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ORIGINAL PAPER

A glassy carbon electrode modified with carbon dots and gold nanoparticles for enhanced electrocatalytic oxidation and detection of nitrite

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Abstract The authors describe a method for the fabrication of a nanohybrid composed of carbon dots (C-dots) and gold nanoparticles (AuNPs) by in-situ reduction of C-dots and hydroauric acid under alkaline conditions. The process does not require the presence of surfactant, stabilizing agent, or reducing agent. The hybrid material was deposited in a glassy carbon electrode (GCE), and the modified GCE exhibited good electrocatalytic activity toward the oxidation of nitrite due to the synergistic effects between carbon dots and AuNPs. The findings were used to develop an amperometric sensor for nitrite. The sensor shows a linear response in the concentration range from 0.1 μmol·L^{-1} to 2 mmol·L^{-1} and a low detection limit of 0.06 μmol·L^{-1} at the signal-to-noise ratio of 3.

Keywords Nanomaterial · Nafion · Nitrite detection · Electrochemical sensor · Glassy carbon electrode · Electrooxidation · Amperometric sensor

Introduction

Rapid, accurate and economic determination of nitrite has attracted much attention for its excess level is hazardous to human health [1]. Many techniques have been reported for determination of nitrite, such as chemiluminescence [2], spectrophotometry [3], sequential injection analysis [4], chromatography [5], electrophresis [6], and electrochemical methods. Among these methods, electrochemical methods are often favored over others due to their relatively low-cost instrument, easy operation, high sensitive and fast response. The unmodified glassy carbon (GC) is highly active towards the direct electro-oxidation of nitrite. However, the working potential is quite higher and the selectivity is poor in the presence of other oxidizing compounds and thus decreases the sensitivity and accuracy. Hence, various chemically modified electrodes for the determination of nitrite by electrochemical oxidation have been explored to overcome the above limitations.

Carbon-based nanomaterials such as grapheme and carbon nanotubes have been employed in the development of nitrite sensor. For example, Chen et al. showed that nitrogen-doped reduced graphene oxide nanosheets modified electrode was favorable to the activation of nitrite and facilitated the charge transfer kinetics of nitrite [7]. Bai et al. showed that the oxidation peak of nitrite on polyhedral oligomeric silsesquioxane/reduced graphene oxide nanocomposite modified electrode due to the large surface area and the hydrophobic interface of polyhedral oligomeric silsesquioxane [8]. Kuralay et al. prepared poly(vinylferrocenium)/multi-walled carbon nanotubes coated disposable pencil graphite electrode for nitrite sensor and demonstrated its electrocatalytic activity towards nitrite due to carbon nanotubes [9]. The electrocatalytic activity towards nitrite have been improved by growth and anchoring of metal (Au [10, 11], Pd [12], Ag [13], Pt [14], Cu [15], Au-Pd [16], Pd-Co [17]) nanoparticles on carbon-based nanomaterials because of the unique physical and chemical properties, including excellent electronic conductivity, large surface area, high mechanical strength, and good electrocatalytic activity of metal nanoparticles.

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Carbon dots (CDs) have attracted tremendous attention owing to their outstanding optical properties, excellent biocompatibility, simple synthesis and remarkable conductivity. Many efforts have been devoted to exploring their application in the fields of optoelectronic devices, bioimaging and biosensing. Carbon dots have been used in electrochemical sensors to accelerate the electron transfer process between sensing interface and the electrode and promote the redox reaction processes. For example, N-doped carbon dots exhibited a highly sensitive electrochemical response toward dopamine in phosphate buffered saline [18]. The nanocomposite of carbon dots, hexadecyltrimethyl ammonium bromide and chitosan introduced a favorable access for the electron transfer and exhibited excellent electrocatalytic activity toward the oxidation of 2,4-DC dichlorophenol [19]. Nafion/multi-walled carbon nanotubes/carbon dots/multi-walled carbon nanotubes modified electrode can be used for simultaneous determination of hydroquinone, catechol and resorcinol in phosphate buffer solutions [20]. Reduced graphene oxide-carbon dots composite can be used as an enhanced material for electrochemical determination of dopamine [21]. Moreover, CDs also offer the possibility of combining metal component to obtain a binary hybrid nanomaterial, which merging different properties into a single new material can provide superior properties over their single components in various applications. Li et al. showed that the CDs/octahedral Cu_2O nanocomposites exhibited excellent electrocatalytic performance to glucose oxidation and H_2O_2 reduction compared with the only octahedral Cu_2O [22]. Huang et al. demonstrated that Au@carbon dots–chitosan modified glassy carbon electrode had higher catalytic activity toward the oxidation of dopamine compared with CDs–CS/GCE [23]. Gao et al. reported that polyamidoamine dendrimers capped-carbon dots nanocomposites with excellent conductivity, stability and biocompatibility on the surface of electrode can be designed as an immobilized matrix for sensitive immunosensing of alpha-fetoprotein [24]. Yang et al. prepared a nanomaterial of thiol functional ferrocene derivative stabilized Au NPs/carbon dots nanocomposite coupling with graphene modified glassy carbon electrode for ultrasensitive and simultaneous determination of ascorbic acid, dopamine, uric acid and acetaminophen [25].

CD-metal nanohybrids were usually prepared by reducing the mixing solution of metal precursors and carbon dots with a variety of reducing agents, such as citrate [23], sodium borohydride [26]. Actually, CDs can be used as a reducing agent and stabilizing agent during the reaction [27]. Au NPs/carbon dots nanocomposite [25], platinum/CD hybridnanoparticles [28] and carbon based-AuPd bimetallic nanocomposite [29] have been fabricated by using carbon dots as the reductant and stabilizing agent. Silver/carbon nanocomposite synthesized by using carbon dots as the reductant was used for the detection of nitrite by differential pulse voltammetry [30]. Au-carbon nanocompositions are usually employed as electrochemical interfaces to effectively accelerate electron transfer between electrodes and nitrite ions because of their desirable properties, including excellent electronic transport properties, and good biocompatibility [10, 11] In this paper, Au decorated on the surface of carbon dots were synthesized by simply heating CDs and metal precursors under alkaline conditions, without adding any additional reducing agents, stabilizing agent and surfactant. Herein, CDs are used as reducing agents, stabilizing agent and carrier for in situ growing of CD/Au nanohybrids. This one-pot strategy provides a new pathway for the fabrication of CD-metal nanohybrids. What's more, the obtained CD/Au nanohybrids exhibited an outstanding electrocatalysis towards the oxidation of nitrite. Based on the obtained nanohybrids, a simple and sensitive amperometric sensor for nitrite has been developed.

Experimental

Chemicals and reagents

All chemicals were purchased from Aladin Ltd. (Shanghai, China, http://www.aladdin-e.com). All the reagents were of analytical grade and used as received without further purification. Ultrapure water purified by a Millipore-Q System and used as solvent throughout all experiments. All glassware was cleaned in a bath of freshly prepared aqua regia solution (HCl/HNO_3, 3:1), and then rinsed thoroughly with ultra pure water. Acetate buffer was prepared with CH_3COONa and CH_3COOH. Sodium nitrite solution was prepared before used.

Apparatus

Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were taken from a FEI model Tecnai G2 F20 TEM at 200 kV. Elemental composition was characterized using the energy-dispersive X-ray analysis (EDX) equipment that was coupled to the Tecnai G2 F20 TEM system.

Electrochemical measurements were carried out on a CHI660D electrochemical workstation (Shanghai, China) with a conventional three electrode system comprised of platinum wire as the counter electrode, Ag/AgCl (3 $mol\cdot L^{-1}$ KCl) as the reference electrode and modified glassy carbon electrode (GCE, 3 mm in diameter) as the working electrode.

Synthesis of carbon dots

The electrochemical preparation of CDs was performed according to the literature [31]. NaOH solution (2.0 $mol\cdot L^{-1}$) was used as the supporting electrolyte. The graphite rod (GR) was inserted into 2.0 $mol\cdot L^{-1}$ NaOH as working electrode, the other graphite rod as the counter electrode, and a Ag/AgCl (3 mol·L^{-1} KCl) as reference electrode. The applied potential at the GCE was cycled between −2.0 and 2.0 V at 0.1 V·s^{-1}. With increasing oxidation time, the color of the electrolyte solution changed from colorless to light yellow. The light yellow solution was centrifuged (4000 g) for 10 min to remove the precipitated graphite oxide and graphite particles. The supernatant was collected and loaded into dialysis bags (molecular weight cut off =3500) and dialyzed against ultrapure water for 48 h. Finally, the obtained solution was water soluble fluorescent CDs and stored at 4 °C for further use. The carbon dots exhibit yellow fluorescence when exposed to 365 nm UV light.

Preparation of CD/Au nanohybrids

In a typical synthesis, 2.0 mL of 10 mmol·L^{-1} $HAuCl_4$ solution were added into 2.0 mL of the obtained CDs and stirred for 2 min at room temperature. Then sodium hydroxide solution was added into this mixture dropwise to adjust the pH to 11. After another 2 min stirring, the mixture solution was refluxed at 37 °C with stirring for 48 h. It is noteworthy to point out that we did not use any other reducing and stabilizing agent during the reaction.

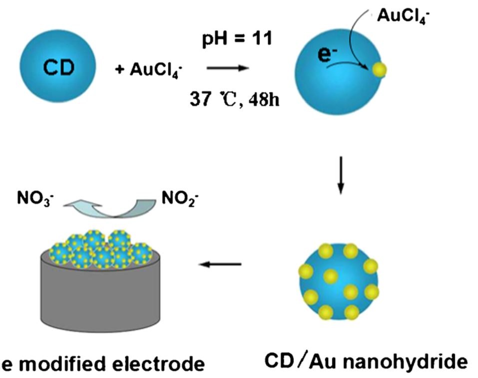
Preparation of modified electrode

GCE was polished to a mirror-like surface with 0.5 μm and 0.03 μm, α-alumina slurry, respectively, then washed successively with ultra pure water, ethanol and ultra pure water in an ultrasonic bath, and dried in air before use. Subsequently, 5 μL CD/Au nanohybrids were coat onto the surface of the GCE, and dried in the air at room temperature. And then, 5 μL of Nafion solution was deposited onto the CD/Au nanohybrids modified electrode surface to entrap the CD/Au nanohybrids The obtained electrode was stored at 4 °C before use. Similarly, nafion and CDs-nafion modified GCE were also prepared for comparison.

Result and discussion

Principles

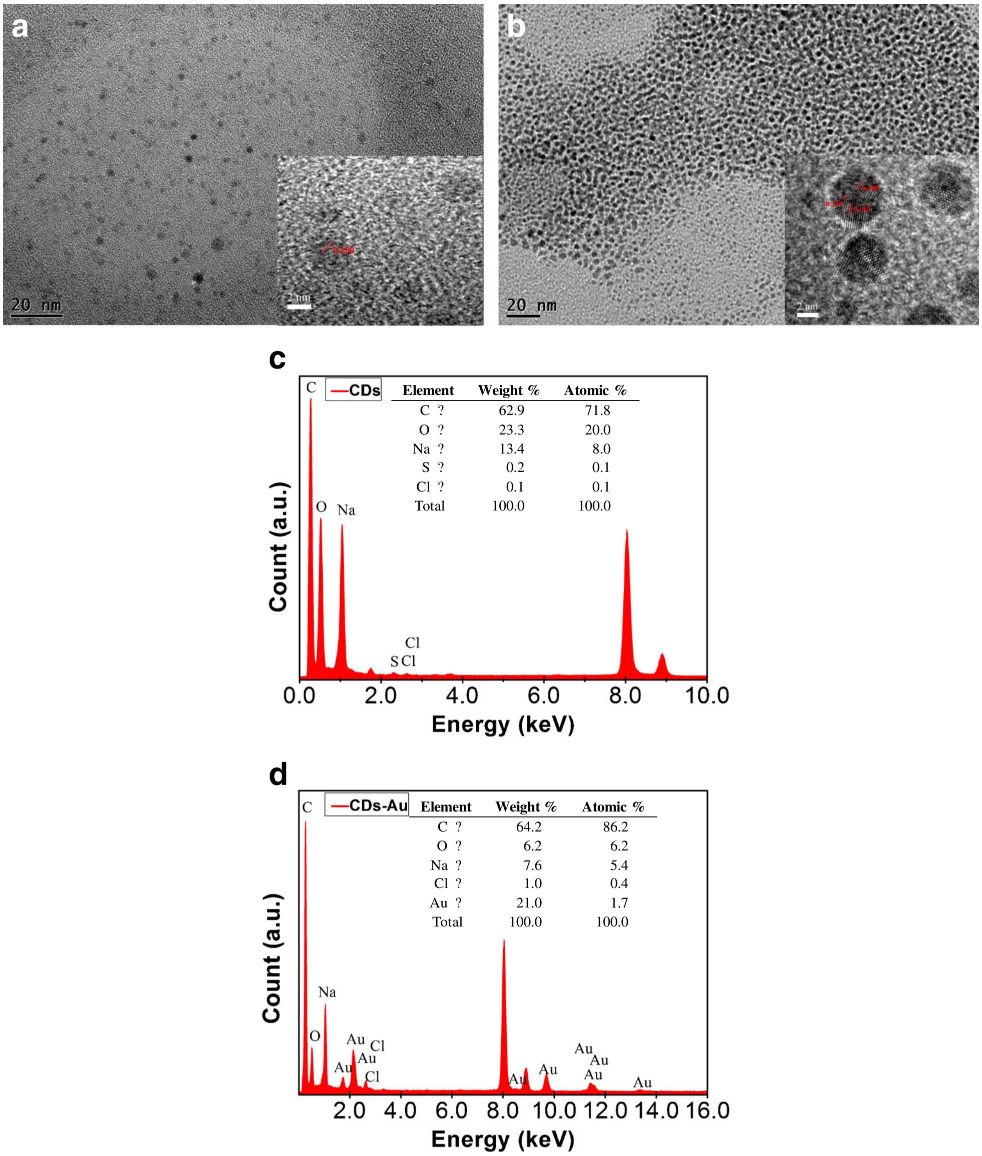
In a simple and facile method, CD/Au nanohybrids were fabricated by heating the CDs and $HAuCl_4$ under alkaline conditions. The obtained CD/Au nanohybrids were used to construct a sensor for the detection of nitrite, Scheme 1 is schematic of the preparation of CD/Au nanohybrids and the principle of determination nitrite. CDs can act as an excellent electron acceptor and electron donor [32], and therefore they have promising potential to be oxidation or reduction agents [27]. Herein, the abundant functional groups (−OH,-COOH, C = O) on the surface of CDs provide anchor sites for the nucleation and growth of Au nanoparticles. In the process of heating and refluxing, Au nanoparticles were in situ generated on the surface of CDs under alkaline conditions. It is noteworthy that not only alkaline conditions with heating but also CDs help to reduce $HAuCl_4$ to Au nanoparticles. The obtained CD/Au nanohybrids are highly stable and well dispersible in water. In our case, none of additional surfactant, stabilizing agent and reducing agents was employed, and CDs can be used as reductant and stabilizer for synthesizing Au nanoparticles on the surface of CDs. It provides a new pathway for simply and effectively preparing of CD-based nanohybrids. The obtained CD/Au nanohybrids subsequently were coated on the GCE surface for determination of nitrite.



Scheme 1 Schematic illustration for the preparation of CD/Au nanohybrids and nitrite sensor application

Characterization of CD/Au nanohybrids

The morphologies and microstructures of CDs and CD/Au nanohybrids were investigated by TEM. As shown in Fig. 1, it can be found that CDs (Fig. 1a) and CD/Au nanohybrids (Fig. 1 b) were well-dispersed and nearly spherical in shape with diameters of about 3–4 nm and 4–5 nm, respectively. The HRTEM image of one nanoparticles (Fig. 1a, inset) showed a crystalline structure with the lattice spacing of 0.200 nm, which can be attributed to the (102) diffraction planes of graphitic (sp^2) carbon. However, for the HRTEM of CD/Au nanohybrids (Fig. 1b, inset), the clear lattice spacing of 0.230 and 0.150 nm was found which can be attributed to the (111) and (220) lattice space of metallic Au [33]. The lattice spacing of 0.200 nm can also be observed, which implied Au was decorated on the surface of carbon dots and therefore prevent the aggregation of CD/Au nanohybrids. EDX were further employed to examine the chemical composition of the obtained nanohybrids. As shown in Fig.1c and d, the nanohybrids were composed of C and Au, and the content of C and O decreased compared with the only CDs.



—CDs

Element	Weight %	Atomic %
C ?	62.9	71.8
O ?	23.3	20.0
Na ?	13.4	8.0
S ?	0.2	0.1
Cl ?	0.1	0.1
Total	100.0	100.0

—CDs-Au

Element	Weight %	Atomic %
C ?	64.2	86.2
O ?	6.2	6.2
Na ?	7.6	5.4
Cl ?	1.0	0.4
Au ?	21.0	1.7
Total	100.0	100.0

Fig. 1 TEM images of CDs **a** and CD/Au nanohybrids **b**. The energy-dispersive X-ray (EDX) spectroscopy spectrum of CDs **c** and CD/Au nanohybrids **d**

Furthermore, UV-vis and fluorescence spectra of CDs and CD/Au nanohybrids (shown in ESM) also proved the generation of CDs/Au nanohybrids.

Electrochemical response of nitrite on the CD/Au nanohybrids modified electrode

The electrochemical response of nitrite at GCE, nafion/GCE, CDs/nafion/GCE and CD/Au nanohybrids/nafion/GCE were examined using CV in 1.0 mmol·L^{-1} nitrite solution. As shown in Fig. 2, the bare GCE showed a catalytic oxidation peak for 1 mmol·L^{-1} nitrite at 1.00 V. However, the anodic peak disapeared on nafion modified GCE maybe due to the cation perm-selectivity of nafion. When CDs were coated onto the electrode surface, small anodic peak of nitrite at 0.90 V can be observed. A significant shift in overpotential

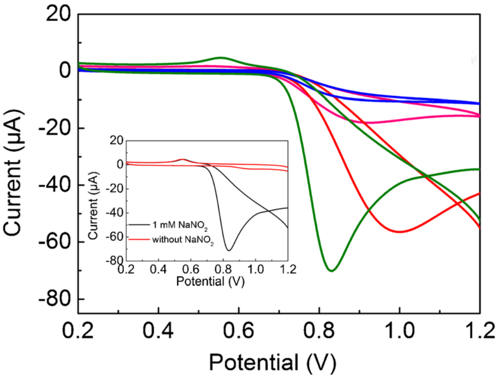


Fig. 2 CVs response of bare (*red curve*), nafion (*blue curve*), CDs/nafion (*pink curve*) and CD/Au nanohybrids/nafion (*olive curve*) modified electrodes in 0.1 mol·L^{-1} acetate buffer (pH 6.0) in the presence of 1.0 mmol·L^{-1} NaNO$_2$. Inset: CVs of CD/Au nanohybrids/nafion/GCE in the absence (*red curve*) and presence (*black curve*) of 1.0 mmol·L^{-1} NaNO$_2$ in 0.1 mo l L^{-1} acetate buffer (pH 6.0). Scan rate: 100 mV s^{-1}

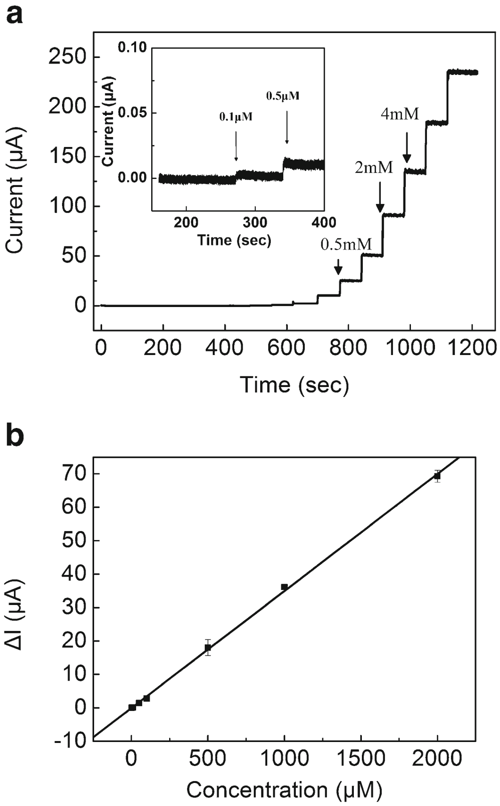


Fig. 3 **a** Steady-state current–time responses of nitrite at the CDs/Au nanohybrids/nafion/GCE at 0.90 V vs. Ag/AgCl (3 mol·L^{-1} KCl) subject to various concentrations of nitrite in 0.1 mol·L^{-1} acetate buffer (pH 6.0) under constantly stirring. Top inset displays the response to 0.1 and 0.5 µmol·L^{-1} nitrite. **b** the calibration curve of nitrite at the CDs/Au nanohybrids/nafion/GCE at 0.90 V vs. Ag/AgCl (3 mol·L^{-1} KCl)

Table 1 Comparison of the proposed CD/Au nanohybrids/nafion/GCE performance with those previously reported for the determination of nitrite

Electrode material	Linear range (µmol·L^{-1})	Detection limit (µmol·L^{-1})	Refs.
MWCNTs-TiN/Cyt c/GC	1–2000	0.0014	[34]
PEDOT/AuNP	0.2–1400	0.06	[35]
PEDOT-AuNP	3.0–300	0.1	[36]
Au-ZnO-MWCNTs	0.78–400	0.4	[37]
Pt-RGO/GCE	0.25–90	0.1	[38]
Cu/f-RGO/GCE	0.15–10,500	0.06	[39]
Au-MA	10–1000	0.89	[40]
AuCu NCN	10–4000	0.2	[41]
CDs-Au-N	0.1–2000	0.06	This work

Abbreviation: *AuCu NCN* gold-copper nanochain networks: *f-RGO* flower-like reduced graphene oxide: *MA* Melamine: *N* Nafion: *PEDOT* Poly(3,4-ethylenedioxythiophene)

toward less positive region for nitrite oxidation on CDs/nafion/GCE in comparison to bare GCE indicates the CDs facilitated the electrochemical oxidation of nitrite. For CD/Au nanohybrids/nafion modified electrode, it showed a catalytic oxidation peak for 1 mmol·L^{-1} of nitrite at 0.83 V and however, it did not show any voltammetric response around 0.83 V in the absence of nitrite (insert in Fig. 2). The sharp oxidation peak at around 0.83 V may be attributed to the conversion of NO_2^- to NO_3^-. Compared with GCE, nafion/GCE and CDs/nafion/GCE, a substantial negative shift of the anodic peak potential and obvious increase of current signal were observed on the CD/Au nanohybrids/nafion modified electrode as depicted in Fig. 2 (olive curve). The enhancement of the electrochemical activities to nitrite may be attributed to the synergistic effect of Au and CDs.

In order to improve its performance, various factors affecting the response of the sensor were investigated such as the pH value of the electrolyte solution and the applied potential used. As shown in ESM (in Fig. S2a), the peak current increased with pH in the range from 3.5 to 6.0 and then decreased with the further increased of pH value. The maximum oxidation current of nitrite appeared at pH 6.0. The optimal value of the applied potential was obtained by amperometric measurement of nitrite concentration in acetate buffer (0.1 mol·L^{-1}, pH 6.0) at applied potentials from 0.80 to 1.05 V. The response of the sensor at different applied potentials is shown in the ESM (in Fig. S2b). The results demonstrated that the response sensitivity was increased with the increase of applied potentials; however, the noise and interference will become more serious for the detection of nitrite at higher applied potentials. As such, 0.1 mol·L^{-1} acetate buffer (pH 6.0) and an applied potential of 0.90 V were chosen for subsequent experiments.

Figure 3a displays a typical amperometric response curve of nitrite in 0.1 mol·L^{-1} acetate buffer (pH 6.0) at CD/Au nanohybrids modified electrode. A well-defined, stable and

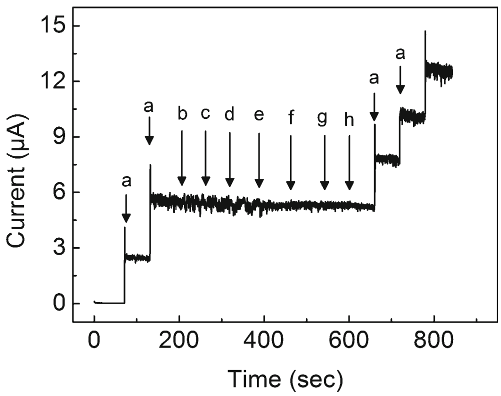


Fig. 4 Amperometric response of CDs/Au nanohybrids/nafion/GCE in 0.1 mol·L^{-1} acetate buffer (pH 6.0) by adding different species at 0.90 V vs. Ag/AgCl (3 mol·L^{-1} KCl). Arrow stands for the point of sample addition. a: 0.1 mmol·L^{-1} nitrite, b-h: 5 mmol·L^{-1} KNO_3, C_2H_5OH, $MgSO_4$, $CaCl_2$, $(NH_4)_2SO_4$, glucose and Na_2CO_3

Table 2 Results for determination of nitrite in the lake water sample

Sample	The proposed method					optical method* (μmol·L^{-1})
	Detected (μmol·L^{-1})	Added (μmol·L^{-1})	Found (μmol·L^{-1})	RSD (%)	Recovery (%)	
1	3.88	10	13.95	4.45	100.70	4.10
2	4.10	10	13.64	1.09	95.40	3.98
3	3.99	10	13.21	5.01	92.20	3.92

*Optical method was performed by the PRC National Standard (GB7493–87)

fast amperometric response can be observed at 0.90 V with successive additions of nitrite into 0.1 mol·L^{-1} acetate buffer (pH 6.0). The time required to reach the stable response was less than 2 s, which is much faster than the other nitrite sensors [31–35]. The calibration curve for the nitrite sensor is shown in Fig. 3b. The current responses are proportional to the nitrite concentration in a range from 0.1 μmol·L^{-1} to 2 mmol·L^{-1}, and the regession equation is Ip (μA) = −0.032 + 0.035 [NO^{2-}](μmol·L^{-1}) (R^2 = 0.9994.). The detection limit is estimated to be 60 nmol·L^{-1} with a signal/noise ratio of 3. The performance of the present sensor was compared with the other previously reported sensors for the detection of nitrite in Table 1 and the LOD of present sensor is comparable to other sensor materials. All the data from this sensor reveal the properties of high sensitivity, low detection limit and fast response time, attributed to the synergistic catalytic effect of Au and CDs which promoted the oxidation of nitrite.

The reproducibility and stability of the sensor was evaluated. Six CD/Au nanohybrids/nafion modified electrode were made and their current responses to 1.0 mmol·L^{-1} nitrite at 0.90 V were investigated. The relative standard deviation (RSD) was 5.7 %, confirming that the fabrication method was reproducible. Three successive measurements of 1.0 mmol·L^{-1} nitrite solution on one CD/Au nanohybrids/nafion modified electrode yielded an RSD of 1.9 %, demonstrating that the sensor was stable. The long-term stability of the sensor was evaluated by measuring its sensitivity to nitrite among 20 days. The sensor was stored in air at 4°C and its sensitivity was tested every 10 day. The result demonstrated that the sensitivity was 89 % of its initial sensitivity after being stored 20 days, indicating good stability after long-term storage. The good reproducibility and long-term stability of the sensor are desirable for most routine analysis.

The selectivity of the CD/Au nanohybrids/nafion modified electrode was evaluated in the presence of different possible interfering molecules and ions, such as KNO_3, C_2H_5OH, $Mg(CH_3COO)_2$, $CaCl_2$, $(NH_4)_2SO_4$, glucose and Na_2CO_3. As shown in Fig. 4, it is obvious that only the spiking of nitrite produced current signal and the others failed to produce the current response in i–t curve even at 50 times higher concentration than the concentration of nitrite. Moreover, the presence of higher concentration of interfering ions did not disturb the current signal of nitrite and almost same magnitudes of current response were reproduced. These results indicated that the developed sensor possessed high selectivity for determination of nitrite. To demonstrate the feasibility of the present sensor applied to the practical samples, the detection of nitrite in lake water was performed. The water sample was filtered and used for the real sample analysis. Water quality-determination of nitrogen (nitrite)-spectrophotometric method of PRC National Standard (GB7493–87) was adopted to estimate the accuracy. The results shown in Table 2 revealed good accordance between the spectrophotometric method and this method. It can be clearly observed that the developed sensor produced satisfactory recoveries with an average recovery of 96.7 % suggesting reliability of the proposed electrode. These results implied that the sensor can be used for practical applications.

Conclusion

We have shown the fabrication of CD/Au nanohybrids by using CDs as reducing agents, stabilizing agent and carrier. The obtained CD/Au nanohybrids modified GCE was used as the electrochemical sensor for the detection of nitrite and it produced a synergistic catalytic current in nitrite oxidation with significant negative shift in overpotential. The sensor was stable, reproducible and sensitive toward the detection nitrite. Although CD/Au nanohybrids modified electrode were not capable enough to prevent the interference from ascorbic acid, dopamine, and acetaminophen, the present sensor can be applied for the detection of nitrite in real lake water sample with good recoveries.

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Compliance with ethical standards The author(s) declare that they have no competing interests.

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