



A glassy carbon electrode modified with N-doped carbon dots for improved detection of hydrogen peroxide and paracetamol

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Abstract

Nitrogen doped carbon dots (NCDs) were synthesized using a low temperature approach and used to modify a glassy carbon electrode (GCE) via dipping. The oxygen groups on the surface of the NCDs, and the charge delocalization of the NCDs warrant an excellent electrocatalytic activity of the GCE toward oxidation of paracetamol (PA) and reduction of H₂O₂. PA and H₂O₂ were detected at 0.34 V and −0.4 V (both vs. Ag/AgCl) using differential pulse voltammetry and amperometric I-T measurement, respectively. The modified GCE has a linear response to PA in the 0.5 to 600 μM concentration range, and to H₂O₂ in the 0.05 μM to 2.25 mM concentration range. The detection limits are 157 nM and 41 nM, respectively. In our perception, the modified GCE holds promise for stable, selective and sensitive determination of PA and H₂O₂ in pharmaceutical analysis.

Keywords Low temperature synthesis · Surface functional group · Electrode modification · Cyclic voltammetry · Differential pulse voltammetry · Pharmaceutical analysis · H₂O₂ disinfectant · Electrochemical sensor · Nanomaterial

Introduction

Carbon-derived nanomaterials have been used to develop a myriad of chemical sensing applications due to their excellent electrochemical properties and stability. As a new type of nanocarbon material, carbon dots (CDs) have attracted interest

due to their low cytotoxicity, high chemical stability, easy preparation, green synthesis and stable photoluminescence [1–3]. Although most of the sensing applications based on CDs have focused on bioimaging and optical sensing due to their highly tunable photoluminescence properties, studies have also explored the potential of using CDs for electrochemical sensing

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[4–7]. For example, Huang et al. [8] fabricated a Cu₂O-CD nanocomposite and successfully used it for the determination of dopamine in human serum. Wei et al. [9] reported a Nafion/multi-walled carbon nanotube/CD/multi-walled carbon nanotube nanocomposite as an electrode surface modifier for detecting hydroquinone, catechol and resorcinol. However, CDs possess abundant surface functional groups and behave as a semiconductor, and thus, they may not be an ideal electrode surface modifier for enhancing electrochemical properties. Therefore, only limited reports have focused on the direct usage of CDs for electrochemical sensing application [10, 11].

To tailor the electronic and electrocatalytic properties of CDs, chemical doping is an effective approach. Earlier work has shown that chemical doping of carbon materials results in a higher density of free charge carriers. This, consequently, improves their thermal and electrical properties [12–15]. Therefore, a low-temperature method was used to synthesize the nitrogen-doped CDs (NCDs) in a good yield.

Then, a dipping fabrication method was applied for the glassy carbon electrode (GCE) surface modification. The absorbed NCDs on the GCE surface serve as electrocatalytic sites for electrochemical reactions. Pharmaceutical sensing is extremely important in clinical fields [16, 17]. The potential pharmaceutical sensing performance of the fabricated NCDs/GCE was tested using hydrogen peroxide (H₂O₂) and paracetamol (PA) as the analytes. The cyclic voltammetry studies indicated that the NCDs/GCE exhibited remarkable electrocatalytic activities for PA oxidation and H₂O₂ reduction because of the N-doping-induced charge delocalization. Under the optimized conditions, the NCDs/GCE exhibits linear detection ranges of 0.5 to 600 μM and 0.05 μM to 2.25 mM and limit of detections of 140 nM and 33 nM for PA and H₂O₂, respectively.

Experimental

Citric acid, urea, dopamine, glucose, acetylsalicylic acid, bacitracin zinc, ibuprofen, H₂O₂ and paracetamol were purchased from Sinopharm Chemical Reagent Co., Ltd. (<http://en.reagent.com.cn>). All reagents were analytical grade, and the solutions were prepared with deionized water. The paracetamol tablet (Coles Brand, 500 mg, <https://www.coles.com.au>) was ground using a mortar and pestle, and the obtained powders were dissolved in 100 mL of water by sonication. Then, different amounts of the prepared solutions were diluted to 5 mL with 0.1 M PB for the determinations.

For the NCDs synthesis, 2 g of citric acid and 2 g of urea were pre-mixed and heated to 180 °C for 10 min. Then, 100 mL of water was added to disperse the reaction product. After centrifugation (5000 rpm, 15 min), the supernatant was collected and filtered through a cellulose acetate filter. The solution was then dialyzed in a dialysis bag (cut off molecular

weight of 3500 Da) in deionized water for 2 days. The quantitative yield of the NCDs was approximately 37%. A 0.5 mg·mL⁻¹ NCDs solution was prepared for the GCE surface modification. A dipping method was conducted by immersing the GCE in the NCDs solution for 5 min and was followed by a N₂ drying process.

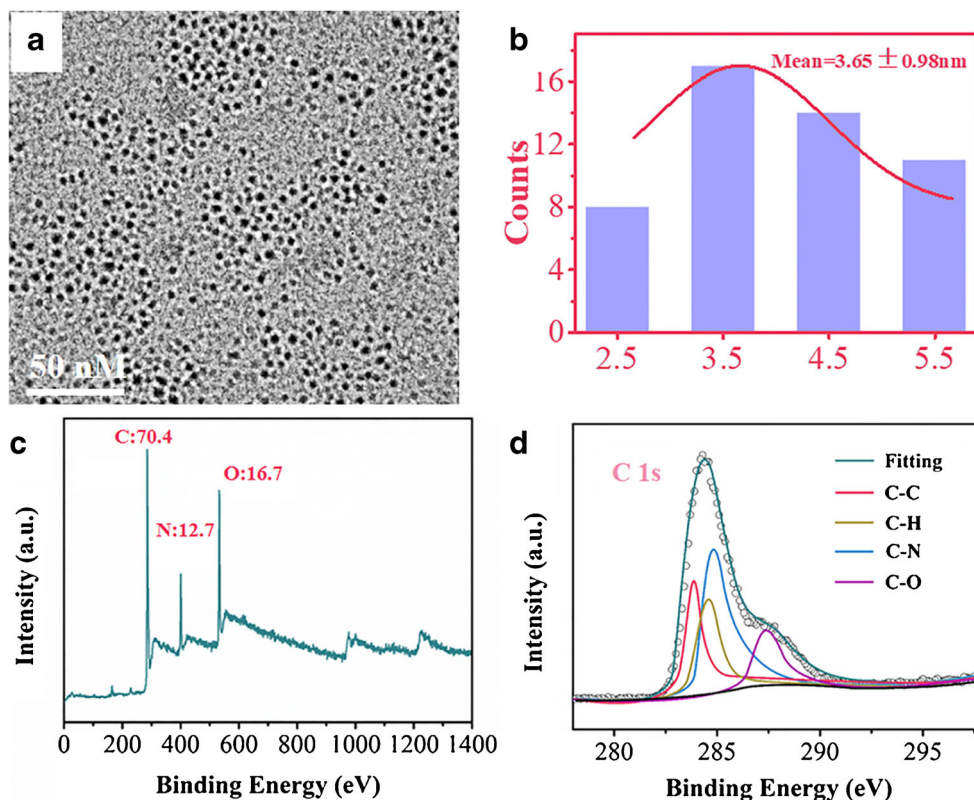
The morphology and size observations were conducted by a transmission electron microscope (JEOL 2100, USA). The surface chemical status of the NCDs was characterized by X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250Xi USA) using a monochromatic Al-K X-ray source. All electrochemical experiments were conducted using a CHI 832 electrochemical workstation with a conventional three-electrode system comprised of a platinum wire auxiliary electrode, a 3 M Ag/AgCl reference electrode and a GCE working electrode. Cyclic voltammetry (CV) was performed at scan rates from 20 to 200 mV·s⁻¹ with sample intervals of 1 mV. Differential pulse voltammetry (DPV) measurements were carried out with an amplitude, pulse width, sampling width and pulse period of 30 mV, 0.02 s, 0.015 s and 0.05 s, respectively.

Results and discussion

Carbon nanomaterials are excellent electrode materials and modifiers for electrochemical sensing applications because they increase the electroactive surface area, enhance the electron transfer, and promote the adsorption of molecules. They exhibit better electrical properties than common conducting polymers, but they are cheaper than noble metal nanomaterials. Among carbon nanomaterials, CDs can be prepared using a very cheap precursor. The preparation of CDs can be achieved using a simple instrument without a catalyst. Moreover, CD doping can be manipulated during the synthesis. Therefore, the sensing properties of NCDs are worth studying.

The morphology of the NCDs was characterized using a TEM. As shown in Fig. 1a, the size of the NCDs ranged from 2.0 to 6.0 nm. The average diameter of the NCDs was 3.65 ± 0.98 nm based on 50 individual NCDs (Fig. 1b). The successful nitrogen doping was confirmed using X-ray photoelectron spectroscopy (XPS). As shown in Fig. 1c, the elemental survey shows C, N and O are the prominent elements in the prepared NCDs, and the percentages of C, N, O are 59.1%, 19.5% and 20.71%, respectively. The high-resolution survey spectra of C 1s are shown in Fig. 1d. The dominant peak at 284.7 eV corresponds to graphitic sp² carbon, suggesting the carbon atoms in the NCDs are arranged in a π-conjugated lattice. The peaks located at 285.2 eV and 287.2 eV are assigned to N-sp² carbon and N-sp³ carbon [10, 18], respectively. The results show that the nitrogen doping during the low-temperature synthesis was successful.

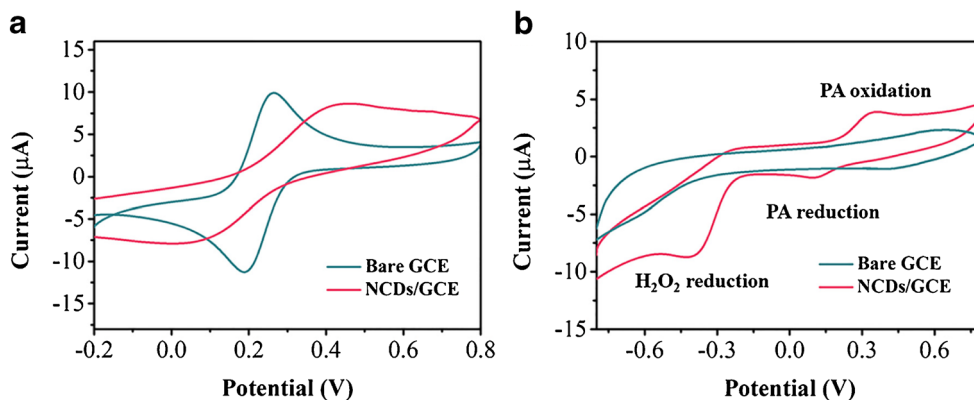
Fig. 1 **a** TEM image of the NCDs. **b** Diameter distribution of the NCDs calculated based on 50 individual NCD. **c** XPS elemental survey of the NCDs. **d** High-resolution C survey spectra of the NCDs



After the dipping fabrication process, cyclic voltammetry (CV) was used to investigate the electrochemical behavior changes of the GCE. CV scans were performed in a 1 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ solution with 0.1 M KCl. As shown in Fig. 2a, the CV profile of the GCE exhibits well-defined redox peaks as expected. However, a clear decrease in the peak current was observed for the NCDs/GCE with enlarged peak-peak splitting. This observation indicated the NCDs modification decreased the electron transfer rate of the pristine GCE, which contradicted some previous reports [19, 20]. The oxygen containing groups were detected by XPS (Fig. 1d). Their presence on the NCDs facilitates electron transfer [10]. Therefore, NCDs are not good electrode surface modifiers to enhance the electrode conductivity. Next, the GCE electrocatalytic

activity changes in the presence of H_2O_2 and paracetamol (PA) were tested. Figure 2B shows the CV behaviors of 0.4 mM H_2O_2 and 0.2 mM PA at the GCE and the NCDs/GCE in 0.1 M PB. On the bare GCE, only one peak was observed at $E_{\text{pa}} = 0.52$ V, which was attributed to the irreversible oxidation of PA. In contrast, PA underwent a well-defined, partial oxidation at the NCDs/GCE with $E_{\text{pa}} = 0.34$ V and $E_{\text{pc}} = 0.1$ V. A clear H_2O_2 reduction enhancement with a larger current response and lower reduction potential was also recorded at the NCDs/GCE compare with that at the bare GCE. Therefore, the electrocatalytic reactions of both molecules occurred at the NCDs/GCE. Previous research has reported that the surface defects and surface oxygen-containing functional groups of carbon materials can act as

Fig. 2 **a** CV profiles of the GCE and NCDs/GCE at 1 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ + 0.1 M KCl. **b** CV recorded at the GCE and NCDs/GCE with 0.4 mM H_2O_2 and 0.2 mM PA in 0.1 M PB (pH 7.0). Scan rate: $50 \text{ mV}\cdot\text{s}^{-1}$



active sites for electrocatalytic reactions [21–24]. Therefore, the surface functional groups on the NCDs acted as regulators of the observed electrocatalytic behavior. For the PA oxidation, the oxygen-containing groups withdraw two protons from the endiol group and facilitate the PA oxidation reaction [25]. For H_2O_2 , the surface-functionalized NCDs increase the adsorption energy for H_2O_2 and improve its reduction reaction [24, 26]. Moreover, doping with nitrogen also induces charge delocalization in the CDs and accelerates the electrocatalysis [27].

The electrochemical behavior of the NCDs/GCE can be affected by the fabrication process. The pristine GCE surface behavior must be ensured for the NCDs modification. The precision of the NCDs concentration and the accuracy of the dipping time are two important steps in ensuring the final NCDs/GCE performance. Fig. S1 shows the effect of the dipping time on both the PA oxidation and H_2O_2 reduction. Both the PA oxidation and H_2O_2 reduction clearly increased when the dipping time increased from 2 min to 4 min. A slight decrease in the reduction current of H_2O_2 was observed when a 5 min dipping time was applied, but the PA oxidation continued to increase. Further increasing the dipping time results in a significant decrease in the H_2O_2 reduction. A decrease in the PA oxidation was observed when 8 min was used. Therefore, a 4 min dipping time was chosen for the fabrication.

Figure 3A shows the effect of the scan rate on the electrocatalysis of H_2O_2 and PA. The peak currents for the PA oxidation at the NCD/GCE increased as the scan rate increased from 20 to $200 \text{ mV}\cdot\text{s}^{-1}$. Linear relationships were recorded for the scan rate versus the peak current (Fig. 3b), which suggested the PA oxidation occurring on the NCDs/GCE was controlled by adsorption [28, 29]. A linear relationship was also recorded for the scan rate versus the peak current for the H_2O_2 reduction at the NCDs/GCE (Fig. 3c). Therefore, the H_2O_2 reduction that occurred at the NCDs/GCE was also controlled by adsorption. The carry-over effect was further tested, as shown in Fig. S2. One NCDs/GCE (a) was tested for sensing

$0.4 \text{ mM } \text{H}_2\text{O}_2$ and 0.2 mM PA from 20 to $100 \text{ mV}\cdot\text{s}^{-1}$, while another NCDs/GCE (b) was tested direct using $100 \text{ mV}\cdot\text{s}^{-1}$. The two CV curves have similar profiles. This can be ascribed to the thin NCDs layer that formed on the GCE surface, which avoided a carry-over effect for the NCDs/GCE.

As shown in Fig. 2b, the oxidation of PA is more distinct than the reduction. Therefore, the differential pulse voltammetry (DPV) of the PA oxidation was chosen to illustrate the analytical performance of the NCDs/GCE for PA. The optimization of the DPV parameters is discussed in S1. Figure 4a shows the DPV curves of the NCDs/GCE with different concentrations of PA. The data were recorded at 0.34 V (vs. 3 M Ag/AgCl) and collected for the representative PA concentrations. The current responses increased linearly with the increase in the PA concentration from 0.5 to $600 \text{ }\mu\text{M}$ (inset of Fig. 4a). The linear regression equation was $I_{\text{pa}} = 0.01123C_{(\text{PA concentration, }\mu\text{M})} + 0.93598$. ($R^2 = 0.999$), and the limit of detection was 157 nM based on the National Institute of Standards and Technology report [30]. Several typical electrochemical PA sensors are listed in Table S1 for comparison. The electrocatalytic determination of PA using NCDs/GCE exhibits a competitive performance.

An investigation of the analytical performance of the NCDs/GCE for the electrocatalytic reduction of H_2O_2 was carried out. Figure 4b displays a typical amperometric response curve of the NCDs/GCE with a continuous addition of H_2O_2 at -0.4 V (vs. 3 M Ag/AgCl). Fast amperometric responses were achieved after successive additions of H_2O_2 . The inset of Fig. 4b shows the plot of the current versus the H_2O_2 concentration. An excellent linear relationship was observed for H_2O_2 concentrations between $0.05 \text{ }\mu\text{M}$ and 2.25 mM . The sensitivity of the NCDs/GCE declines when the H_2O_2 concentration is above 2.25 mM . This may be caused by the limitation of the number of electrocatalytic sites for the reaction to occur [31, 32]. The limit of detection was calculated to be 41 nM . The analytical performance of the NCDs/GCE for H_2O_2 detection was compared with that in other reports and is summarized in Table S2. Carbon-based

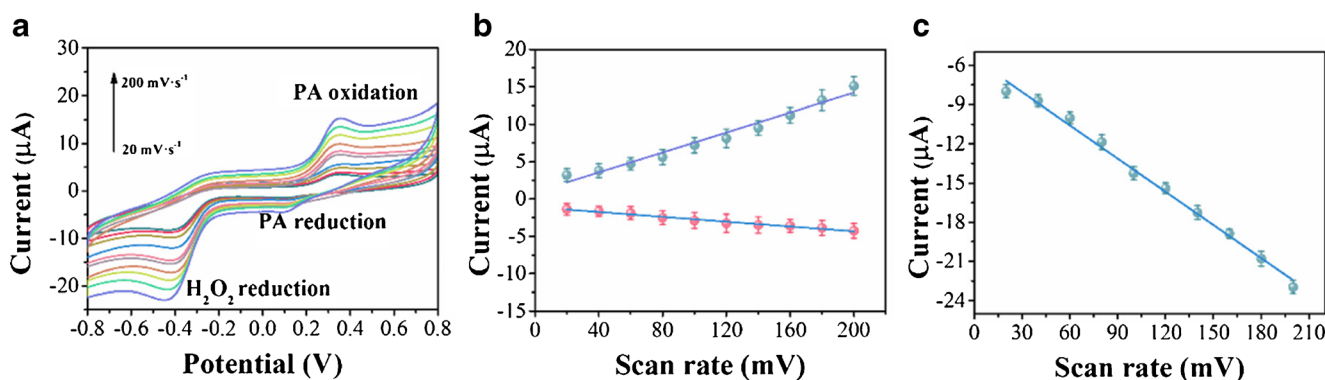


Fig. 3 a CV profiles of the NCD/GCE for $0.4 \text{ mM } \text{H}_2\text{O}_2$ and 0.2 mM PA in 0.1 M PB with a scan rate from 20 to $200 \text{ mV}\cdot\text{s}^{-1}$. b Plots of the PA oxidation and reduction peak currents versus the scan rate. c Plot of the H_2O_2 reduction peak currents versus the scan rate

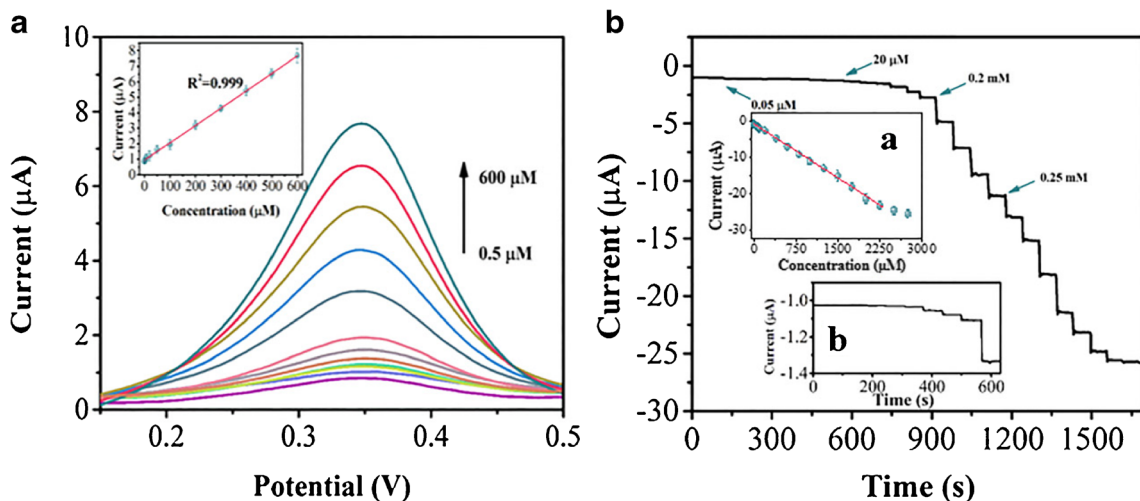


Fig. 4 **a** DPV of NCDs/GCE with 0.5, 1, 2, 4, 8, 20, 50, 100, 200, 300, 400, 500 and 600 μM PA. Amplitude: 30 mV; pulse width: 0.02 s; sampling width: 0.015 s; pulse period: 0.05 s. Inset: Calibration curve of the current response versus the PA concentration. **b** Typical I-T curve of the NCDs/GCE upon successive injection of H_2O_2 (from 0.05 μM to

2.75 mM). Applied potential: -0.4 V (vs. 3 M Ag/AgCl). Inset: (a) Calibration curve of the current response versus the H_2O_2 concentration. (b) I-T curve of the NCD/GCE for H_2O_2 additions in the concentration range from 0.05 μM to 20 μM

materials have been widely used for electrode modification, such as CuO-doped graphene/cerium oxide nanocomposite [33], Mn-Co oxide-decorated graphene [34] and Co_3O_4 NPs/mesoporous carbon nanofibers [35]. The detection limit and linear range of the NCDs/GCE are comparable and even better than those of many of the carbon material-based H_2O_2 electrochemical sensors.

The reproducibility of the NCDs/GCE was tested by six individual dip-fabricated sensors. The relative standard deviations (RSD) of the NCDs/GCE for PA and H_2O_2 determinations were 3.2% and 3.7%, respectively. The operational stability of the NCDs/GCE was studied by ten successive determinations of PA, and the RSD was 3.5%, which suggested the interaction between GCE and the NCDs is strong enough for multiple sensing uses. The long-term stability of the NCDs/GCE was tested once per week for 3 weeks. The current signals for PA and H_2O_2 decreased by 5.7% and 6.2%, respectively.

Avoiding interferences from other common biological species is important for applying an electrochemical sensor in practical applications. The selectivity of the NCDs/GCE was studied for the PA and H_2O_2 determinations in the presence of other electroactive biological species. Figure 5A displays the detection of PA and H_2O_2 in the presence of 20-fold excesses of uric acid (UA), ascorbic acid (AA), glucose and dopamine (DA). The current responses of the PA and H_2O_2 showed negligible changes in the presence of glucose and AA. The 20-fold excesses of UA, DA and AA induced current changes of less than 5%. The effect of some common inorganic ions, such as Na^+ , K^+ , Cl^- , CH_3COO^- and CO_3^{2-} , was investigated. The results are given in Fig. 5b. According to the obtained results, the presence of 20-fold excess concentrations of Na^+ , K^+ , Cl^- and CO_3^{2-} did not significantly interfere with the determination of PA and H_2O_2 . The presence of a 20-fold excess of CH_3COO^- caused an approximately 7% change in the detection current. In addition, the selectivity of the NCD/

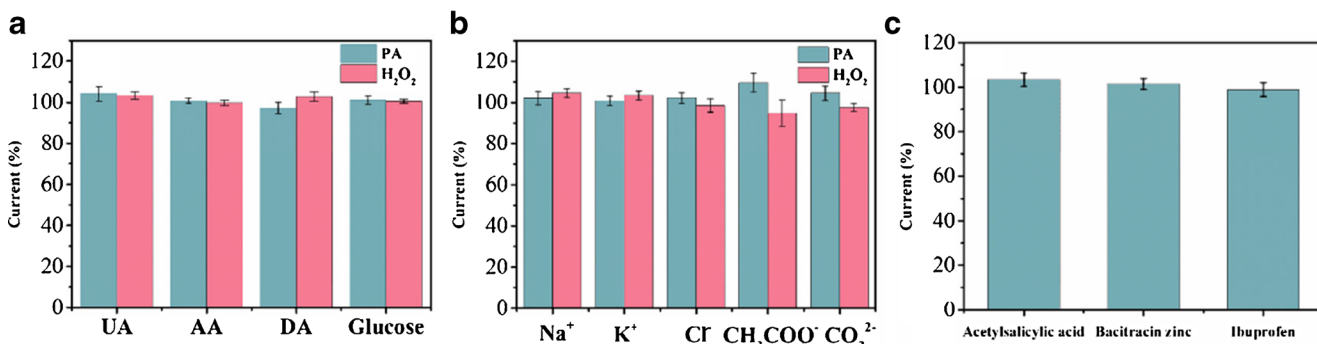


Fig. 5 Relative current changes of the NCDs/GCE for PA and H_2O_2 determination in the presence of (a) UA, AA, DA and glucose; (b) Na^+ , K^+ , Cl^- , CH_3COO^- and CO_3^{2-} . (c) Relative current changes of the NCD/

GCE for PA determination in the presence of acetylsalicylic acid, bacitracin zinc and ibuprofen ($n = 5$)

Table 1 DPV determination of PA in tablet samples ($n = 3$)

Labeled (μM)	Added (μM)	Detected (μM)	Recovery (%)	RSD (%)
0.5	5	5.421	98.56	4.5
1	10	10.458	95.07	2.2
20	100	117.541	97.95	4.9

GCE for PA was further tested in the presence of some ingredients commonly used in paracetamol-based products. As shown in Fig. 5c, the results showed negligible current changes. The DPV and amperometric profiles for the selectivity tests are also shown in Fig. S3 and Fig. S4. Therefore, the NCDs/GCE has a reliable sensing ability for both analytes.

The practical feasibility of using the electrode for the determination of PA in a tablet (Coles Brand) was investigated by a standard addition method. The results are listed in Table 1. The applicability of the NCDs/GCE for 1% and 3% H_2O_2 disinfectant samples was also investigated (Table 2). As shown in the tables, the NCDs/GCE showed good recovery results, which confirmed that the sensor is capable of determining PA and H_2O_2 concentrations in real samples.

Conclusion

A room-temperature method was used to synthesize NCDs. The synthesized NCDs were fabricated on a GCE surface using a direct dipping process. Although the NCDs modification did not improve the electro-conductivity of the GCE, distinct electrocatalytic performances were observed for PA oxidation and H_2O_2 reduction. The superior electrocatalytic activity of the NCDs can be ascribed to their surface functional groups. Moreover, the electrocatalysis process was facilitated by the nitrogen-doping-induced charge delocalization. The electrochemical behavior of the NCDs/GCE was ensured by a careful GCE polishing process and by controlling the NCDs concentration and dipping time. The NCDs/GCE showed a comparable linear detection range and limit of detection for PA and H_2O_2 with an excellent stability and reproducibility. The detection performance of the NCDs/GCE was not affected by most biological species and inorganic ions, except for CH_3COO^- . Moreover, the NCDs/GCE was successfully applied for real sample sensing with good results.

Table 2 Amperometric determination of H_2O_2 in the disinfectant samples ($n = 3$)

Labeled (μM)	Added (μM)	Detected (μM)	Recovery (%)	RSD (%)
882.4	100	978.5	99.60	3.2
294.1	200	499.4	101.07	1.10

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

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