present CL system was investigated under the optimal reaction conditions. As shown in Figure 10 the analytical signal increased with increasing QD concentrations, but for the highest concentrations the repeatability was impaired. Use of 20 mg L⁻¹ ZnS QD solution led to reproducible signals (r.s.d. ~ 1.5%). The ZnS QDs concentration was then fixed as 20 mg L⁻¹, which assured a compromise between sensitivity, analytical dynamical concentration range, and precision.

3.5. Possible Reaction Mechanism. The CL-generation mechanism for QDs oxidation in aqueous solution has been

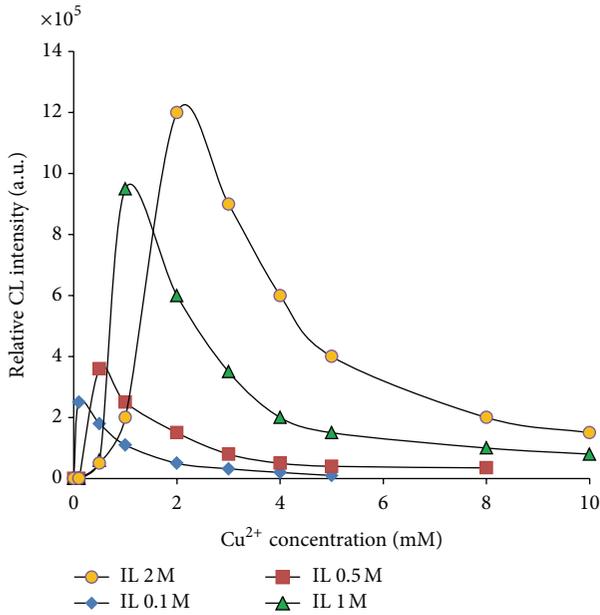


FIGURE 8: Light intensity as a function of different copper and IL concentrations in phosphate buffer (0.1 M, pH 8.0); ZnS QDs, 20 mg L⁻¹, H₂O₂, and 0.5 M.

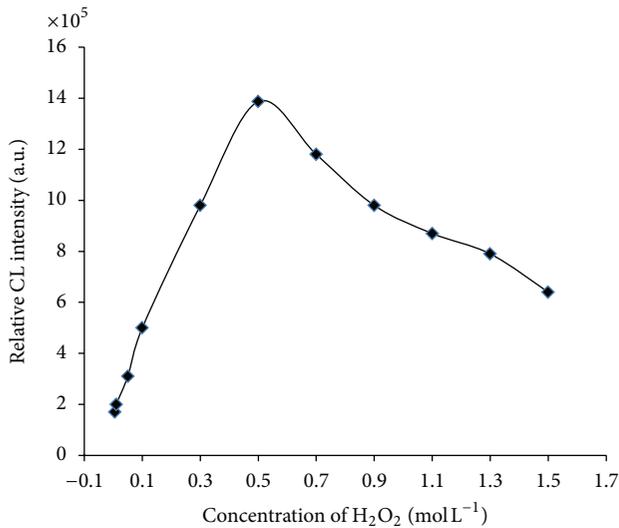


FIGURE 9: Effect of H₂O₂ concentration on the CL intensity of the ionic liquid/copper-ZnS QDs-H₂O₂ system in phosphate buffer (0.1 M, pH 8.0); ZnS QDs, 20 mg L⁻¹.

extensively studied [17, 19, 21]. Some important oxygen-related radicals, such as superoxide radical anion O₂^{•-} and the hydroxyl radical OH[•], have been reported to be important intermediates leading to luminescence [17, 19, 21]. Under a basic condition, based on Sawyer and Kazarnovskii's reports [47] an OH[•] radical can be produced by the reaction of a base with hydrogen peroxide:

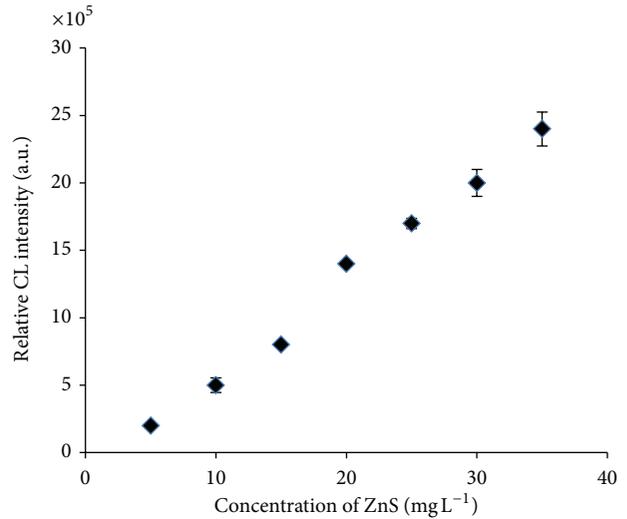
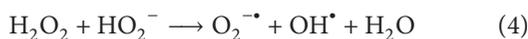
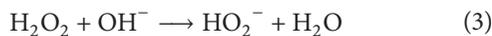
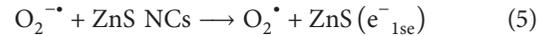


FIGURE 10: Effect of ZnS QDs concentration on the CL system in phosphate buffer (0.1 M, pH 8.0), H₂O₂, 0.5 M. The CL intensity was obtained from the average of three replicates.

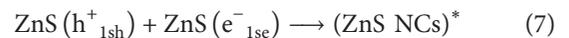
On the other hand, transition metal ions with two available oxidation states usually catalyze the radical decomposition of H₂O₂ [48, 49]. Based on findings of Neeraj and coworker, there is a complexation reaction between copper(II) ion and imidazole ring in presence of phosphate buffer [45]. Copper(II) organic complex has activity more than Copper(II) ion in the radical decomposition of H₂O₂, as it can be detected by CL reaction [50]. So [(1,3-Pr₂im)Br]/Cu²⁺ complex catalyzes the production of reactive oxygen species. The resulted superoxide ion (anion radical, O₂^{•-}) is produced by the radical decomposition of H₂O₂ [47, 48, 51]. The formed superoxide ions are quite stable in high pH aqueous solution, and their lifetime is about 1 min [52]. They can easily donate one electron and lead to the injection of an electron from the superoxide ion into the 1Se quantum-confined orbital of ZnS NCs [16]:



The formed OH[•] radical should be able to inject a hole in the 1Sh quantum-confined orbital of the ZnS NCs at the optimum pH value is used [16]:



Then the excited state of the ZnS NCs occurs containing one electron and one hole which occupies the 1Se (ZnS(e⁻_{1se})) and 1Sh (ZnS(h⁺_{1sh})) quantum-confined orbital, respectively [53]. When the excited state of ZnS NCs returns to its ground state, CL may be produced:



In this study, it is found that [(1,3-Pr₂im)Br]/Cu²⁺ complex can enhance the sensitivity of ZnS QDs-H₂O₂ system (Figure 6). Enhancement of CL by adding IL solution [(1,3-Pr₂im)Br] purposed to have two reason: (1) more efficient

reaction of QDs with the $O_2^{\cdot-}$ by forming surfactant aggregate in presence of IL, similar to micelle effect [54, 55], (2) the catalyst effect of the formed [(1,3-Pr₂im)Br]/Cu²⁺ complex in producing superoxide anion radical $O_2^{\cdot-}$ by the radical decomposition of H₂O₂ [47, 48, 51].

4. Conclusion

The use of QDs as CL emitter is a topic of considerable interest in CL research field. In this study, it has been found that 1,3-dipropylimidazolium bromide/copper can enhance the sensitivity of ZnS QDs-H₂O₂ system. It is possible that [(1,3-Pr₂im)Br]/copper can prolong the radical lifetime and, thus, as a chemiluminescence sensitizer have the potential to interact with the nanodots affecting their photochemical properties and/or reactivity and make possible chemiluminometric determination of compounds. The most QDs CL reactions are classically performed in basic conditions (NaOH 0.1 M). The IL, in addition to the reaction buffer, allows lowering of the reaction pH to 8 that is beneficial toward biological analysis. This may intrigue researchers into gaining a new interest in investigating the chemiluminescence property of semiconductor nanocrystals. This work is important for the study of new and efficient catalysts and luminophore for chemiluminescent reactions and promoting the steps towards its application in various fields.

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