Quantum Dot Electrochemiluminescence in Aqueous Solution at Lower Potential and Its Sensing Application

Lihua Zhang, Xiangqin Zou, Erbo Ying, and Shaojun Dong*

State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry. Graduate School of the Chinese Academy of Sciences, Chinese Academy of Sciences, Changchun, 130022, China

The unique strategy for electrochemiluminescence (ECL) sensor based on the quantum dots (QDs) oxidation in aqueous solution to detect amines is proposed for the first time. Actually, there existed two QDs ECL peaks in anhydrous solution, one at high positive potential and another at high negative potential. However, here we introduced the QDs oxidation ECL in aqueous solution to fabricate a novel ECL sensor. Such sensor needed only lower positive potential to produce ECL, which could prevent the interferences resulted from high potential as that of QDs reduction ECL in aqueous solution. Therefore, the present work not only extended the QDs oxidation ECL application field from anhydrous to aqueous solution but also enriched the variety of ECL system in aqueous solution. Furthermore, we investigated the QDs oxidation ECL toward different kinds of amines, and found that both aliphatic alkyl and hydroxy groups could lead to the enhancement of ECL intensity. Among these amines, 2-(dibutylamino)ethanol (DBAE) is the most effective one, and accordingly, the first ECL sensing application of the QDs oxidation ECL toward DBAE is developed; the as-prepared ECL sensor shows wide linear range, high sensitivity, and good stability.

Introduction

Semiconductor nanocrystals (NCs), often referred to as quantum dots (QDs), have attracted extensive interest because of their variety of size- and shape-dependent optical and electrical properties.[1−5] QDs can be utilized as an emitting material in light-emitting diode and display devices.[6,7] The color emission can be tuned by size variation without altering their chemical properties.[8,9] High fluorescence quantum yields are achieved by introducing defects on the surface of the QDs.[10,11] Moreover, electrochemical methods of characterizing semiconductor NCs can often complement the optical methods that are usually employed. While absorption and fluorescence spectroscopies mainly probe the interior of the particle and provide information about the electronic transitions (band gap) of the material, electrochemistry predominately probes the particle surface.[12]

Electrochemiluminescence (ECL), the production of light from electrochemically generated reagents, has been paid considerable attention during the past several decades due to its versatility, simplified optical setup, very low background signal, and good temporal and spatial control.[13] Many chemiluminescent reagents were applied in ECL reactions, such as luminol, polyaromatic hydrocarbons (PAH), and metal complexes.[14−16] Recently, more people began to be aware of the potential application of QDs in ECL field. Bard's group found that QDs could be oxidized and reduced during the potential cycling or pulsing. Light emission occurs when electrogenerated reduced species (R$^{\bullet-}$) are in collision with the oxidized species (R$^{\bullet+}$) in an annihilation process that produces excited states (R*).[17−20]

$$R^{\bullet-} + R^{\bullet+} \rightarrow R* + R \qquad (a)$$

---

* Corresponding author.

$$R* \rightarrow R + h\nu \qquad (b)$$

These works were carried out in nonaqueous media, since the potential window for the electrochemical oxidation and reduction of water is simply too small to conveniently generate these two species (i.e., the radical anions and cations) needed for annihilation ECL.

An alternative approach to generate QDs ECL is through the use of a coreactant. The purpose of the coreactant in ECL is to overcome either the limited potential window of a solvent or the poor stability of radical anions or cations.[21] Thereafter, ECL emission can be generated by a single direction potential sweep with the addition of coreactant. For example, the oxidation of oxalate produces a strong reducing agent, CO$_2{}^{\bullet-}$, which can then react with the radical cation R$^{\bullet+}$ to emit light. Similarly, the reduction of peroxydisulfate releases a strong oxidizing agent SO$_4{}^{\bullet-}$, which can interact with the radical anion R$^{\bullet-}$, and finally leads to ECL signal.[17] The electron-transfer reaction between electrochemically formed QDs and coreactants implies that QDs have great potential for development of ECL sensors. According to this principle, a novel kind of QDs ECL sensor was developed to detect the concentration of H$_2$O$_2$ in aqueous solution.[22−24] The prepared ECL sensor shows high sensitivity, good stability, and reproducibility, indicating QDs could be a new and promising material for ECL application. In their work, QDs are first reduced to R$^{\bullet-}$ and then reacted with H$_2$O$_2$ to emit light. However, in order to produce R$^{\bullet-}$, the potential has to be scanned to as negative as −1.5 V, at which water began to electrolyze. The produced bubbles could absorb onto the electrode surface and might impact the results to a certain extent.

Here, for the first time, the novel strategy for ECL sensor based on the CdTe NCs oxidation in aqueous solution to detect 2-(dibutylamino)ethanol (DBAE) has been proposed. Moreover, such sensor could be sensitively functioned at lower positive potential not exceeding 1.0 V, avoiding the interferences from
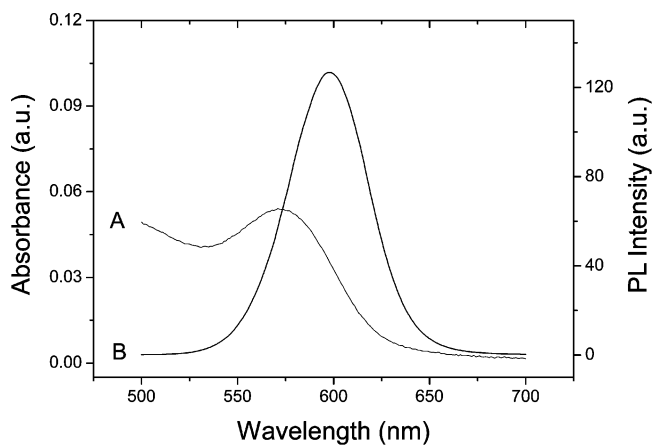
Figure 1. Absorption (A) and photoluminescence (B) spectra of the as-prepared CdTe NCs. Excitation wavelength: 400 nm.

high potential either positive or negative. Once the DBAE is introduced into the solution, a great enhancement of ECL signal was observed at 0.9 V, and the ECL enhancement has good linear relationship with the concentration of DBAE in solution.

Experimental Section

Materials. Mercaptosuccinic acid and tripropylamine were purchased from Aldrich. DBAE was obtained from Sigma. Sodium borohydride was purchased from Acros. Na_2TeO_3 was brought from Germany. Cadmium chloride, trisodium citrate dihydrate, diethylamine, triethylamine, ethanolamine, and tri-ethanolamine were bought from Beijing Reagent Company. All other chemicals were of analytical grade, and the aqueous solutions were prepared with doubly distilled water.

Apparatus. Cyclic voltammetric experiments were performed with a CH Instruments 832 voltammetric analyzer. All experiments were carried out with a conventional three-electrode system. Glassy carbon electrode, platinum wire, and Ag/AgCl (saturated KCl) were used as working electrode, counter electrode, and reference electrode, respectively. The ECL signal produced in the electrolytic cell was detected and recorded by a flow injection chemiluminescence analyzer (IFFD, Xi an Remax Electronic Science Tech. Co. Ltd.), and the photomul-tiplier tube was biased at 900 V.

UV–vis spectra were recorded using a Cary 50 Scan UV–vis spectrophotometer (Varian). Emission spectra data were obtained from a LS 55 luminescence spectrometer (Perkin-Elmer, U.K.) at room-temperature, and the excitation wavelength was selected at 400 nm.

Preparation of CdTe NCs. CdTe NCs were prepared according to the reported method.[25] In a typical synthesis, cadmium chloride ($CdCl_2$, 0.04 M, 4 mL) was diluted to 50 mL in a one-necked flask, and trisodium citrate dihydrate (100 mg), Na_2TeO_3 (0.01 M, 1 mL), mercaptosuccinic acid (50 mg), and sodium borohydride ($NaBH_4$, 100 mg) were added with stirring. When the color of the solution changed to green, the flask was attached to a condenser and refluxed under open-air conditions for 5 h. The resulting CdTe NCs were washed with ethanol and separated by centrifugation. Finally, the prepared CdTe NCs were dispersed in the water.

Results and Discussion

Characterization of CdTe NCs. Figure 1 shows typical absorption and photoluminescence (PL) spectra of CdTe NCs aqueous solution. The sharp UV and PL peaks indicate a highly monodisperse sample. The band gap from the absorption peak
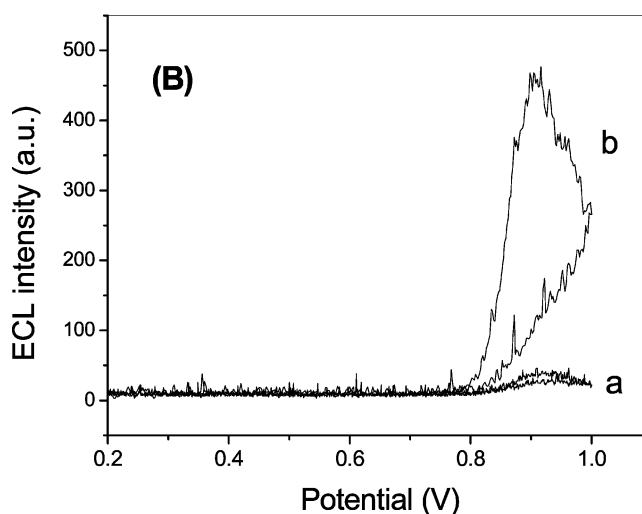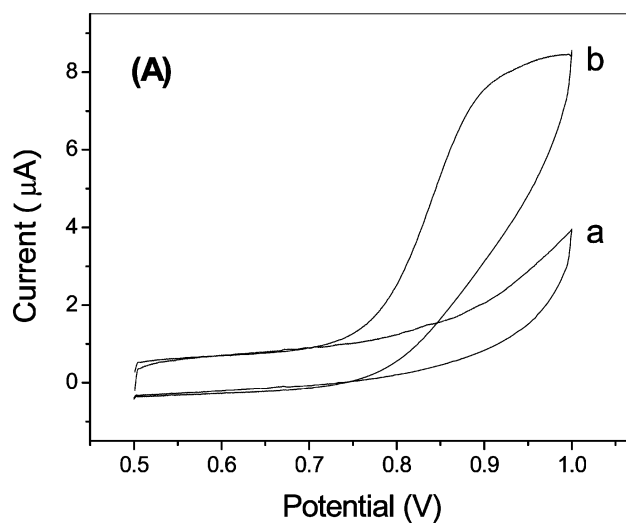

Figure 2. (A) CV and (B) ECL of (a) CdTe NCs in PBS (pH 7.5), (b) 1.5×10^{-4} M DBAE added to (a). Scan rate: 100 mV/s.
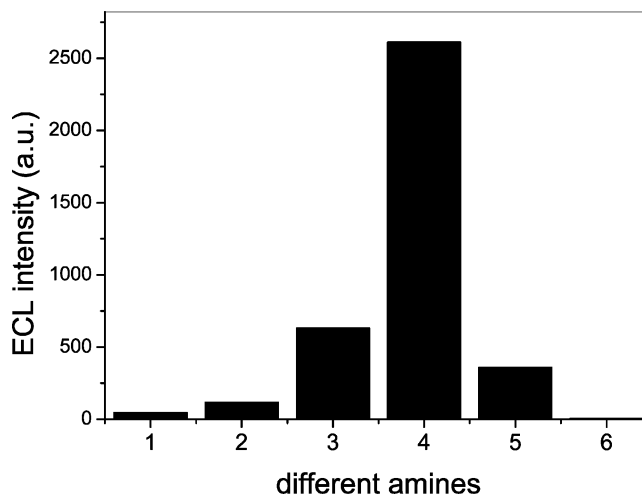
Figure 3. ECL intensities of CdTe NCs with different kinds of amines with the same concentration of 3 mM. (1) diethylamine, (2) triethy-lamine, (3) tripropylamine, (4) DBAE, (5) triethanolamine, (6) etha-nolamine, measured in 0.1 M PBS (pH 7.5) and the potential was scanned from 0 to 1.0 V.

is 2.2 eV (571 nm) and is shifted to higher energy from the band gap of bulk CdTe (1.5 eV), representing the quantum size effect of the nanoparticles.[26] A particle size of 3.4 nm is estimated from this spectrum, based on the first absorption peak
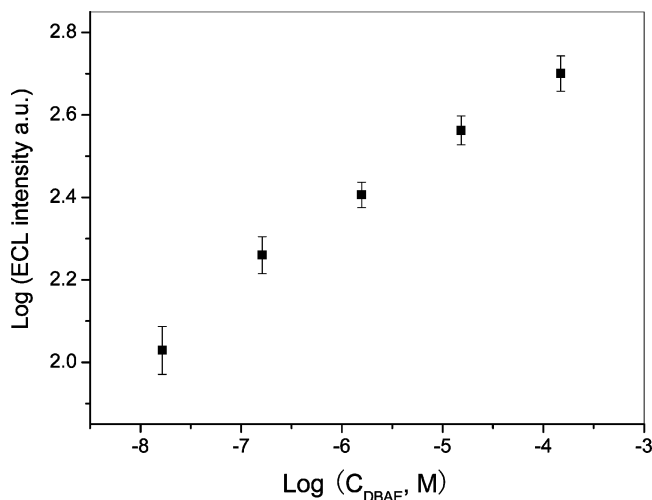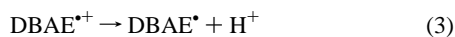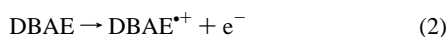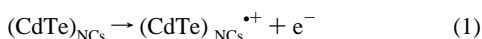
Figure 4. ECL intensities of CdTe NCs with different concentrations of DBAE in PBS (pH 7.5) at the scan rate of 100 mV/s.

Figure 5. ECL intensity of CdTe NCs in PBS (pH 7.5) containing 5 × 10⁻⁵ M DBAE under continuous cyclic voltammetry for 9 cycles with the scan rate of 500 mV/s.

wavelength.[27] Furthermore, the PL of CdTe NCs exhibits a peak at 598 nm when excited at 400 nm.

Electrochemistry and ECL of CdTe NCs. In CdTe NCs phosphate buffer solution (PBS), a scan between 0 and 1 V is featureless as shown in Figure 2A. However, ECL shows a distinct signal around 0.9 V as demonstrated in Figure 2B. Once 1.5×10^{-4} M DBAE is introduced into the solution, an irreversible anodic peak is emerged around 0.87 V, which could be attributed to the oxidation of DBAE. Meanwhile, the corresponding ECL increases greatly. The onset of luminescence occurs near 0.8 V, and then the ECL intensity rises up steeply from 0.8 V until it reaches a maximum near 0.9 V.

However, in previous study of CdTe NCs annihilation process in anhydrous solution, when potential is scanned between −2.46 and 1.5 V, ECL response was not observed at positive potential region, although there existed a significant ECL signal around −1.85 V.[20] Surprisingly, here, the ECL signal of CdTe NCs occurring at 0.9 V in aqueous PBS is found. When DBAE is used as coreactant with the CdTe NCs system, we suppose the reaction mechanism as the following equations:

$$(CdTe)_{NCs} \rightarrow (CdTe)_{NCs}^{\bullet+} + e^- \quad (1)$$

$$DBAE \rightarrow DBAE^{\bullet+} + e^- \quad (2)$$

$$DBAE^{\bullet+} \rightarrow DBAE^{\bullet} + H^+ \quad (3)$$

$$(CdTe)_{NCs}^{\bullet+} + DBAE^{\bullet} \rightarrow (CdTe)_{NCs}^* + DBAEfragments \quad (4)$$

$$(CdTe)_{NCs}^* \rightarrow (CdTe)_{NCs} + h\nu \quad (5)$$

As the electrode potential is scanned to more positive, $(CdTe)_{NCs}$ are oxidized to $(CdTe)_{NCs}^{\bullet+}$. Concurrently, DBAE is oxidized and then undergoes a chemical reaction generating the powerful reducing agent $DBAE^{\bullet}$. Since the reduction potential of $(CdTe)_{NCs}^{\bullet+}$ was less negative than the that of $DBAE^{\bullet}$, $(CdTe)_{NCs}^{\bullet+}$ could receive electrons from $DBAE^{\bullet}$ to populate the excited state $(CdTe)_{NCs}^*$.[28] While CdTe NCs fall from excited state $(CdTe)_{NCs}^*$ to ground state $(CdTe)_{NCs}$, light is emitted. Before the addition of DBAE, the presence of impurities might act as coreactant to produce ECL signal, but during this process, the oxidation current of CdTe NCs might be too slight to be discernible in cyclic voltammogram (CV) (Figure 2Aa). On the other hand, when DBAE is introduced into the system, the oxidation current of CdTe NCs might be overshadowed by
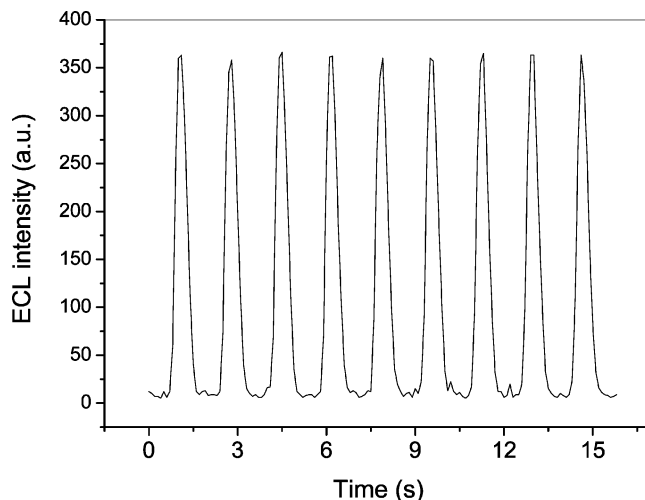
the relatively high DBAE oxidation current (Figure 2Ab). Furthermore, we took the control experiment to verify the ECL is originated from CdTe NCs. When 1.5×10^{-4} M DBAE is added to the PBS (pH 7.5, without CdTe NCs), no ECL signal occurs although there exists an irreversible anodic peak around 0.87 V, which could be attributed to the oxidation of DBAE.

Moreover, we investigated the dependence of CdTe NCs ECL intensities on 6 coreactant amines at 1.0 V in PBS, and all of these amines were with the same concentration of 3 mM. As demonstrated in Figure 3, different ECL responses were emerged toward different amines. As we proposed the reaction mechanism of CdTe NCs-DBAE (eqs 2 and 3), amine is first oxidized to produce a short-lived radical cation, and then it is deprotonated to form a strong reducing intermediate. This intermediate is the source of the chemical energy to produce the excited-state of CdTe NCs in the ECL reaction. It is reported that electron-donating substituents attached to the nitrogen of the amine would stabilize positive or electron-deficient radical ions.[29] Therefore, since aliphatic alkyl groups are electron donating by an inductive effect, an increase in the number and length of alkyl chains attached to the nitrogen atom would enhance the stability of the radical ions and finally lead to an increased ECL response. Hence, tertiary amines are the most ECL active, followed by secondary and finally primary amines. As illustrated in Figure 3, from diethylamine, triethylamine to tripropylamine, the ECL intensity increased accordingly. Furthermore, as the hydroxy group could catalyze the oxidation of amines, when the hydroxy group was attached to the amine, its ECL response is much higher than the corresponding amine without hydroxy group.[30]

As shown in Figure 3, DBAE could most effectively enhance the CdTe NCs ECL response, besides it is an environmental friendly reagent.[30] Therefore, we developed CdTe NCs ECL sensor for DBAE in aqueous solution at lower potential. Each point as shown in Figure 4 is a mean of three ECL signals obtained by three successive measurements. It could be seen that ECL intensity had good linearity with the DBAE concentration and the linear range was wide extending from 1.7×10^{-8} to 1.5×10^{-4} M ($R = 0.995$) with a remarkable detection limit (S/N = 3) of 8 nM. Moreover, under continuously cyclic potential scanning for 9 cycles in CdTe NCs PBS (pH 7.5) containing 5×10^{-5} M DBAE, the ECL response changes only 2.2% as demonstrated in Figure 5.

4454 *J. Phys. Chem. C, Vol. 112, No. 12, 2008*

Zhang et al.

Conclusions

In previous works, QDs ECL signals were found mainly in anhydrous solution and required high potential both positive and negative. In our work, we extended the application field of QDs ECL from anhydrous solution to aqueous solution to detect amines for the first time. The ECL signal of mercaptosuccinic acid protected CdTe NCs emerged around 0.9 V, and the signal responds sensitively with the existence of amines. The as-prepared ECL sensor demonstrated a linear response extending from 1.7×10^{-8} to 1.5×10^{-4} M with a remarkable detection limit (S/N = 3) of 8 nM toward DBAE. Furthermore, we also studied the CdTe NCs ECL responses toward different kinds of amines and concluded that amines with aliphatic alkyl and hydroxy groups could lead to the enhancement of ECL intensity.

References and Notes

(1) Colvin, V. L.; Schlamp, M. C.; Alivisatos, A. P. *Nature* **1994**, *370*, 354.

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

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

(4) Huynh, W. U.; Dittmer, J. J.; Alivisatos, A. P. *Science* **2002**, *295*, 2425.

(5) Achermann, M.; Petruska, M. A.; Kos, S.; Smith, D. L.; Koleske, D. D.; Klimov, V. I. *Nature* **2004**, *429*, 642.

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

(7) Tessler, N.; Medvedev, V.; Kazes, M.; Kan, S. H.; Banin, U. *Science* **2002**, *295*, 1506.

(8) Dabbousi, B. O.; Thomas, E. L.; Bawendi, M. G.; Onitsuka, O.; Rubner, M. F. *Appl. Phys. Lett.* **1995**, *66*, 1316.

(9) Schlamp, M. C.; Peng, X.; Alivisatos, A. P. *J. Appl. Phys.* **1997**, *82*, 5837.

(10) Spanhel, L.; Haase, M.; Weller, H.; Henglein, A. *J. Am. Chem. Soc.* **1987**, *109*, 5649.

(11) Peng, X.; Schlamp, M. C.; Kadavanich, A. V.; Alivisatos, A. P. *J. Am. Chem. Soc.* **1997**, *119*, 7019.

(12) Bard, A. J.; Ding, Z.; Myung, N. *Struc. Bond.* **2005**, *118*, 1.

(13) Faulkner, L. R.; Bard, A. J. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1977; Vol. 10, p 1.

(14) Cui, H.; Xu, Y.; Zhang, Z. *Anal. Chem.* **2004**, *76*, 4002.

(15) Moret, S.; Conte, L. S. *J. Chromatogr. A* **2000**, *882*, 245.

(16) Zu, Y.; Bard, A. J. *Anal. Chem.* **2000**, *72*, 3223.

(17) Ding, Z.; Quinn, B. M.; Haram, S. K.; Pell, L. E.; Korgel, B. A.; Bard, A. J. *Science* **2002**, *296*, 1293.

(18) Myung, N.; Ding, Z.; Bard, A. J. *Nano. Lett.* **2002**, *2*, 1315.

(19) Myung, N.; Lu, X.; Johnston, K. P.; Bard, A. J. *Nano. Lett.* **2004**, *4*, 183.

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

(21) Bard, A. J.; Faulkner, L. R. *Electrochemical methods, fundamentals and applications*; Wiley: New York, 2001.

(22) Zou, G.; Ju, H. *Anal. Chem.* **2004**, *76*, 6871.

(23) Jie, G.; Liu, B.; Miao, J.; Zhu, J. *Talanta* **2007**, *71*, 1476.

(24) Dai, Z.; Zhang, J.; Bao, J.; Huang, X.; Mo, X. *J. Mater. Chem.* **2007**, *17*, 1087.

(25) Bao, H.; Wang, E.; Dong, S. *Small* **2006**, *2*, 476.

(26) Zanio, K. *Semiconductors and Semimetals*; Academic: New York, 1978; p 13.

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

(28) Shin, I.; Kim, J.; Kwon, T.; Hong, J.; Lee, J.; Kim, H. *J. Phys. Chem. C* **2007**, *111*, 2280.

(29) Knight, A. W.; Greenway, G. M. *Analyst* **1996**, *121*, 101R.

(30) Liu, X. Q.; Shi, L. H.; Niu, W. X.; Li, H. J.; Xu, G. B. *Angew. Chem., Int. Ed.* **2007**, *46*, 421.