

Research Article

Electrochemical Investigation of Anthraquinone-Based Chemodosimeter for Cu^{2+} Metal Ion

Yeo Woon Yoon,¹ Jong Seung Kim,² and Tae Hyun Kim¹

¹ Department of Chemistry, Soonchunhyang University, Asan 336-746, Republic of Korea

² Department of Chemistry, Korea University, Seoul 136-701, Republic of Korea

Correspondence should be addressed to Jong Seung Kim; jongskim@korea.ac.kr and Tae Hyun Kim; thkim@sch.ac.kr

Received 13 September 2013; Revised 6 December 2013; Accepted 6 December 2013

Academic Editor: Fernanda Carvalho

Copyright © 2013 Yeo Woon Yoon et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The electrochemical properties of an anthraquinone-containing Cu^{2+} -promoted desulfurization chemodosimeter (AQCD) in the presence of various metal ions were investigated by voltammetry. AQCD showed voltammetric changes toward divalent metal ions (M^{2+}), which are similar to those of anthraquinone (AQ) and 1-aminoanthraquinone (AQNH_2) with the metal ions except Cu^{2+} . This can be explained on the electrostatic interaction (AQCD-M^{2+}) and chemodosimetric reaction (AQCD-Cu^{2+}).

1. Introduction

Chemodosimeters are used for sensing an analyte through a usually rapid response, highly selective, and irreversible chemical reaction between dosimeter molecule and the target material, leading to an observable signal [1–5]. Most have been utilized as optical sensors to monitor the target by UV/Vis and fluorescence spectroscopic measurements [1, 2]. These methods are usually sensitive, easy to perform, and inexpensive, but they have limitations in portability and mobility in terms of practical sensor devices.

Alternatively, analytical techniques based on electrochemical detection are suitable for the development of convenient, sensitive, selective, and low cost tools that could be exploited for rapid monitoring, ultimately applicable to hand-held or autonomous operation. However, only a few examples of electrochemical sensors using chemodosimeters have been reported [6–11]. These studies utilized ferrocene [6, 7], iridium(III) complex [8, 9], and pyridine-4-thione [10] as redox units. Previously, we reported an anthraquinone-containing chemodosimeter (AQCD) responsible for Cu^{2+} ion-induced desulfurization to exhibit highly selective UV and fluorescence changes (Scheme 1) [12].

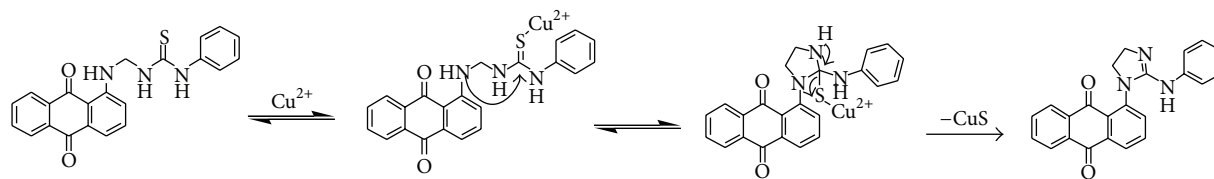
The anthraquinone unit can serve not only as a chromofluorescent unit but also as a redox center. It has largely

proved to be an effective, remarkable and promising redox-signaling unit for electrochemical applications due to its robust electrochemistry [13–15].

Here, we report now the redox properties as well as cation sensing behavior of AQCD in the absence and the presence of alkali, alkaline earth, Cu^{2+} , and other metal ions by voltammetry. The present study aims to investigate the electrochemical influence of various metal ions on AQCD behavior in terms of chemodosimetric reaction confirmed previously by optical methods [12] and consequently to check the feasibility of anthraquinone-based chemodosimeter as an electrochemical sensor for metal ions. In the pursuit of this goal, electrochemical behavior of AQCD was also compared with the results of anthraquinone (AQ) and 1-aminoanthraquinone (AQNH_2) in the various metal ions.

2. Experimental

Electrochemical measurements were carried out with a Model 660D electrochemical workstation (CH Instruments, Austin, TX, USA). The three-electrode system consists of a glassy carbon working electrode, an Ag/Ag^+ (in 0.1M AgNO_3) reference electrode, and a Pt wire counter electrode. The surface of the working electrode was polished with 0.03 and 0.05 μm alumina (CH Instruments, Austin, TX, USA)



SCHEME 1: Anthraquinone-based chemodosimeter (AQCD) and its reaction mechanism upon Cu^{2+} ion addition.

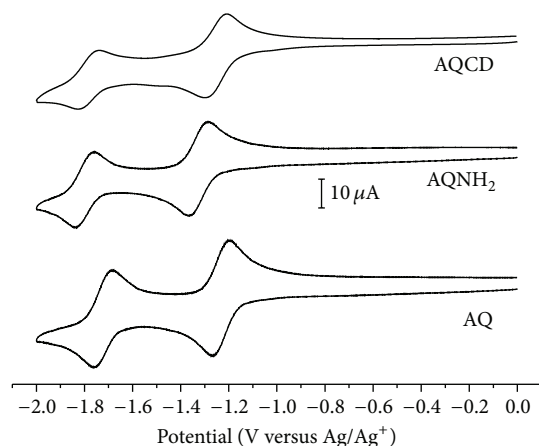


FIGURE 1: Cyclic voltammograms (CVs) of 0.5 mM AQCD, AQNH₂, and AQ in 0.1 M TBAPF₆/CH₃CN. Scan rate: 50 mV/s.

and rinsed with deionized water. Residual alumina particles were thoroughly removed by positioning the electrode in an ultrasonic bath for 10 min. Then, the electrode was dried and washed with pure acetonitrile before use. The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) in acetonitrile solution (CH₃CN). The concentration of AQCD was 0.5 mM and stock solution of metal perchlorate salts with various concentrations was prepared using acetonitrile. Test solutions were prepared by placing 2 mL of the AQCD solution into an electrochemical cell and adding appropriate aliquot of each metal stock solution with a microsyringe. All experiments were carried out in a nitrogen atmosphere at room temperature. Synthesis and identification of AQCD were described in the previous paper [12]. All reagents were purchased from Aldrich and used without further purification.

3. Results and Discussion

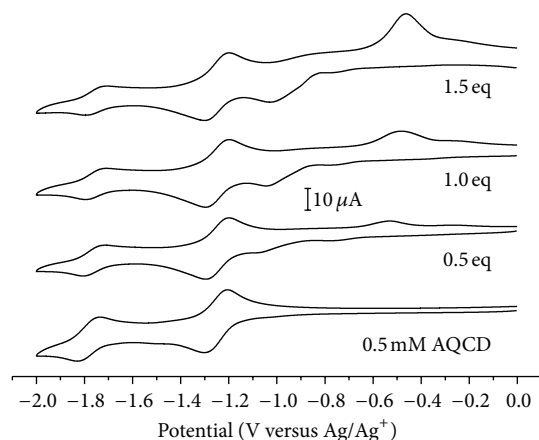
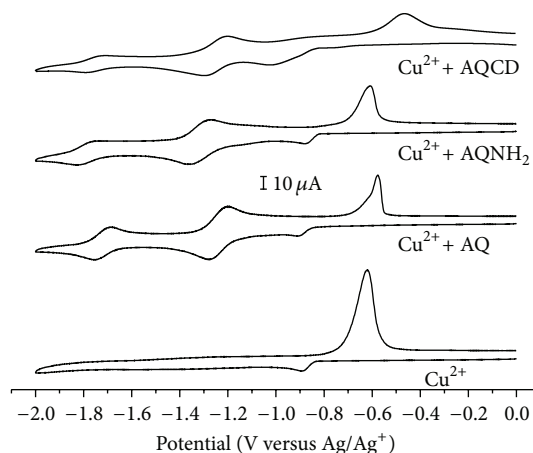
The redox chemistry of AQCD was investigated in CH₃CN with TBAPF₆ as a supporting electrolyte in a nitrogen atmosphere. Cyclic voltammogram (CV) of 0.5 mM AQCD is presented in Figure 1, and, for comparison, CVs of AQ and AQNH₂ are also exhibited in Figure 1. The reason for the comparison between AQCD, AQ, and AQNH₂ is to clarify the electrochemical results of AQCD by using AQ as a useful reference and to confirm the role of 1-amino substituent (1-NHR') of AQCD in the absence and the presence of metal ions. AQCD shows reversible first and second waves, of which

shape agrees with those of AQ and AQNH₂. But only a slight negative shift is observed in the redox potentials of AQCD and AQNH₂, compared with those of AQ. This is thought to be due to the existence of electron-donating amine groups (1-NHR') in AQCD and AQNH₂. The first and second waves are separated by about 525 mV for AQCD, 475 mV for AQNH₂, and 489 mV for AQ. The cyclic voltammetric data for the two waves for all three anthraquinones in 0.1 M TBAPF₆/CH₃CN are summarized in Table 1. Two reduction peaks of AQCD, AQNH₂, and AQ correspond to two single reductions to give the semiquinone and then dianion in agreement with well-known redox chemistry of quinone compounds [16]. But for a shade difference, electrochemical behaviors of all three anthraquinones show typical redox chemistry of quinone compounds. This shows that neither amine group and electroinactive lariat influence the redox of anthraquinone. Therefore, there is no factor affecting the electrochemical reduction and oxidation of AQCD, AQNH₂, and AQ except the characteristic interaction between the anthraquinones and metal ions.

Electrochemical properties of AQCD in the presence of alkali, alkaline earth, Cu^{2+} , and other metal ions were also investigated in 0.1 M TBAPF₆/CH₃CN by voltammetry. As a chemodosimeter, AQCD showed high selectivity toward Cu^{2+} over other competitive cations in aspects of colorimetric and fluorometric chemodosimetry [12]. Addition of Cu^{2+} ion to AQCD solution exhibited a rapid color change along with its blue-shifted absorption band. This is caused by the fact that a planar intramolecular charge-transfer (ICT) structure of AQCD becomes difficult to be adopted due to the cyclization assisted by Cu^{2+} , resulting in reducing the ICT character in the anthraquinone moiety (Scheme 1). One can expect the same behavior of AQCD toward Cu^{2+} and other metal ions in the electrochemistry. Thus, we first investigated an electrochemical reaction between AQCD and Cu^{2+} ion by cyclic voltammetry. Figure 2 shows voltammetric variation of 0.5 mM AQCD upon gradual addition of Cu^{2+} (0.25, 0.5, and 0.75 mM). AQCD shows significant voltammetric changes and increase of the intensity of redox wave at a potential between -0.1 and -1.1 V as the concentration of Cu^{2+} increases. Redox waves, however, assigned to anthraquinone unit at a potential between -1.1 and -2.0 V exhibit no significant change even with the increase of Cu^{2+} concentration. This indicates that transformation of the aminoethylthiourea unit of AQCD into imidazoline (Scheme 1) causes no influence on redox chemistry of anthraquinone unit. The redox waves at a potential between -0.1 and -1.1 V are presumably due to the redox reaction of copper species (CuS).

TABLE 1: The values of $E_{1/2}$ for the redox peaks for AQCD, AQNH₂, and AQ in 0.1 M TBAPF₆/CH₃CN. Scan rate: 50 mV/s.

	Cathodic peak potential (V)		Anodic peak potential (V)		Peak separation (V)		Half wave potential (V)	
	E_{pc1}	E_{pc2}	E_{pa1}	E_{pa2}	ΔE_1	ΔE_2	$E_{1/2}$ (1)	$E_{1/2}$ (2)
AQ	-1.265	-1.757	-1.200	-1.687	0.065	0.070	-1.233	-1.722
AQNH ₂	-1.363	-1.835	-1.287	-1.764	0.076	0.071	-1.325	-1.800
AQCD	-1.307	-1.820	-1.208	-1.745	0.099	0.075	-1.258	-1.783

FIGURE 2: CVs of 0.5 mM AQCD in the absence and presence of 0.25, 0.5, and 0.75 mM Cu²⁺ in 0.1 M TBAPF₆/CH₃CN. Scan rate: 50 mV/s.FIGURE 3: CVs of 0.75 mM Cu²⁺ in the absence and the presence of 0.5 mM AQ, AQNH₂, and AQCD in 0.1 M TBAPF₆/CH₃CN. Scan rate: 50 mV/s.

To gain an insight into the voltammetric properties of AQCD with Cu²⁺, CV experiments have been also performed with AQ and AQNH₂ in the presence of Cu²⁺ (Figure 3). The CV data of AQ and AQNH₂ also show two distinctive patterns. Firstly, the characters of the redox curves of anthraquinone unit remain intact even when the concentration of Cu²⁺ ions increases. This confirms that Cu²⁺ leads to no significant effect on redox reaction of anthraquinone unit, indicating no structural change of anthraquinone moiety in AQCD, as described in Scheme 1. The second redox features at a potential between -0.5 and -1.0 V in AQ and AQNH₂ are caused by copper reduction (Cu²⁺ → Cu⁰) and oxidation (Cu⁰ → Cu²⁺), which is confirmed by the CV of Cu²⁺ itself (Figure 3). But compared with those in AQ and AQNH₂, the copper redox reaction in AQCD shows negative shift in reduction and positive shift in oxidation, meaning more difficult redox reactions, attributable to the production of CuS resulting from chemodosimetric reaction. This also confirms the mechanism described in Scheme 1.

The addition of alkali metal ions to free AQCD solution leads to little change in both CVs and square wave voltammograms (data not shown). But the presence of alkaline earth and other metal ions (Cd²⁺, Fe²⁺, Pb²⁺, and Zn²⁺) alters both the reduction/oxidation peak potentials and currents of AQCD, which is different behavior in the presence of Cu²⁺ in terms of redox chemistry of anthraquinone unit. Typical example of CVs of AQCD with divalent metal ions (alkaline earth and other metal ions except Cu²⁺) is presented in Figure 4(a), and for comparison, CVs of AQ and AQNH₂

with the same metal ion are also illustrated in Figures 4(b) and 4(c). Significant changes in potentials and currents of AQCD were observed in the presence of Mg²⁺ ion with change in concentration. As the concentration of Mg²⁺ increases, a new reduction wave appears at a potential less negative than that of the original waves (Figure 4(a)). At high concentration of Mg²⁺, the new wave dominates and the peak at the more negative potential disappears. A similar behavior also occurs in the redox reaction of AQ and AQNH₂ with Mg²⁺. This indicates that the electrochemical reaction of AQCD and divalent metal ions except Cu²⁺ is associated only with the redox chemistry of anthraquinone unit and not with electroinactive lariat in AQCD, which confirms the chemodosimetric mechanism for selective detection of Cu²⁺ in Scheme 1.

Typically, by reduction of quinone in aprotic media, addition of increasing concentrations of a strong proton donor such as a strong acid causes new prior wave and leads to positive shift of E_1 wave with irreversibility, until merging with the new wave and disappearing of E_2 wave [16]. This is generally due to fast protonation of semiquinone (Q^{•-})/dianion (Q²⁻) and reduction of the more easily reduced QH[•]/QH₂ at the same potential. As shown in Figure 4, the electrochemical characteristics of anthraquinones in the presence of divalent Mg²⁺ ion are very similar to those of quinone with proton donor, which is so called proton-coupled reaction. That is, the electrochemistry of anthraquinone in the presence of divalent metal ion shows divalent metal ion-coupled reaction.

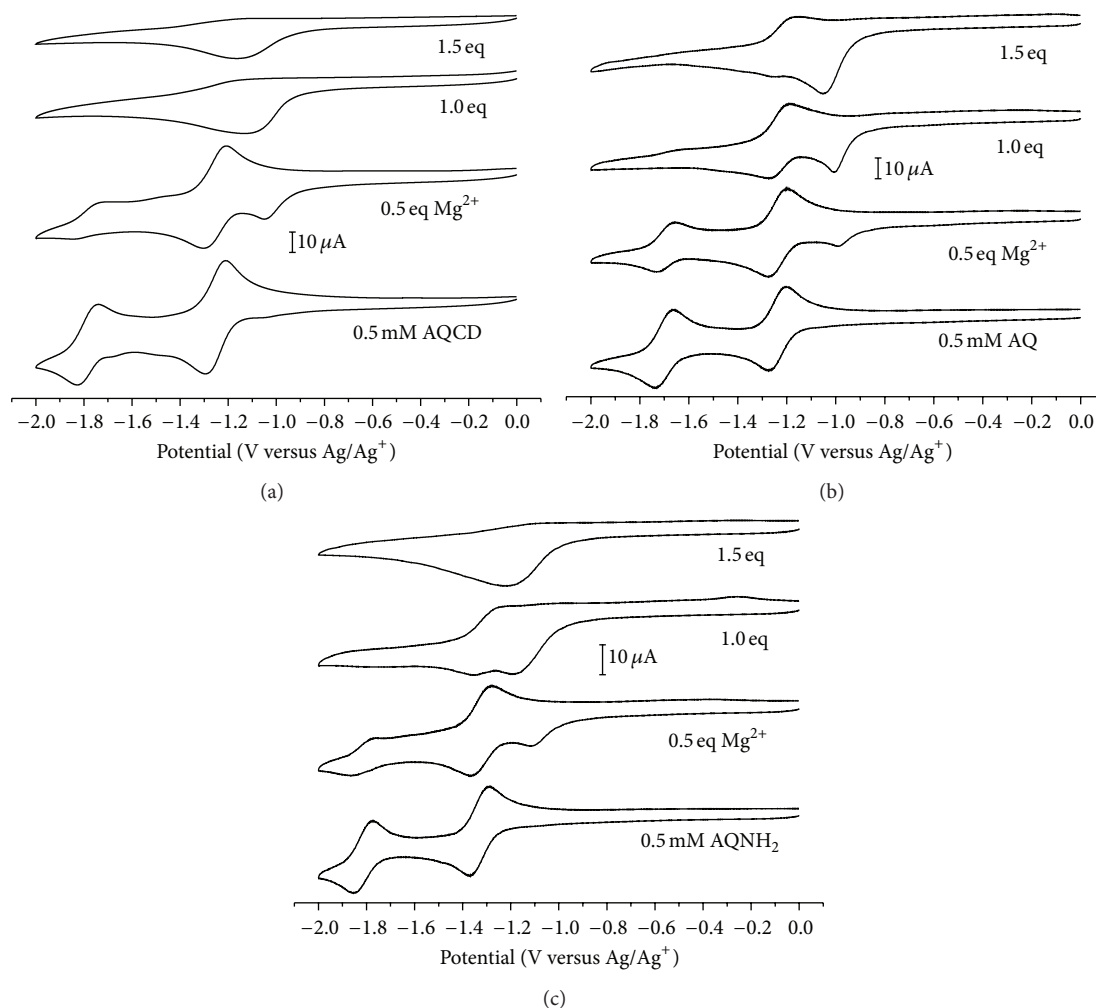


FIGURE 4: CVs of 0.5 mM (a) AQCD, (b) AQ, and (c) AQNH₂ in the absence and presence of 0.25, 0.5, and 0.75 mM Mg²⁺ in 0.1 M TBAPF₆/CH₃CN. Scan rate: 50 mV/s.

It is noted that with divalent Cu²⁺ AQ does not show the coupled reaction because Cu²⁺ ions are already reduced to Cu⁰ at a more positive potential before interacting with AQ, as shown in Figure 3. In case of other divalent metal ions (alkaline earth, Cd²⁺, Fe²⁺, Pb²⁺, and Zn²⁺ metal ions) the reduction occurs at a more negative potential than that of the reduction of AQ, thus leading to divalent metal ion-coupled redox reaction of AQ. As shown in Figure 5, Ca²⁺ in 0.1 M TBAPF₆/CH₃CN does not exhibit reduction at a potential between 0 and -2.0 V, thus resulting in the coupled reaction of anthraquinones. Except for subtle differences, other divalent metal ions also show similar voltammetric behaviors of divalent metal ion-coupled reaction with AQ, AQNH₂, and AQCD (data not shown). This means, in essence, that AQCD interacts with Cu²⁺ ion via *chemodosimetric reaction* and with other divalent ions via *metal ion-coupled reaction*. Even with the difference of electrochemical mechanisms between AQCD with Cu²⁺ and AQCD with other divalent metal ions, it seems inappropriate to apply AQCD to electrochemical sensor for Cu²⁺ ion due to signal changing in the presence of other divalent metal ions, as well as Cu²⁺.

4. Conclusion

We have investigated the electrochemical behaviors of an anthraquinone bearing chemodosimeter for Cu²⁺ ion-induced desulfurization with metal ions. Differently from the results by optical measurements showing only colorimetric and fluorometric changes toward Cu²⁺, the electrochemical measurements of AQCD gave two different types of voltammetric changes toward divalent metal ions and Cu²⁺. This is attributed to the chemodosimetric reaction for Cu²⁺ and the divalent metal ion-coupled electrochemical reaction for other metal ions in the redox chemistry of AQCD. Therefore, to develop the electrochemical chemodosimeter for metal ions using anthraquinone derivatives, one should consider the metal ion-coupled electrochemical reaction as the interference for selective detection.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

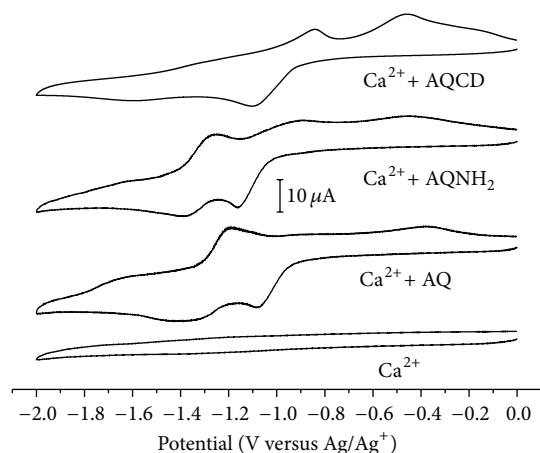


FIGURE 5: CVs of 0.75 mM Ca^{2+} in the absence and the presence of 0.5 mM AQ, AQNH_2 , and AQCD in 0.1 M $\text{TBAPF}_6/\text{CH}_3\text{CN}$. Scan rate: 50 mV/s.

Acknowledgments

This work was supported by the Soonchunhyang University Research Fund. This work (Grant no. C0119167) was also supported by Business for Cooperative R&D between Industry, Academy, and Research Institute funded Korea Small and Medium Business Administration in 2013.

References

- [1] J. J. Du, M. M. Hu, J. L. Fan, and X. J. Peng, "Fluorescent chemodosimeters using "mild" chemical events for the detection of small anions and cations in biological and environmental media," *Chemical Society Reviews*, vol. 41, no. 12, pp. 4511–4535, 2012.
- [2] D. T. Quang and J. S. Kim, "Fluoro- and chromogenic chemodosimeters for heavy metal ion detection in solution and biospecimens," *Chemical Reviews*, vol. 110, no. 10, pp. 6280–6301, 2010.
- [3] K. Kaur, R. Saini, A. Kumar et al., "Chemodosimeters: an approach for detection and estimation of biologically and medically relevant metal ions, anions and thiols," *Coordination Chemistry Reviews*, vol. 256, no. 17–18, pp. 1992–2028, 2012.
- [4] R. Martínez-Máñez and F. Sancenón, "Chemodosimeters and 3D inorganic functionalised hosts for the fluoro-chromogenic sensing of anions," *Coordination Chemistry Reviews*, vol. 250, no. 23–24, pp. 3081–3093, 2006.
- [5] Y. Yang, Q. Zhao, W. Feng, and F. Li, "Luminescent chemodosimeters for bioimaging," *Chemical Reviews*, vol. 113, no. 1, pp. 192–270, 2013.
- [6] M. Alfonso, A. Tárraga, and P. Molina, "Ferrocenylbenzobisimidazoles for recognition of anions and cations," *Inorganic Chemistry*, vol. 52, no. 13, pp. 7487–7496, 2013.
- [7] Q.-Y. Cao, M. H. Lee, J. F. Zhang, W. X. Ren, and J. S. Kim, "Ferrocene-based novel electrochemical chemodosimeter for mercury ion recognition," *Tetrahedron Letters*, vol. 52, no. 21, pp. 2786–2789, 2011.
- [8] Y. Liu, M. Li, Q. Zhao, H. Wu, K. Huang, and F. Li, "Phosphorescent iridium(III) complex with an $\text{N}^{\wedge}\text{O}$ ligand as a Hg^{2+} -selective chemodosimeter and logic gate," *Inorganic Chemistry*, vol. 50, no. 13, pp. 5969–5977, 2011.
- [9] B. Lou, Z.-Q. Chen, Z.-Q. Bian, and C.-H. Huang, "Multisignaling detection of cyanide anions based on an iridium(III) complex: remarkable enhancement of sensitivity by coordination effect," *New Journal of Chemistry*, vol. 34, no. 1, pp. 132–136, 2010.
- [10] T. K. Khan and M. Ravikanth, "3-(Pyridine-4-thione)BODIPY as a chemodosimeter for detection of Hg(II) ions," *Dyes and Pigments*, vol. 95, no. 1, pp. 89–95, 2012.
- [11] Y.-R. Kim, H. J. Kim, M. H. Lee et al., "Electrochemically programmed chemodosimeter on ultrathin platinum films," *Chemical Communications*, vol. 46, no. 44, pp. 8448–8450, 2010.
- [12] H. J. Kim, S. J. Lee, S. Y. Park, J. H. Jung, and J. S. Kim, "Detection of Cu^{II} by a chemodosimeter-functionalized monolayer on mesoporous silica," *Advanced Materials*, vol. 20, no. 17, pp. 3229–3234, 2008.
- [13] G. Dryhurst, *Biological Electrochemistry*, vol. 1, Academic Press, New York, NY, USA, 1982.
- [14] M. Quan, D. Sanchez, M. F. Wasylkiw, and D. K. Smith, "Voltammetry of quinones in unbuffered aqueous solution: reassessing the roles of proton transfer and hydrogen bonding in the aqueous electrochemistry of quinones," *Journal of the American Chemical Society*, vol. 129, no. 42, pp. 12847–12856, 2007.
- [15] R. H. Thomson, *Naturally Occurring Quinones IV: Recent Advances*, Balckie Academic & Professional, New York, NY, USA, 4th edition, 1997.
- [16] N. Gupta and H. Linschitz, "Hydrogen-bonding and protonation effects in electrochemistry of quinones in aprotic solvents," *Journal of the American Chemical Society*, vol. 119, no. 27, pp. 6384–6391, 1997.

