Determination of catechol in tea based on the inhibition of CS@Cd composites electrochemiluminescence

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Research Article

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Abstract

To address growing concerns about food safety, sensors for catechol (CA) have been urgently needed. In this work, cadmium-supported carbon spheres (CS@Cd) composites are prepared via hydrothermal synthesis and further used to fabricate a CS@Cd modified glassy carbon electrode (CS@Cd/GCE). Importantly, CS@Cd has good sensitization effect on the electrochemiluminescence (ECL) of luminol-$\text{H}_2\text{O}_2$ system. Besides, CA is able to inhibit the ECL of CS@Cd/GCE owing to the consumption of $\text{H}_2\text{O}_2$ induced by CA, and thus a novel strategy for ECL detection of CA is formulated. At optimum conditions, CS@Cd/GCE exhibits excellent linear relationship in the range of $1.0\times10^{-11}$ ~ $1.0\times10^{-4}$ mol·L$^{-1}$ for CA detection with a low limit of detection of $2.5\times10^{-12}$ (S/N = 3). Finally, this method achieves a satisfactory outcome for the detection of CA in tea samples.

1. Introduction

Catechol (CA), or o-diphenol, widely exists in vegetables, tea, fruits and nicotiana tabacum plants (Yang, He, Sui, & Chen, 2017). Meanwhile, as a typical phenolic compound, it is an important intermediate or raw material in the fields of medicine, food, coatings, resins and fragrance industry (Liang, Zhang, Zhang, et al., 2022; Zhou, Shan, Jiang, et al., 2020). However, CA has posed a serious threat to ecological environment and human health due to its degradation-resistant and cytotoxicity (Chen, Lei, Xu, Yang, Dong, Li, et al., 2022). Therefore, simple, quick and accurate detection of CA is of great significance. So far, various approaches, including electrochemical detection, fluorescence analysis, high performance liquid chromatography (HPLC), gas chromatographic method and surface plasmon resonance (Marrubini, Calleri, Coccini, et al., 2005; Moldoveanu & Kiser, 2007; Pathak & Gupta, 2020; Rao, Liu, Zhong, Zhang, et al., 2017; Wu, Cheng, & Tseng, 2007), have been proposed to detect CA. However, in principle, most of these approaches are not without major drawbacks, especially in terms of their need for costly equipment, complex pretreatments and suitably qualified personnel. Accordingly, it would be of practical significance to develop alternative methods for the fast, simple and sensitive detection of CA.

Electrochemiluminescence (ECL) is a chemiluminescence process triggered by electrochemical technology. It means that ECL reagents is excited on the electrode surface by applying a certain voltage, and further participate in a luminescence reaction with each other or with the co-reactant (Dong, Tian, Ren, Dai, et al., 2014; Huang, Li, Chen, Xu, et al., 2021; Kong, Lee, Kim, & Kang, et al., 2017; Wu, Han, Wei, Sun, et al., 2020). Compared with other methods, ECL detection has the advantages of high sensitivity, good selectivity, low cost, strong controllability, simple operation and no need for pre-treatment (Gao, Wang, Li, et al., 2019; Liu, Wang, Ge, Zhang, et al., 2023; Peng, Huang, Wu, Liu, et al., 2019; Zhao, Zeng, Chai, et al., 2020), and thus has evolved progressively into a valuable method in analytical chemistry. Especially, the ECL system of luminol-$\text{H}_2\text{O}_2$ has proved to be useful for detecting various analytes because of its strong ECL emission and ease of fabricating an sensor. For example, Robinson et al. reported a nitric oxide detector and its application in breath analysis using luminol-$\text{H}_2\text{O}_2$. Wang et al.
pointed out that the ECL of luminol can be significantly enhanced by a combination of cobalt-based organic framework and nano-silver particles, and was further applied to the ultra-sensitive detection of cardiac troponin I (Robinson, Bollinger, & Birks, et al., 1999; Wang, Zhao, Wang, Li, Saqib, et al., 2019). As such, we further expand the potential application of luminol-\( \text{H}_2\text{O}_2 \) in CA detection.

Carbon materials have a wide range of applications in contemporary research, especially carbon sphere (CS) material research has attracted much attention in recent years. Currently, various forms of carbon materials, such as carbon fiber, carbon aerogel, carbon nanotubes and fullerenes (Karimi-Maleh, Beitollahi, Senthil, et al., 2022; Karimi Estahbanati, Feilizadeh, Shokrollahi, & Iliuta, et al., 2019; Park., Thorgaard, Zhang, & Bard, 2013; Shi, Liang, Feng, Wang, & Stucky, 2008; Sun, Kiourti, Wang, et al., 2016; Tao, Endo, & Kaneko, 2009; Wang, Li, Wang, Chai, et al., 2019; Wang, Zhou, Gao, et al., 2022), are popular due to their unique structure and properties. In this work, we focus on carbon nanosphere composites on account of their uniform spherical morphology, controllable porosity, adjustable particle size, outstanding chemical and thermal stability, good conductivity and adsorption (Karimi Estahbanati, Feilizadeh, Shokrollahi, & Iliuta, et al., 2019; White, Tauer, Antonietti., & Titirici, 2010). These advantages indicate that carbon spheres have broad application prospects in ECL fields.

In the current study, CS@Cd composites are synthesized via hydrothermal method, taking niacin, glucose and cadmium chloride as raw materials, and are finally successfully applied to prepare an ECL sensor of CS@Cd/GCE. Herein, CS@Cd composites act as an ECL enhancer in luminol-\( \text{H}_2\text{O}_2 \) system, oppositely, CA can inhibit the ECL signal by the interaction between CA and \( \text{H}_2\text{O}_2 \). On this basis, sensitive detection of CA is achieved under the optimal conditions. Finally, CA in tea samples is analyzed to demonstrate the effectiveness of the proposed CS@Cd/GCE. In view of its simplicity, rapidity, sensitivity and specificity, the ECL sensor has significant potential in the analysis of \( \text{H}_2\text{O}_2 \) consumers for monitoring food quality.

2. Experimental Section

The detailed reagents, instruments, preparation of cadmium-supported carbon spheres (CS@Cd) composites are displayed in the Supplementary Materials.

2.1 Fabrication of CS@Cd/GCE

The glass carbon electrode (3 mm in diameter) was carefully polished with \( \text{Al}_2\text{O}_3 \) (0.05 \( \mu \text{m} \)) powder slurry on a suede to a mirror finish, and ultrasonicated with ultra-pure water for 5 min. The as-prepared CS@Cd powders and chitosan (a binder) solution were mixed. Further, ultrasonic treatment was conducted for 20 min to form an uniform dispersion solution. A clean electrode was subsequently incubated with 2.5 \( \mu \text{L} \) of
the mixture and air-dried at room temperature for 2 hours. After every step, the CS@Cd/GCE was fabricated and thoroughly cleaned with PBS buffer before use.

2.2 ECL Measurements

The three-electrode system was immersed into a PBS (0.1 M, pH 7.5) solution containing $1.00 \times 10^{-3}$ mol·L$^{-1}$ luminol, $1.00 \times 10^{-3}$ mol·L$^{-1}$ H$_2$O$_2$ and CA with given concentrations. The applied potential of the photomultiplier tube (PMT) was set at 700 V. Thereafter, the ECL emission was triggered and measured when the ECL sensor was scanned from $-0.5$ to $-1.5$ V with the scan rate of 0.18 V·s$^{-1}$.

3 Results And Discussion

3.1 Characterization of structure and morphology

The microstructure of the prepared CS (a) and CS@Cd (b) composites was characterised by SEM and TEM images. Both CS (Fig. 1A) and CS@Cd (Fig. 1B) consist of smooth microspheres with a mean diameter of about 400 nm. Besides, as can be seen from Fig. 2, CS@Cd are solid spheres. Additionally, the corresponding the elemental mapping images indicates that CS@Cd possesses C, O and Cd elements which are relatively uniform distributed in the CS@Cd composites.

The chemical composition of CS@Cd was also studied by XPS measurements and shown in Fig. 3. The full XPS spectrum (Fig. 3A) clearly shows that CS@Cd contain the elements of C, O and Cd, which is consistent with mapping images. The spectrum of C 1s in the CS@Cd (Fig. 3B) is deconvoluted into three single peaks that correspond to C-C (284.7 eV), C-N (286.0 eV) and C=O (288.5 eV) functional groups, respectively (Lv, Zhang, Wang, et al., 2018; Zhou, Wang, Yang, et al., 2018). In the high-resolution XPS spectra of Cd 3d, as shown in Fig. 3C, the characteristic peaks at 405.40 eV and 412.19 eV are attributed to the Cd 3d5/2 and Cd 3d3/2 orbits, respectively. The spin orbit separation ($\Delta$) of the Cd 3d orbit is 6.79 eV, implying that cadmium existed mostly in the form of Cd($^+$) (Zhou, Wang, Yang, et al., 2018).

Meanwhile, spectrum of O 1s region of CS@Cd (Fig. 3D) shows that the characteristic peaks at 531.61 eV, 532.77 eV and 533.70 eV, attributing to adsorbed oxygen (Oads), -C-O and C-OH, respectively (Haq, Din, Khan, et al., 2021).

3.2 ECL behavior

The ECL behaviors of CS/GCE and CS@Cd/GCE was studied in luminol-H$_2$O$_2$ system. As can be seen in Fig. 4, the ECL signal of CS@Cd/GCE (curve a) is strong in comparison with CS/GCE (curve c), which may attribute to the sensitization effect of CS@Cd composites. Importantly, when $1.00 \times 10^{-9}$ mol·L$^{-1}$ CA was added to the solution, the ECL signals of both CS@Cd/GCE and CS/GCE decrease obviously, as shown in curve b and curve d, respectively, arising from the chemical depletion of H$_2$O$_2$ induced by CA (specific explanation in Supplementary Materials). Therefore, the efficient inhibition supports the detection of CA in a ECL system of luminol-H$_2$O$_2$ using CS@Cd/GCE.
3.3 ECL analysis for CA

Under optimal detection conditions (Supplementary Materials), the linearity performance of CS@Cd/GCE for CA quantification was studied. In the existence of CA with various concentrations, ECL intensity progressively decreases with the CA concentration increases (Fig. 5A). Meanwhile, the intensity of ECL ($\Delta I_{ECL}$) difference shows a good linear negative association with the logarithmic concentration of CA (Fig. 5B). The regression equation is $\Delta I_{ECL} = 1.238 \lg C + 14.19$ ($\Delta I_{ECL} = I_0 - I$, $\Delta I_{ECL}$: the change of ECL intensity with CA concentration, $I_0$: the original ECL intensity, and $I$: the catechol-induced ECL intensity decrease; $C$: concentration of CA, $r = 0.9901$) in a range of $1.0 \times 10^{-11} \sim 1.0 \times 10^{-4}$ mol·L$^{-1}$, and the detection limit ($S/N = 3$) is $2.5 \times 10^{-12}$ mol·L$^{-1}$.

3.2.5 Selectivity and stability of the ECL sensor

In order to further study the specific selectivity of CS@Cd/GCE for CA. Possible interfering substances were added to $1.00 \times 10^{-6}$ mol·L$^{-1}$ CA solution and their ECL responses exhibited that the 1-fold concentration of hydroquinone, resorcinol, p-nitrophenol, 50-fold concentration of L-lysine, arginine, valine and threonine, 100-fold concentration of glucose, ascorbic acid, urea, Cu$^{2+}$ and Ca$^{2+}$ had no interference, suggesting that CS@Cd/GCE had strong selectivity to CA. The long-term stability was then studied by testing the ECL response of three ECL sensors to $1.00 \times 10^{-6}$ mol·L$^{-1}$ CA after 10 days of storage at 4°C. A 4.7% attenuation in the ECL signal was noted, thus indicating satisfactory stability of the ECL sensor.

3.2.6 Sample analysis

The tea (Liu'an Guapian from China) was dried in an oven, and then ground into powder with a mortar. After that, 0.1 g of tea powder was dispersed in a aqueous solution containing 30 mL 20% methanol, and further stirred and heated at 80 ℃ for 20 min, followed by filtering, and the filtrate was diluted to 50 mL. According to the above method, the content of CA in tea samples was determined with standard addition method. The results in Table 1 indicate that the proposed strategy is feasible, with CA recoveries in the range of 98.0%~103.5% as well as an relative standard deviation (RSD) within satisfactory rang. These findings further indicate that CS@Cd/GCE was reliable and satisfactory for analyzing CA in real samples.
Table 1
Determination of CA in tea samples (n = 7).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Original (mol·L(^{-1}))</th>
<th>Added (mol·L(^{-1}))</th>
<th>Found (mol·L(^{-1}))</th>
<th>RSD (%)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>tea</td>
<td>3.706×10(^{-6})</td>
<td>1.800×10(^{-6})</td>
<td>5.470×10(^{-6})</td>
<td>4.3</td>
<td>98.0</td>
</tr>
<tr>
<td></td>
<td>3.000×10(^{-6})</td>
<td>6.844×10(^{-6})</td>
<td></td>
<td>5.2</td>
<td>104.6</td>
</tr>
<tr>
<td></td>
<td>7.000×10(^{-6})</td>
<td>1.095×10(^{-5})</td>
<td></td>
<td>3.8</td>
<td>103.5</td>
</tr>
</tbody>
</table>

4. Conclusion

In conclusion, CS@Cd composites are first synthesized via hydrothermal method and is able to fabricate an ECL sensor for detecting CA, in which ECL signal inhibition is based on the chemical depletion of H\(_2\)O\(_2\) induced by CA. The as-prepared CS@Cd/GCE possesses good reproducibility, high sensitivity, wide linear range, and low detection limit. Additionally, the ECL sensor provides a method for fast detection of CA in tea samples, which can be applied to analyze not only CA but also some other H\(_2\)O\(_2\)-consuming substances. Thus, this work will pave an avenue for future development of other ECL sensors referring to food assay.

Declarations

Funding

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Author Contribution


Compliance with Ethical Standards

Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Ethical Approval
This article does not contain any studies with human participants or animals performed by any of the authors.

**Informed Consent**

Informed consent was obtained from all individual participants included in the study.

**Data availability**

Data will be made available on request.

**Appendix A. Supplementary data**

Supplementary material related to this article can be found, in the online version, at doi:https://XXX/XXXXX

**References**


Figure 1

SEM images of CS (A) and CS@Cd (B) composites.
Figure 2

TEM image of CS@Cd and the elemental mapping images of C, O and Cd.
Figure 3

XPS spectra of the CS@Cd. (A) Survey spectrum; (B) C1s spectrum; (C) Cd 3d spectrum and (D) O1s spectrum.
Figure 4

ECL behavior of CS/GCE and CS@Cd/GCE.

Figure 5
(A) The ECL responses to CA with different concentrations (from a to p: 0, 1.0×10^{-11}, 5.0×10^{-11}, 1.0×10^{-10}, 5.0×10^{-10}, 1.0×10^{-9}, 5.0×10^{-9}, 1.0×10^{-8}, 5.0×10^{-8}, 1.0×10^{-7}, 5.0×10^{-7}, 1.0×10^{-6}, 5.0×10^{-6}, 1.0×10^{-5}, 5.0×10^{-5}, 1.0×10^{-4} \text{ mol}\cdot\text{L}^{-1}). (B) The calibration plot between ΔI_{ECL} and lnC

Supplementary Files

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- ElectronicSupplementaryMaterials02.01.doc