Chemiluminescence of CdTe Nanocrystals Induced by Direct Chemical Oxidation and Its Size-Dependent and Surfactant-Sensitized Effect

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CdTe nanocrystals (NCs) capped with thioglycolic acid (TGA) were synthesized via a microwave-assisted method. The chemiluminescence (CL) of CdTe NCs induced by directly chemical oxidation and its size-depended and surfactant-sensitized effect in aqueous solution were then investigated. It was found that oxidants, especially hydrogen peroxide and potassium permanganate, could directly oxidize CdTe NCs to produce strong CL emission in basic conditions. The oxidized CL of CdTe NCs displayed size-dependent effect and its intensity increased along with increasing the sizes of the NCs. Moreover, the CL intensity could, if surfactants CTAB or β-cyclodextrin were added to the above CL system, be sensitized to some degree. The sensitized CL induced by CTAB and β-cyclodextrin is mainly contributing to the formation of aggregate nanostructure and the micellar micronanoenvironment, respectively. The possible oxidized CL mechanisms were further examined by means of photoluminescence spectra, CL spectra, and transmission electron microscopy studies. The CL properties of CdTe NCs not only will be helpful to study physical chemistry properties of semiconductor nanocrystals but also are expected to find use in many fields such as luminescence devices, bioanalysis, and multicolor labeling probes.

1. Introduction

Semiconductor nanocrystals (NCs) with excellent luminescent properties have attracted an increased attention because of its application in many areas of fundamental and technical importance.[1–5] Luminescent properties of semiconductor nanocrystals are usually investigated by photoluminescence (PL) produced using photoexcitation,[6,7] electrochemiluminescence (ECL) generated by electron injection,[8–10] and cathodoluminescence given from electron impact.[11] However, chemiluminescence (CL) generated from chemical energy excitation is rarely used to study the luminescent property of semiconductor nanocrystals to date. To the best of our knowledge, only Talapin et al. recently described the chemiluminescence property of CdSe/CdS core/shell nanostructure dealing with the emitting state related to the quantum-confined orbitals.[12] The other reports about chemiluminescence in the presence of the micro- or nanosized particles involved in different luminescent mechanisms, such as catalysis effect, without relationship to the state of the particle.[13–16]

In recent years, CL and related analytical technique have intrigued people extensive interest and have been developed to be an important and powerful tool in different fields,[17,18] such as chip technique,[19] drug analysis,[20] environmental monitoring,[21] clinical diagnose,[22] biomedical detection,[23] and biological process,[24] because of its high sensitivity, wide linear range, simple instrumentation, and no background scattering light interference. Many investigations have indicated that chemiluminescent property of novel nanoparticles, due to its high sensitivity, would be promising for new applications.[12,18] If a refitted instruments for chemiluminescence multiple wavelengths monitoring was used for luminescent signal collection, the use of nanocrystals as chemiluminescent emitters can have potential benefits such as easy multicolor labeling for visible and NIR spectral regions without the requirement of external excitation light source.[12]

In the present work, CdTe NCs, one of the novel classes of semiconductor nanocrystals, was chosen to investigate CL properties of semiconductor NCs as light emitter. The directly oxidized CL of CdTe NCs and its size-dependent and surfactant-sensitizing effects in aqueous solution were detailedly studied. CL spectra, PL spectra, UV–visible absorption, and transmission electron microscopy studies were carried out to explore the oxidized CL reaction mechanism. These new phenomena would further enable people to exploit more applications of the semiconductor nanocrystals. In particular, the obtained results would be essential for the development of novel characterization and analysis methods for semiconductor NCs.

2. Experimental Section

2.1. Reagents and Materials. Analytical reagent-grade chemicals and ultrapurification water prepared with an ultra-purification system (Beijing Shuangfeng Ultrapurification Instrument Plant, Beijing, China) were used throughout. Te powder and thioglycolic acid (TGA) were purchased from Acros Organics (Geel, Belgium). $CdCl_2$, $NaHB_4$, H_2O_2, $KMnO_4$, $K_3Fe(CN)_6$, KIO_4, NBS, $Ce(SO_4)_2$, $K_2S_2O_8$, cetyltrimethylammonium bromide (CTAB), sodium dodecyl sulfate (SDS), β-cyclodextrin (β-CD), Tween 80, Triton X-100, and NaOH were obtained from Tianjin Chemical Reagent Plant (Tianjin, China). The likely minimum number of dilution steps was used to prepare more diluted solutions. All other chemicals were of the best grade available and used as received.

2.2. Preparation of CdTe NCs. TGA-capped CdTe NCs were synthesized as the procedure described in refs 25 and 26 with little modification. Briefly, N_2-saturated cadmium chloride solution was added to NaHTe solution which was prepared by

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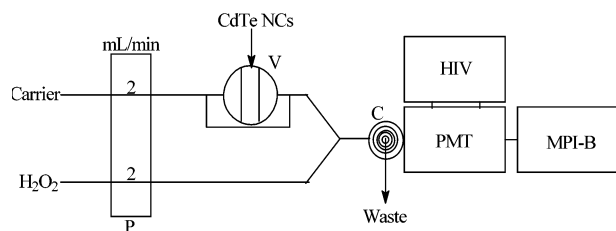
Figure 1. Schematic diagram of lab-built flow-injection chemiluminescence detection system. Key: P, peristaltic pump; V, injection valve; C, flow cell; PMT, photomultiplier tube; HIV, negative high-voltage supply; MPI-B, luminescence analyzer controlled by personal computer.

the reaction between sodium borohydride and tellurium powder in the presence of thioglycolic acid (TGA). The concentration of Cd^{2+} was 2 mM, and the molar ratio of Cd^{2+}:Te^{2-}:TGA was fixed at 1:0.5:2.5. After mixing, the solution was heated with microwaves for different time. The sizes of the CdTe NCs could be tuned by simply varying the heating time.

For the purified CdTe NCs samples, the free CdCl$_2$ and TGA were removed via dialysis for 2 days in 0.01 M NaOH solution. A dialysis membrane with a molecular weight of cutoff 7000 was used for the purification of CdTe NCs. The purified degree of the free CdCl$_2$ and TGA was monitored with an elemental analysis for the dialysate.

2.3. Apparatus. The schematic diagram of the flow system employed in this work is shown in Figure 1. A peristaltic pump was used to deliver flow streams in this system. PTFE tubing (0.8 mm i.d.) was used as connection material in the flow system. CdTe NCs colloid solution (50 μL) was injected into the carrier stream (water) using an eight-way injection valve equipped with a 50 μL sample loop, and then it was merged with H$_2$O$_2$ or KMnO$_4$ and finally reached the flow cell to produce CL emission. The flow cell was made by coiling 30 cm of colorless glass tube (1 mm i.d. and 2 mm o.d.) into a spiral disk shape with a diameter of 2 cm and located directly facing the window of the CR-105 photomultiplier tube (Hammamatsu, Tokyo, Japan). The CL signal produced in the flow cell or the static detection cell in static injection mode was detected and recorded with a computerized ultraweak luminescence analyzer (type MPI-B, manufactured at Remax Electronic Science and Technology Co. Ltd., Xi'an, China). Data acquisition and treatment were performed with MPI-B software running under Windows XP. The CL spectra of the proposed systems were examined by a series of high-energy optical filters (425, 440, 460, 490, 515, 535, 555, 575, 595, 620, 640 nm).

The photoluminescence of CdTe NCs was mornitored by a LS-550 fluorophotometer (PE Elmer, U.K.). UV−vis absorption spectra were achieved with a model UV-2100s spectrophotometer (Shimadzu, Japan).

The size and shape of the CdTe NCs synthesized using the present method were characterized by a model H-800 transmission electron microscope (Hitachi, Japan) operated at 100 kV.

2.4. Procedure for CL Detection. To obtain good mechanical and thermal stability of the flow-injection CL system, the instruments were run for 10 min before the first measurement. Flow lines were inserted into H$_2$O$_2$ solution, water carrier, and CdTe NCs solution, respectively. The flow rate was fed at 2.0 mL/min for all lines. The pumps were then started to wash the whole system until a stable baseline was recorded. The 50 μL of sample solution was injected into the carrier stream. This stream was merged with the H$_2$O$_2$ solution and then reached the flow cell to produce the CL emission. The concentration of CdTe NCs was quantified by the relative CL intensity.
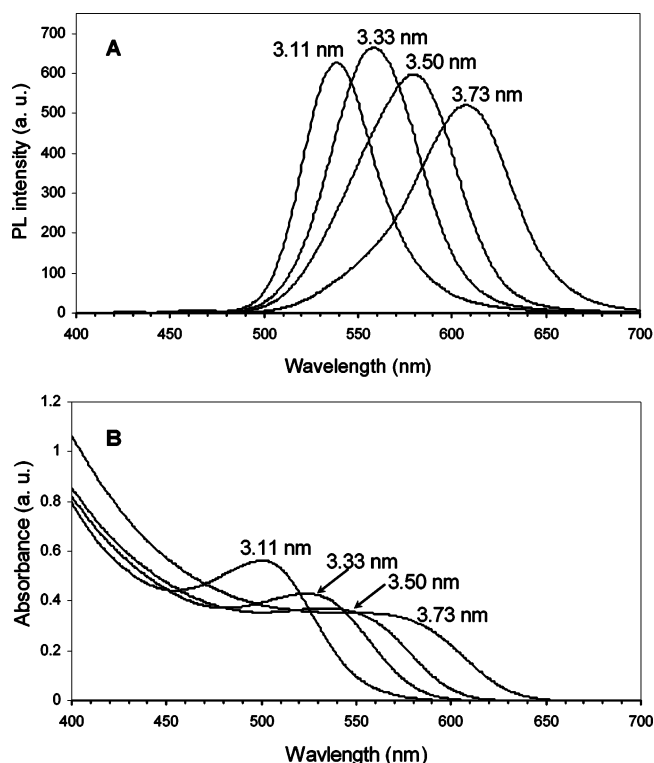
Figure 2. (A) PL spectra and (B) absorption spectra of CdTe NCs with different sizes. The sizes of a, b, c, and d were around 3.11, 3.33, 3.50, and 3.73 nm, respectively. Conditions: A, 5 × 10^{-6} M CdTe colloidal solutions with different sizes; B, 1 × 10^{-3} M CdTe colloidal solutions with different sizes.

The lab-built static CL detection system for the CL reactions consisted of a colorless glass beaker (10 mL) and the MPI-B ultraweak luminescence analyzer. The colorless glass beaker was located directly on the window of the CR-105 photomultiplier tube of the luminescence analyzer. Oxidant solutions were placed into the glass beaker, respectively. Then a 100 μL CdTe colloidal solution was injected into the beaker using a 100 μL injector through the rubber plug in the lid of detector of the luminescence analyzer. Data acquisition and treatment were still performed with MPI-B software running under Windows XP.

3. Results and Discussions

3.1. PL and Absorption Spectra of CdTe NCs. Photoluminescence (PL) and absorption spectra are not only utilized to character semiconductor NCs assisted with TEM and other characterization means, but they are a powerful tool to confirm quantum-confined property of semiconductor NCs. Figure 2 showed PL and absorption spectra of the different sizes of the TGA-stabilized CdTe NCs prepared using a microwave-assisted synthetic process. These CdTe colloids possessed a relative well-resolved absorption maximum of the first electronic transition. And the PL peak (Figure 2A) and absorption maximum (Figure 2B) shifted to longer wavelengths with increasing NCs sizes as a consequence of quantum confinement. According to the literature,[27] the particle size of above-mentioned CdTe NCs was calculated in virtue of the following expression:

$$D = (9.8127 \times 10^{-7})\lambda^3 - (1.7147 \times 10^{-3})\lambda^2 + (1.0064)\lambda - 194.84 \quad (1)$$

The results show that the particle diameters of the as-prepared CdTe NCs are around 3.11, 3.33, 3.50, and 3.73 nm, respec-
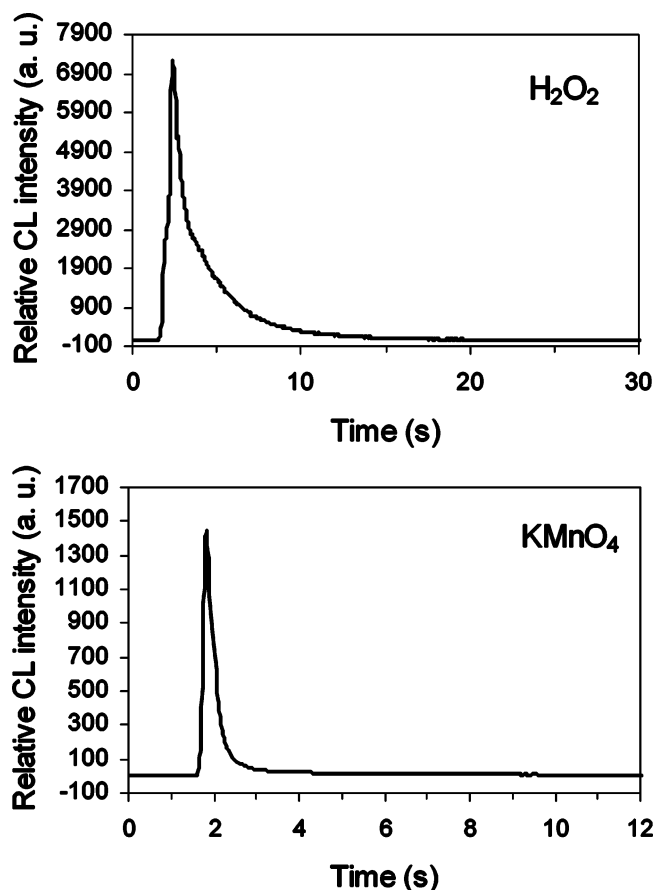
Figure 3. CL intensity profiles via time of H_2O_2−CdTe NCs (a) and KMnO$_4$−CdTe NCs (b) CL reactions in static-injection mode. Conditions: a, 100 μL 1 × 10^{-3} M CdTe NCs with a particle size of around 3.33 nm injected into a 1 M H_2O_2 solution; b, 100 μL 1 × 10^{-3} M CdTe NCs with a particle size of 3.33 nm injected into a 1 × 10^{-3} M KMnO$_4$ solution; high voltage, −500 V.

TABLE 1: CL Response of CdTe NCs to Different Oxidants

oxidant	concentration (mol/L)	relative CL intensity	high voltage (V)
H_2O_2	1	7000	−500
KMnO$_4$	1 × 10^{-4}	1500	−500
KIO$_4$	0.01	350	−500
Ce^{4+}	0.01	80	−500
K$_3$Fe(CN)$_6$	0.01	30	−500
(NH4)$_2$S$_2$O$_8$	0.01	14	−500
K$_2$S$_2$O$_8$	0.01	0	−800
NBS	0.03	0	−800

[a] CdTe colloidal solutions were injected respectively into different oxidants through using a static injection system. Conditions: oxidants, 2 mL; 1 × 10^{-3} M CdTe NCs with a particle size of around 3.33 nm, 100 μL; high voltage, −500 or −800 V.

tively, corresponding with the PL peaks of 539, 559, 580, and 608 nm (a, b, c, d in Figure 2A).

3.2. Directly Oxidized CL. When TGA-capped CdTe colloid solution was mixed with some oxidants, especially 1 M H_2O_2 or 1 × 10^{-4} M KMnO$_4$ in alkaline aqueous solution, strong CL light emission was observed as shown in Figure 3.

The CL reaction between oxidants and CdTe NCs was further investigated with 3.33 nm size CdTe NCs. First, various oxidants usually applied in CL reaction were respectively investigated with a static injection system and the results are listed in Table 1. It could be seen from Table 1 that H_2O_2 and KMnO$_4$ can, in the available concentration range, directly oxidize CdTe NCs
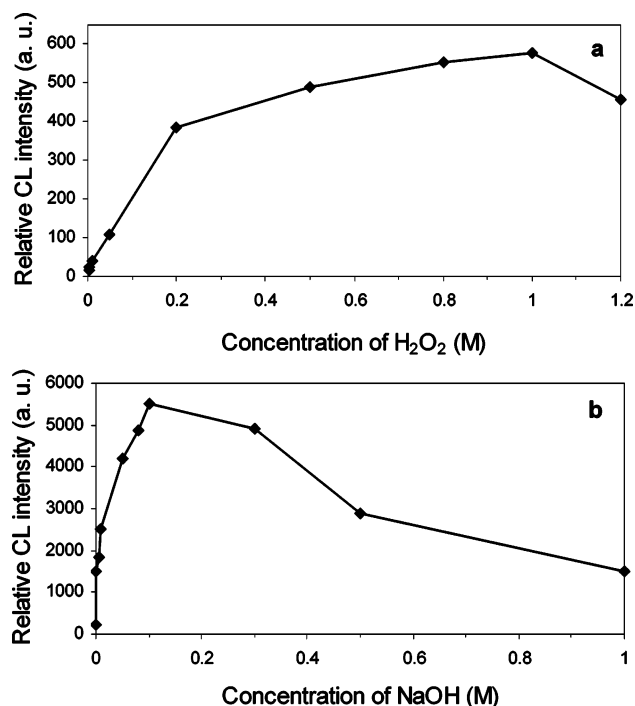
Figure 4. Profiles of oxidized CL intensity via the concentrations of H_2O_2 (a) and NaOH (b) in FIA-CL mode. Conditions: (a) 1 × 10^{-3} M CdTe NCs colloid solution with a particle size of around 3.33 nm as luminescent reagent and water as carrier; (b) 1 M H_2O_2 as oxidant and 1 × 10^{-3} M CdTe NCs colloid solution with a particle size of around 3.33 nm as luminescent reagent; flow rate, 2.0 mL/min; high voltage, −800 V.

to generate strong CL emission. And the CL produced with H_2O_2 was more intensive than that of KMnO$_4$. The dynamic CL intensity−time profiles of the CdTe−H_2O_2/KMnO$_4$ systems acquired in static-injection mode indicated (Figure 3) that the CL reactions were very quick and the CL intensity reached a maximum after ∼0.75 s for CdTe−H_2O_2 system and ∼0.25 s for CdTe−KMnO$_4$ system after initiating the reactions. CdTe NCs can also be oxidized by K$_3$Fe(CN)$_6$ and KIO$_4$ to produce CL signals. But, compared with that of H_2O_2 and KMnO$_4$, the CL induced by K$_3$Fe(CN)$_6$ and KIO$_4$ were quite weak. The consequent experiments therefore selected H_2O_2 as oxidant for the CL reaction. A contrast experiment was also conducted to examine the influence of coexisting substances (e.g., free CdCl$_2$ and TGA) on the oxidized CL system in the unpurified CdTe colloids. With the same static-injection mode, CdCl$_2$ and TGA solution were in turn injected into H_2O_2 solution, and no CL signal was observed. At the same time, the CL response of purified CdTe NCs sample via a dialysis procedure was investigated with proposed FIA-CL system. The results showed that there had no significant difference between the obtained CL signals and that of a comparison of the unpurified CdTe NCs, indicating that the free CdCl$_2$ and TGA in the unpurified CdTe NCs colloids solution show almost no effect on the oxidized CL reaction of CdTe NCs.

Second, the concentration of H_2O_2 was optimized over the range of 0.0001−1.2 M in a FIA-CL mode described in Experimental Section. The results showed that the CL intensity increased along with the increased concentration of H_2O_2 (Figure 4a). However, if the concentration of H_2O_2 was more than 1 M, the CL system would be quite instable possibly attributing to the rapid decomposition of high concentration H_2O_2. Thus, 1 M was selected as optimum concentration of H_2O_2 throughout the study.

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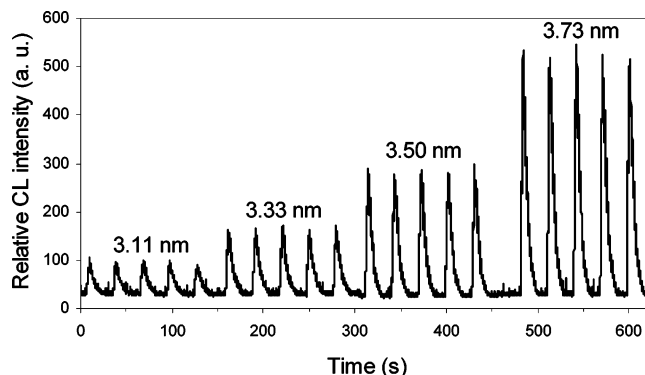*J. Phys. Chem. B, Vol. 109, No. 49, 2005* **23307**
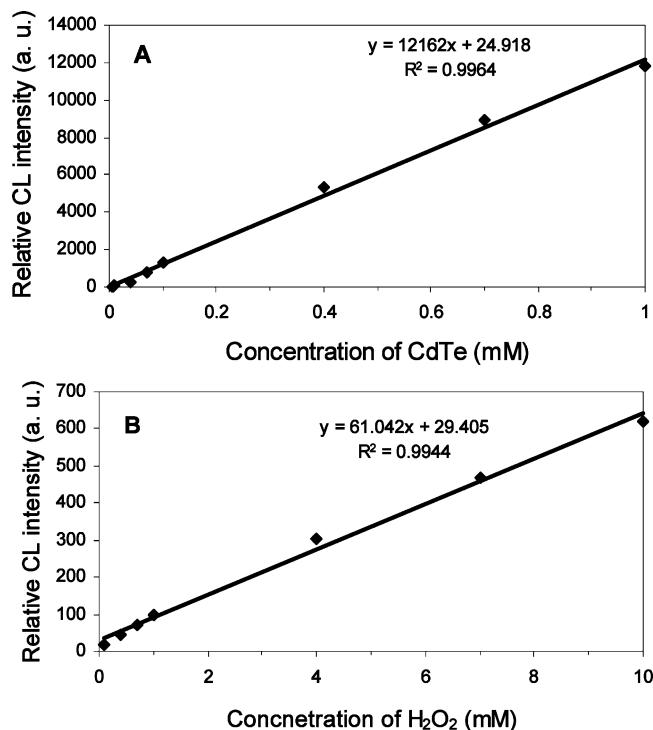
Figure 5. CL intensity profiles via the concentration of CdTe NCs (A) and H_2O_2 (B) in FIA-CL mode. Conditions: (A) 1 M H_2O_2 as oxidant and 0.1 M NaOH solution as carrier; (B) 1×10^{-3} M CdTe NCs colloid solution with a particle size of around 3.33 nm as luminescent reagent and 0.1 M NaOH solution as carrier; flow rate, 2.0 mL/min; high voltage, -800 V.

Figure 6. CL intensity profiles via the particle sizes of CdTe NCs. Conditions: 1×10^{-3} M CdTe NCs with different sizes injected into a proposed FIA-CL system (water as carrier) at a flow rate of 2.0 mL/min, operated at -800 V high voltage.
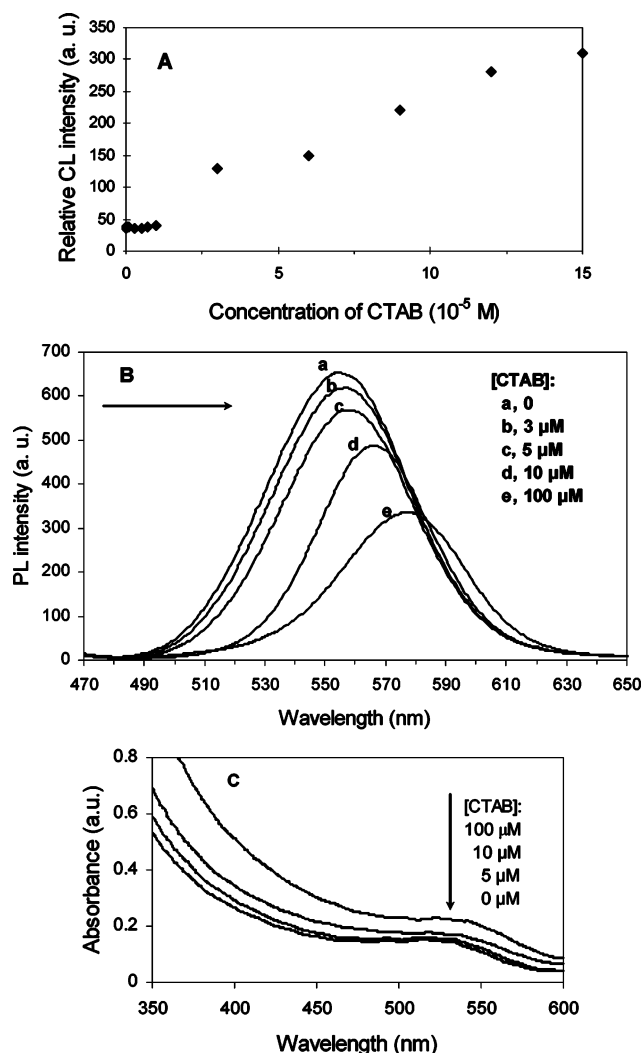
Third, the reaction media was also investigated. Considering the toxicity of HTe in acid condition, the CL response of the proposed CL reaction under the acid media was not tested. When the CL reaction was conducted in alkaline medium, surprisingly, the CL emission enhanced drastically. In the present work, NaOH solution was employed as the reaction medium and the effect of the concentration of NaOH on the CL intensity was further examined. The results (Figure 4b) show that the CL intensity of the oxidized CL would be gradually intensified if the concentration of NaOH was increased from 0.001 to 0.1 M. But, if the concentration of NaOH was more than 0.1 M, the CL intensity decreased instead. Therefore, 0.1 M NaOH was selected as optimal reaction media for the direct oxidized CL of CdTe NCs.

The response of different concentration of CdTe NCs to the present oxidized CL system was investigated under the optimal reaction conditions. It was found (Figure 5A) that the CL intensity linearly increased along with the increased concentration of CdTe NCs in the range of 5×10^{-6} to 1×10^{-3} M. Meanwhile, we also studied the response of the system to different concentration of H_2O_2 using the concentration of 1×10^{-3} M CdTe NCs, showing (Figure 5B) that the CL intensity increased linearly with the concentration of H_2O_2 in the range of 1×10^{-4} to 1×10^{-2} M.

Size effect is a basic characteristic of semiconductor nanocrystals. Large numbers of reports have mentioned the property of semiconductor nanocrystals.[27-31] In the present work, we also wonder whether there is size-dependent effect on the CL response of the as-prepared semiconductor nanocrystals. In a FIA-CL mode, the response of above-mentioned CdTe NCs to the oxidized CL system was investigated using 1 M H_2O_2 as oxidant and water as carrier. It was found (Figure 6) that the CL intensity gradually increased while the particle size of the

CdTe NCs increased, indicating that chemiluminescence of CdTe NCs had size effect. According to CL energy match theory,[17] this probably resulted from the energy matching degree between the chemical energy generated during CL redox reaction and the required excitation energy for the formation of excited state of luminophor. It is known that the energy band gap of semiconductor nanocrystals decreased with the increment of particle size. In this case, the increment of CL intensity is possibly attributed to the chemical energy, generated during the chemical reaction between H_2O_2 and CdTe NCs, more matches the smaller energy band gap of the studied four sizes nanoparticles. The more the chemical energy matches the excitation energy needed, the stronger the CL intensity and efficiency. Meanwhile, the CL intensity was all found to be linear with the concentration of the studied CdTe NCs.

Generally, the use of surfactants often makes the corresponding CL system more sensitive.[32] In a preliminary experiment, the effect of different surfactants whose concentrations were above their cmc on the proposed oxidized CL system, including cationic, anionic, and nonionic surfactants, were examined. The results from the preliminary experiment showed that the addition of micellar cationic CTAB and nonionic β-CD to CdTe colloidal solution resulted in the enhancement of CL intensity, but the others, including anionic SDS, nonionic Tween 80, and Triton X-100, did not show a significant influence on the CL reaction.

At first, we tested the influence of cationic surfactant (e.g., CTAB) on the oxidized CL. It was found when the added CTAB concentration was above 1.5×10^{-4} M, CdTe NCs tended to gradually aggregate and form the precipitation. Therefore, the effect of CTAB on the proposed CL reaction was investigated in the range of 1×10^{-6} to 1.5×10^{-4} M with 1×10^{-3} M CdTe colloidal solution as luminescent reagent and water as carrier. At the same time, PL of CdTe NCs was also examined in the same CTAB concentration range. It was found (Figure 7A) that there was no significant change for the CL intensity when the concentration of CTAB varied from 1×10^{-6} to 1×10^{-5} M. However, once it was above 1×10^{-5} M, the results showed that the oxidized CL intensity increased gradually with the increment of CTAB concentration. A previous contrast experiment has demonstrated that no CL signal was observed when only CTAB was injected into the CL system.

The PL of CdTe NCs in the presence of different concentrations CTAB indicated (Figure 7B) that the PL of CdTe NCs shifted to longer wavelength when we increased the CTAB concentration from 1×10^{-6} to 1.5×10^{-4} M. Figure 7C shows the absorption spectra of CdTe NCs obtained by adding different concentrations CTAB, displaying that the peak absorption

Figure 8. TEM images of CdTe NCs in the absence (A) and presence (B) of CTAB.
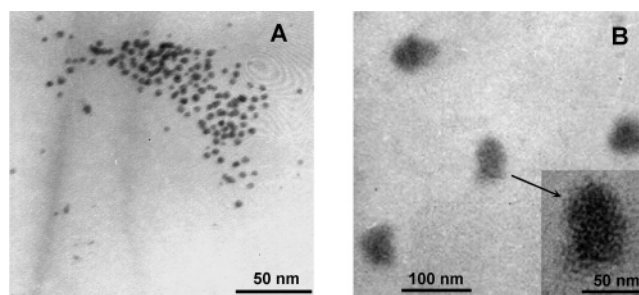
Figure 7. CL intensity profiles (A) PL spectra (B), and absorption spectra (C) of CdTe NCs with a particle size of around 3.33 nm via added CTAB concentration. Conditions: A, different concentrations of CTAB mixed with 1×10^{-3} M CdTe NCs as luminescent reagent and water as carrier in FIA-CL mode, flow rate 2.0 mL/min, -700 V high voltage; B concentration of CdTe NCs, 1×10^{-5} M; C, concentration of CdTe NCs, 5×10^{-4} M.

The compact aggregating nanostructure greatly reduced the distance between nanocrystals, which resulted in the chemical energy generated during the oxidized CL reaction easily transfer between CdTe NCs. And the energy loss via other processes, such as nonradiant transition and collision annihilation, would be greatly reduced, which is in favor of the adequately utilization of the produced chemical energy and enhance the generation of excited state (or exciton) of CdTe NCs. The CL efficiency is consequently enhanced. The authors also examined the effect at above the cmc (9.2×10^{-4} M) of CTAB on the CL intensity of the oxidized CL system. Although the mixture solution appeared little turbid, the stronger CL response was still observed and the CL intensity could be enlarged if the concentration of CTAB continually increased in a certain range. The enhancement CL can be probably attributed to the micelle micronanoemvironment sensitized effect bearing a resemblance to the traditional micelle sensitized CL reaction without considering the size change of the aggregate. These phenomena would be in favor of the development of more sensitive CL system and the preparation of novel long wavelength nanometerials with simple modification.

Then, we also studied the effect of anionic surfactant SDS on the proposed oxidized CL reaction (Figure 9). Figure 9a indicated that there was no significant change for the CL intensity when the concentration of SDS varied in the range of 1×10^{-6} to 5×10^{-3} M. Moreover, the photoluminescence of the mixture of CdTe NCs and different concentration SDS also did not display red shifting or blue shifting for the peak wavelength (Figure 9b). This further confirmed the interaction between the positively charged CTAB and the negatively charged TGA-capped CdTe NCs.

Finally, we examined the effect of nonionic surfactant β-CD on the oxidized CL reaction. The results showed (Figure 10a) that the oxidized CL intensity did not almost alter when the concentration of β-CD below its cmc (1×10^{-3} M) was varied. However, when it was above the cmc of β-CD, the oxidized CL intensity enhanced greatly. It suggested that the micellar nanomicroenvironment was of great importance for the sensitization of the oxidized CL. Similar to other CL systems sensitized by micelle, the micellar micronanoenvironment formed by β-CD made the chemical energy effectively accepted by CdTe NCs and emitted with the manner of light radiation, instead of mass loss via interparticle collision and other nonradiant transition processes. This led to the great enhancement of the CL efficiency and intensity. Meanwhile, the PL spectra of CdTe NCs in β-CD solution were also examined. The results showed (Figure 10b) that the PL did not also display red shifting or blue shifting for the peak wavelength with the concentration of β-CD varied from 1×10^{-6} to 1×10^{-3} M.

All above results demonstrated that the interaction between surfactants and TGA-capped CdTe NCs was dominated by the active force of charges. Positively charged cationic surfactant

wavelength also red shifted to some extent. On the basis of the TEM studies (Figure 8), in the presence of CTAB, CdTe NCs tended to form aggregate nanostructure through the interaction between charges. The aggregation of nanocrystals resulted in the increasing overlap of the electron wave functions in neighboring nanocrystals and further possibly led to the red shift of the spectra.[33,34]

It is well-known that cationic surfactant CTAB is positively charged while the surface of TGA-capped CdTe NCs contains negative charge. It is therefore easily for CTAB molecules to bind onto the surface of TGA-capped CdTe NCs via the static electrification. With the increased amount of the CTAB bounded on the surface of CdTe NCs, the surface of CdTe NCs would gradually show positive charge property and be prone to bind another negatively charged CdTe NCs, which would finally cause the aggregation of CdTe NCs. The aggregation degree associated with the concentration of CTAB and responded to the increased CL intensity. TEM image of CdTe NCs added CTAB solution has proved the aggregation process (Figure 8). Compared with that of in the absence of CTAB (Figure 8A), it can be clearly seen that CdTe NCs easily aggregated to form aggregating nanostructure in the presence of CTAB (Figure 8B).
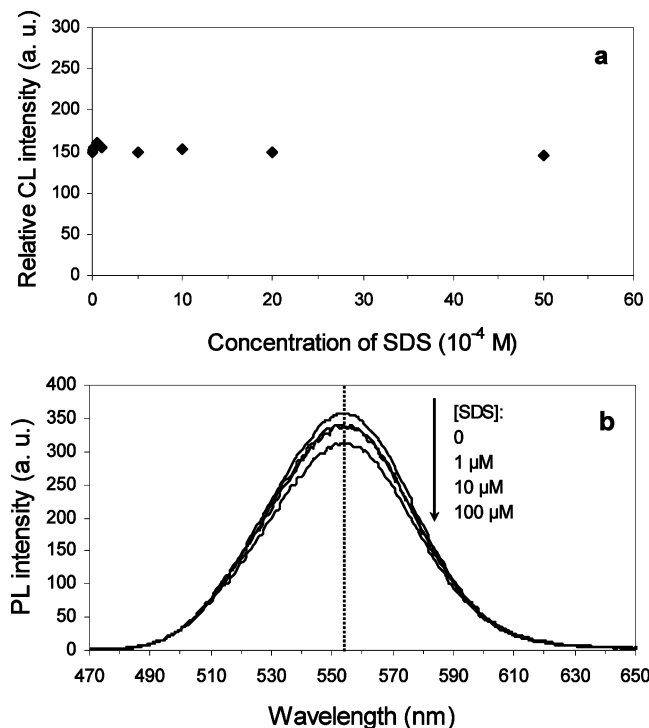
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Figure 9. CL intensity profiles via the added SDS solution (a) and PL spectra of CdTe NCs with the particle size of around 3.33 nm in different concentration SDS solution (b). Conditions: a, different concentrations of SDS mixed with 1×10^{-3} M CdTe NCs as luminescent reagent and water as carrier in FIA-CL mode, flow rate 2.0 mL/min, -800 V high voltage; b, 5×10^{-6} M CdTe NCs in different concentrations of SDS solution.

CTAB of the concentration range of 1×10^{-6} to 1.5×10^{-4} M could bind with TGA-capped CdTe NCs and lead to the change in the oxidized CL behavior and PL behavior, but it is not so for the anionic surfactant SDS and nonionic surfactant β-CD within the same concentration range. Micellar cationic surfactant CTAB and nonionic surfactant β-CD could cause great enhancement of oxidized CL signals. All these phenomena inspired us with an interesting expectation to apply CdTe NCs-like semiconductor nanocrystals to various applications through using their CL or PL properties.

3.3. Possible CL Reaction Mechanism. To explain the primary CL reaction mechanism and confirm the emission species during the oxidized CL reaction, the following experiments were performed. The H_2O_2-oxidized CL spectra of 3.33 nm CdTe NCs were measured using a series of high-energy cutoff filters of various wavelengths as described elsewhere [16] and shown in Figure 11. It could be clearly seen from Figure 11 that there was only one emission band around 490−650 nm and the CL peak was around 555 nm for the CL reaction. It is known that the PL spectra of the stable emitting species should be identical with the CL spectra for common CL reaction. We then investigated the PL of the CdTe NCs. The PL also displayed an emission band similar to the CL spectra with a peak wavelength of around 557 nm. Moreover, the experimental results have indicated that the other coexisting substrates in the CdTe NCs do not possess the oxidized CL or PL properties. Therefore, the emissive species for the observed CL is rather possible that the excited state of CdTe NCs was generated in situ during the chemical reactions in the presence of H_2O_2. The state of CdTe NCs before and after the CL reactions was also examined. We found that the characteristic PL emission peak and UV−vis absorption peak of CdTe NCs disappeared after the CL reactions. Also, TEM studies for the reacted mixture
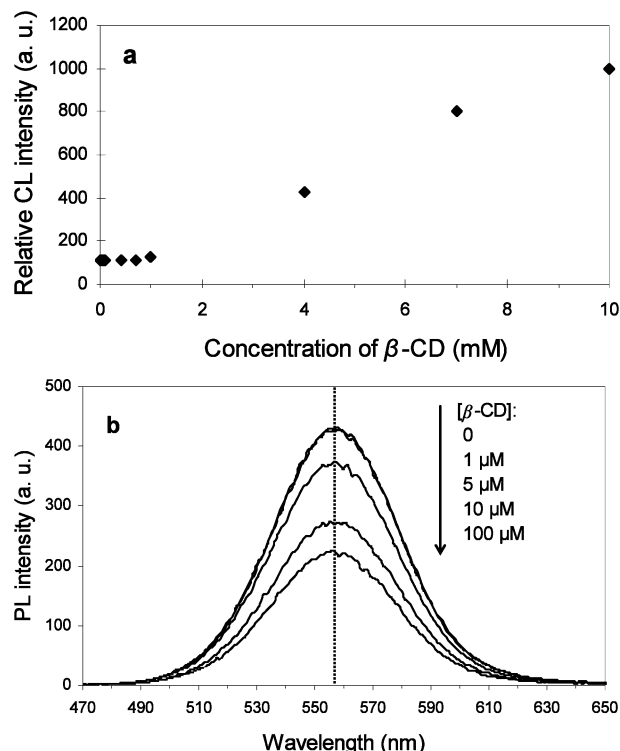

Figure 10. CL intensity profiles via added β-CD concentration (a) and PL spectra of CdTe NCs with a particle size of around 3.33 nm in different concentrations of β-CD solution (b). Conditions: a, different concentrations of β-CD mixed with 1×10^{-3} M CdTe NCs as luminescent reagent and water as carrier in FIA-CL mode, flow rate 2.0 mL/min, -800 V high voltage; b, 5×10^{-6} M CdTe NCs in different concentrations of β-CD solution.
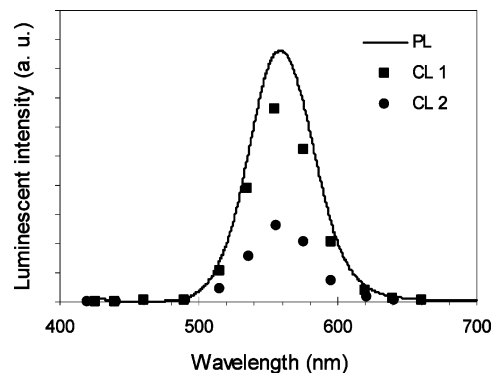
Figure 11. Oxidized CL spectra and PL spectra of CdTe NCs with a particle size of around 3.33 nm. Conditions: CL spectra obtained in FIA-CL mode; solutions of 0.1 M NaOH and 0.001 M CdTe NCs (CL 1), or 0.1 M NaOH and 0.0005 M CdTe NCs (CL 2), mixed on-line with 1 M H_2O_2 solution, respectively; flow rate, 2.0 mL/min; -600 V high voltage. A 5×10^{-6} M CdTe NCs colloid solution was used for PL spectra testing.

solution showed that CdTe NCs did not exist. These demonstrated that the nanocrystal lattice structure of CdTe NCs has been destroyed completely after oxidation by enough H_2O_2. Thus, the CL reaction can be described in its simplest form as follows:

$$\text{oxidant} + \text{CdTe NCs} \rightarrow (\text{CdTe NCs})^* \rightarrow h\nu \qquad (2)$$
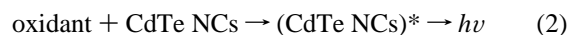
where (CdTe NCs)* refers to the excited state of CdTe NCs.

Some reports on semiconductor nanocrystals ECL indicated that dissolved oxygen played an important role in the ECL reaction. [9] Hereby, the influence of dissolved oxygen on the proposed CL system was also examined. Our experimental

results showed that the CL intensity would decrease about 30% when dissolved oxygen was removed from all solutions by the flow of nitrogen, indicating that dissolved oxygen played an important role in the CL reaction. To examine whether the reactive oxygen species participated in the CL reaction, scavengers of reactive oxygen species, such as ascorbic acid and methanol, were introduced into the CL reaction system, respectively. We found that the CL intensity decreased greatly in the presence of these scavengers, suggesting the existence and participation of reactive oxygen species during the process of the CL reaction. It must be noted that TGA-capped CdTe NCs were used in the present work. The reaction mechanism of thiol-containing compounds with dissolved oxygen in alkaline media has been explored and superoxide radical was proposed as a possible reaction intermediate.[35] In the presence of hydrogen peroxide, the produced superoxide radical can be converted into hydroxyl radical and singlet oxygen (Haber−Weiss reaction).[36] The superoxide radical and hydroxyl radical then induced the generation of $1S_e$−$1S_h$ exciton via electron injection and hole injection. Thus, according to our experiments and related reports about CL of semiconductor nanocrystals and common CL reactions,[12,37] we can put forward the following potential mechanism, i.e., the generation of $1S_e$−$1S_h$ exciton in quantum-confined orbital of CdTe NCs, and accordingly leading to the acquisition of CL in the presence of H_2O_2.

Under a basic condition, TGA reacted with dissolved oxygen to produce reaction intermediate, e.g., superoxide radical $(O_2{}^-)$:[35]

$$RSH + O_2 + OH^- \rightarrow O_2{}^- + RS + H_2O \qquad (3)$$
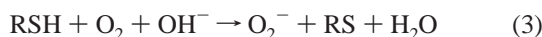
The superoxide ions are quite stable in high pH aqueous solution, and their lifetime approximates 1 min.[38] They can easily donate one electron in the reaction $O_2{}^- \rightarrow O_2 + e^-$ and lead to the injection of an electron (reaction 4) from superoxide ion into the $1S_e$ quantum-confined orbital of CdTe NCs:[12,39]

$$O_2{}^- + CdTe \rightarrow CdTe(e^-{}_{1Se}) + O_2 \qquad (4)$$
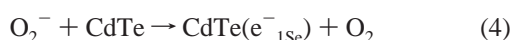
Meanwhile, in the presence of hydrogen peroxide, the produced superoxide radical can be converted into hydroxyl radical ($OH^\bullet$) and singlet oxygen ($^1O_2$) (Haber−Weiss reaction).[36]

$$O_2{}^- + H_2O_2 \rightarrow OH^\bullet + {}^1O_2 \qquad (5)$$
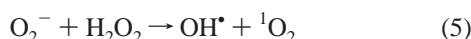
The formed $OH^\bullet$ radical should be able to inject a hole (reaction 6) in the $1S_h$ quantum-confined orbital of the CdTe NCs at the pH values used.[12]

$$OH^\bullet + CdTe \rightarrow OH^- + CdTe(h^+{}_{1Sh}) \qquad (6)$$
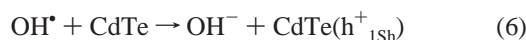
Then the exciton CL reaction arises (reaction 7) accompanying the light emission.

$$CdTe(h^+{}_{1Sh}) + CdTe(e^-{}_{1Se}) \rightarrow (CdTe\ NCs)^* \rightarrow h\nu \qquad (7)$$
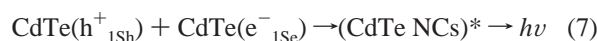
4. Conclusions

In summary, we demonstrated that CdTe NCs could be excited to give rise to chemiluminescence emission through directly chemical oxidation. And the oxidized CL possessed size-dependent and surfactant-sensitized effect. The strong CL response of CdTe NCs in different condition was also investigated and a proposed mechanism of the exciton CL was put forward. The size-dependent CL of CdTe NCs probably resulted

from the generated chemical energy of the CL reaction more matches the smaller energy band gap with a bigger particle size. The sensitized CL induced by CTAB and β-cyclodextrin mainly contributed to the aggregate nanostructure and the micellar micronanoenvironment, respectively. All these phenomena would be helpful to make the CL and even PL behavior of semiconductor nanocrystals find practical applications. Moreover, it gives a new path for further improve the efficiency of nanocrystal CL by optimizing the nanocrystal composition, capping ligands, and the CL system constitution. This may intrigue researchers into gaining a new interest in investigating the chemiluminescence property of semiconductor nanocrystals with different shapes, size, and constitutions and promote the step of its application in various fields based on these CL phenomena, bearing the advantages of relative high sensitivity, simple instrument, no backscattering light interference, and, in particular, easy to multicolor labeling.

References and Notes

(1) Bruchez, M.; Moronne, M.; Gin, P.; Weiss, S.; Alivisatos, A. P. *Science* **1998**, *281*, 2013.

(2) Chan, W. C. W.; Nie, S. M. *Science* **1998**, *281*, 2016.

(3) Han, M.; Gao, X.; Su, J. Z.; Nie, S. *Nat. Biotechnol.* **2001**, *19*, 631.

(4) Coe, S.; Woo, W. K.; Bawendi, M.; Bulovic, V. *Nature (London)* **2002**, *420*, 800.

(5) Chen, S. W.; Truax, L. A.; Sommers, J. M. *Chem. Mater.* **2000**, *12*, 3864.

(6) Qu, L. H.; Peng, X. G. *J. Am. Chem. Soc.* **2002**, *124*, 2049.

(7) Chen, W.; Zhang, J. Z.; Joly, A. G. *J. Nanosci. Nanotech.* **2004**, *4*, 919.

(8) Bae, Y.; Myung, N.; Bard, A. J. *Nano Lett.* **2004**, *4*, 1153.

(9) Zou, G. Z.; Ju, H. X. *Anal. Chem.* **2004**, *76*, 6871.

(10) Miao, J. J.; Ren, T.; Dong, L.; Zhu, J. J.; Chen, H. Y. *Small* **2005**, *1*, 802.

(11) Rodriguez-Viejo, J.; Jensen, K. F.; Mattoussi, H.; Michel, J.; Dabbousi, B. O.; Bawendi, M. G. *Appl. Phys. Lett.* **1997**, *70*, 2132.

(12) Poznyak, S. K.; Talapin, D. V.; Shevchenko, E. V.; Weller, H. *Nano Lett.* **2004**, *4*, 693.

(13) Corrales, T.; Peinado, C.; Allen, N. S.; Edge, M.; Sandoval, G.; Catalina, F. *J. Photochem. Photobiol. A* **2003**, *156*, 151.

(14) Zhu, Y. F.; Shi, J. J.; Zhang, Z. Y.; Zhang, C.; Zhang, X. R. *Anal. Chem.* **2002**, *74*, 120.

(15) McCord, P.; Yau, S. L.; Bard, A. J. *Science* **1992**, *257*, 68.

(16) Cui, H.; Zhang, Z. F.; Shi, M. J. *J. Phys. Chem. B.* **2005**, *109*, 3099.

(17) Garc-Campa, A. M.; Baeyens, W. R. G. *Chemiluminescence in analytical chemistry;* Marcel Dekker: New York. 2001.

(18) Powe, A. M.; Fletcher, K. A.; St. Luce, N. N.; Lowry, M.; Neal, S.; McCarroll, M. E.; Oldham, P. B.; McGown, L. B.; Warner, I. M. *Anal. Chem.* **2004**, *76*, 4614−4634.

(19) Yakovleva, J.; Davidsson, R.; Lobanova, A.; Bengtsson, M.; Eremin, S.; Laurell, T.; Emneus, J. *Anal. Chem.* **2002**, *74*, 2994.

(20) Li, F. M.; Zhang, C. H.; Guo, X. J.; Feng, W. Y. *Biomed. Chromatogr.* **2003**, *17*, 96.

(21) Lv, J. G.; Zhang, Z. J.; Li, J. D.; Luo, L. R. *Forensic Sci. Int.* **2005**, *148*, 15.

(22) Dodeigne, C.; Thunus, L.; Lejeune, R. *Talanta* **2000**, *51*, 415.

(23) Lin, J. H.; Ju, H. X. *Biosens. Bioelectron.* **2005**, *20*, 1461.

(24) Chen, C.; Liu, F. K.; Qi, X. P.; Li, J. S. *World, J. Gastroenterol.* **2003**, *9*, 242.

(25) Li, J.; Hong, X.; Liu, Y.; Li, D.; Wang, Y. W.; Li, J. H.; Bai, Y. B.; Li, T. J. *Adv. Mater.* **2005**, *17*, 163.

(26) Li, J.; Hong, X.; Li, D.; Zhao, K.; Wang, L.; Wang, H. Z.; Du, Z. L.; Li, J. H.; Bai, Y. B.; Li, T. J. *Chem. Commun.* **2004**, 1740.

(27) Yu, W. W.; Qu, L.; Guo, W.; Peng, X. *Chem. Mater.* **2003**, *15*, 2854.

(28) Wang, Y.; Herron, N. *J. Phys. Chem.* **1991**, *95*, 525.

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(29) Alivisatos, A. P. *Science* **1996**, *271*, 933.

(30) Brus, L. *J. Phys. Chem.* **1986**, *90*, 2555.

(31) Poznyak, S. K.; Osipovich, N. P.; Shavel, A.; Talapin, D. V.; Gao, M.; Eychmuller, A.; Gaponik, N. *J. Phys. Chem. B* **2005**, *109*, 1094.

(32) Lin, J. M.; Yamada, M. *Trends Anal. Chem.* **2003**, *22*, 99.

(33) Vossmeyer, T.; Katsikas, L.; Giersig, M.; Popovic, I. G.; Diesner, K.; Chemseddine, A.; Eychmueller, A.; Weller, H. *J. Phys. Chem.* **1994**, *98*, 7665.

(34) Sarkar, S. K.; Hodes, G. *J. Phys. Chem. B* **2005**, *109*, 7214.

(35) Shen, J. M.; Wu, Z. Q. *Pharmaceutical Structure and Reagent;* Chinese Medicine Science and Technology Press: Beijing, 1989; p 341.

(36) Mo, J. *Free Radical Biology in Medicine;* People's Health Press: Beijing, 1989; p 22.

(37) Du, J. X.; Li, Y. H.; Lu, J. R. *Anal. Chim. Acta* **2001**, *448*, 79.

(38) Ono, Y.; Matsumura, T.; Kitajima, N.; Fukuzumi, S. I. *J. Phys. Chem.* **1977**, *81*, 1307.

(39) Sawada, Y.; Iyanagi, T.; Yamazaki, I. *Biochemistry* **1975**, *14*, 3761.