



## Short communication

## Carbon nanotubes/carbon paper composite electrode for sensitive detection of catechol in the presence of hydroquinone

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## ABSTRACT

The fabrication and application of carbon nanotubes/carbon paper (CNTs/CP) composite electrochemical sensors are reported. This sensing platform allows the sensitive determination of catechol in the range of 1  $\mu\text{M}$  to 100  $\mu\text{M}$  with a detection limit of 0.29  $\mu\text{M}$ . The catechol detection in tea samples demonstrates the applicability of this method. The present study explores an interesting and significant application of CNTs/CP composite in electroanalysis.

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## 1. Introduction

Due to their intrinsic physical, chemical, and mechanical properties, carbon nanotubes (CNTs) hold tremendous potential for various applications [1–4], including nanoelectronics, biomedicine, biosensing, energy conversion and storage etc. Recently, direct growth of CNTs onto electrically conductive substrates (e.g. metallic substrates, carbon cloth, and carbon paper (CP)) via chemical vapor deposition (CVD) method have been developed and applied as electrodes for electrocatalysis, supercapacitors, and fuel cells [5–10]. More recently, CNTs paper-based enzymatic bioanodes were facily developed to enhance biofuel cell conversion efficiency [11].

Catechol is a diphenolic compound, which extensively exists in teas, vegetables, fruits, and tobaccos. Catechol is of great biological importance with respect to anti-oxidation, antivirus and enzyme activities; however the excessive intake may cause some health problems [12]. Thus, it is critical to establish effective methods to identify and quantify trace catechol. This can be addressed with the development of simple, sensitive and inexpensive sensors [13–22].

Although CNTs/conductive substrate composites have the advantages of ease of fabrication, low production cost, large electroactive surface area, and excellent electrical conductivity [5–11], the application of CNTs directly grown on conductive substrates for electrochemical sensors has rarely been explored [6]. In this work, CNTs/CP was prepared and subsequently applied to the construction of a voltammetric sensor. The proposed sensor exhibits excellent performance for the detection of

catechol. Therefore the CNTs/CP sensing platform shows great promise in the application of rapid detection of electroactive substrates.

## 2. Experimental

CP was obtained from Zhuzhou Chenxin Induction Equipment Company. Catechol and hydroquinone were purchased from Sigma-Aldrich. Green tea samples were purchased from local market, and catechol in tea was extracted with methanol for 20 min at 80 °C. All other reagents were obtained from Sinopharm Chemical Reagent Co., Ltd.. All reagents were used without further purification.

CVD method was used to prepare the CNTs/CP composite. Typically, a dilution of nickel acetate ethanol solution (10 mM) was spin-coated onto a CP substrate, which was then placed into a tube furnace and annealed at 900 °C for 2 h in argon/hydrogen (95:5). At 900 °C,  $\text{Ni}^{3+}$  was reduced to Ni nanoparticles serving as growth catalysts. Then, hydrogen/acetylene (4:1) was introduced into the chamber; meanwhile the furnace temperature was kept constant to allow the growth of CNTs. CNTs/CP was finally obtained and then tailored to proper size for use.

Electron microscopy experiments were performed on a HITACHI S-4800 SEM and a HITACHI H-7650 TEM, respectively. High-performance liquid chromatography (HPLC) analyses were performed on a Waters 1525 system. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed on a CHI 630E electrochemical workstation with a traditional three-electrode system. Phosphate buffered saline (PBS, pH 7.0) was used in electrochemical sensing tests. Electrochemical impedance spectroscopy (EIS) measurements were conducted on a ZAHNER ZENNIUM electrochemical workstation with a three-electrode system in 5.0 mM  $[\text{Fe}(\text{CN})_6]^{4-/3-}$  solution at

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open circuit voltage and amplitude of 5 mV over a frequency range from 0.01 Hz to 100 kHz.

### 3. Results and discussion

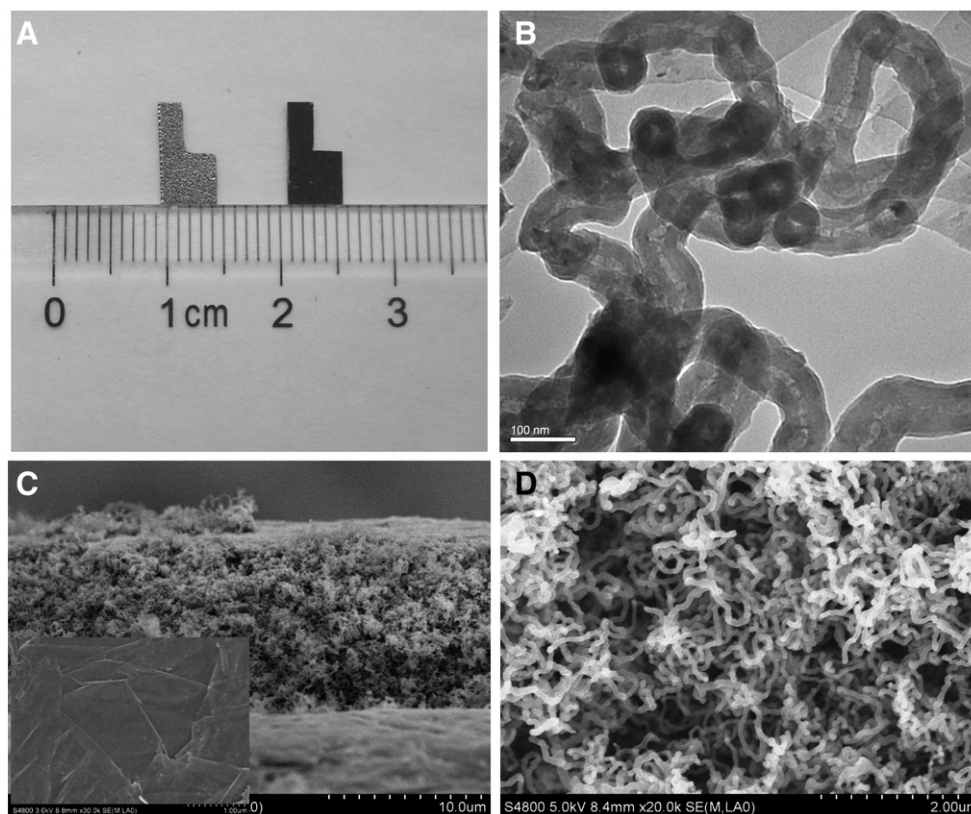
After CVD growth, the surface color of CP changed from gray to black (Fig. 1A), indicating the formation of a carbon layer. The TEM image exhibits a typical structure of multiwalled CNTs (Fig. 1B), confirming the formation of CNTs/CP but not carbon nanofibers/CP. The SEM images show that CNTs directly grown on CP have a smooth structure and form a spaghetti-like network (Fig. 1C, D). The outer diameters of CNTs range from 50 nm to 100 nm; while lengths are larger than 1  $\mu\text{m}$ . Typically the CNTs/CP composite with a  $\sim 10 \mu\text{m}$  thick CNTs layer is adopted for the sensing applications.

EIS was employed to characterize the electrochemical processes of the CNTs/CP electrode (Fig. 2A). The semicircle diameter of CNTs/CP is clearly smaller than that of CP alone, suggesting faster electrochemical reaction kinetics at CNTs/CP. The fitted values of  $R_{ct}$  (the charge transfer resistance) for CNTs/CP and CP are 28.4  $\Omega$  and 142.8  $\Omega$  respectively, providing clear evidence that CNTs/CP has an accelerated electron transfer process.

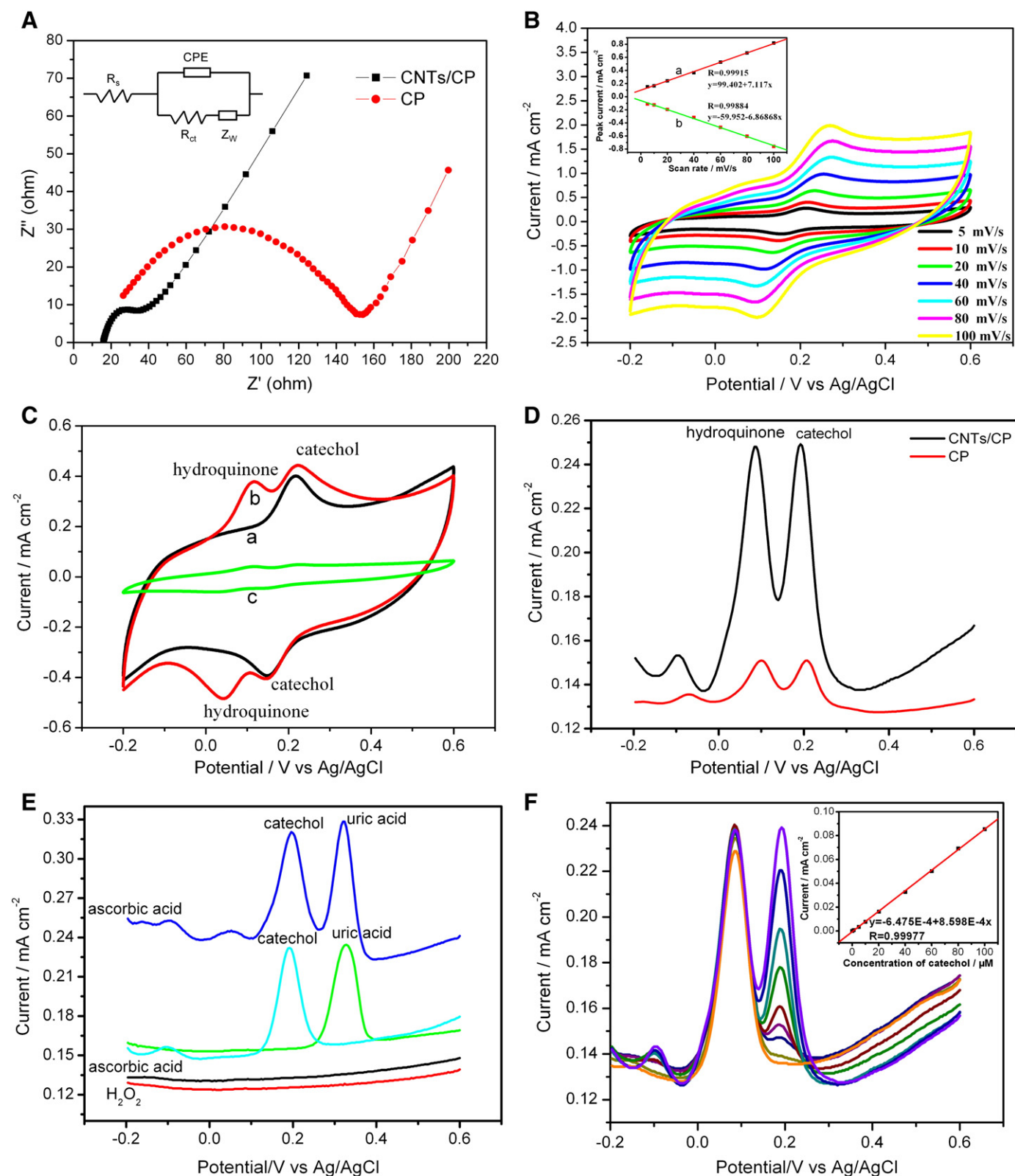
Considering the large electroactive surface area and excellent conductivity of the CNTs/CP composites, it is very interesting to explore their sensing application. CV tests of catechol at CNTs/CP were initially performed. In Fig. 2B, a pair of well-defined redox peaks can be observed at the CNTs/CP electrode at a range of scan rates from 5 to 100 mV/s, which are attributed to the quasi-reversible redox reactions of catechol to 1, 2-benzoquinone [15]. As depicted in the inset of Fig. 2B, peak current is linearly proportional to the scan rate, indicating that the electrochemical reaction of catechol at CNTs/CP is an adsorption-controlled process.

It remains a challenge to electrochemically determinate catechol by avoiding the interference of hydroquinone [13]. The intrinsic structure and property endows the CNTs/CP composite as an alternative to address this challenge. The addition of hydroquinone does not affect the electrochemical behavior of catechol at CNTs/CP (Fig. 2Ca, Cb), and well-defined, separated redox peaks of both catechol and hydroquinone can be observed [16]. The current intensities of catechol and hydroquinone at CNTs/CP are much larger than that at CP (Fig. 2C and D), providing evidence that CNTs/CP has a greater gain in sensitivity against the bare CP. The huge specific surface area of CNTs on CP can further enhance the electrochemical reaction of dihydroxybenzenes, leading to the increased sensitivity [17,19]. The CNTs/CP composite indicates no gain in selectivity against the bare CP, which is reasonable and might be attributed to lamellar structure of the expanded graphite CP we used (the inset of Fig. 1C). The different space resistances to different dihydroxybenzenes and the fast electrochemical reaction kinetics of CNTs/CP are beneficial to the separation of different dihydroxybenzenes. Additionally, the lower electron cloud density of hydroquinone than catechol leads to its lower oxidized potential. Therefore, the voltammetric waves for catechol and hydroquinone can be separated [17,19,22]. It is also worth noting that some other possible interferences including ascorbic acid, uric acid and  $\text{H}_2\text{O}_2$  show no influence on the detection of catechol at CNTs/CP (Fig. 2E), further indicating the good anti-interference ability of CNTs/CP.

Then, as a more sensitive technique than CV, DPV was employed for detecting trace catechol (Fig. 2F). The current density of catechol increases linearly with concentration in the range of 1  $\mu\text{M}$  to 100  $\mu\text{M}$  with a detection limit of 0.29  $\mu\text{M}$  at a signal-to-noise ratio of 3, while the existence of 100  $\mu\text{M}$  hydroquinone did not affect the sensing of catechol. The derived relationship between current intensity and concentration has a correlation coefficient of 0.99977, and a relative standard deviation (RSD) of 3.7% for 10-time tests of 100  $\mu\text{M}$



**Fig. 1.** Photograph (A) of CP (left) and CNTs/CP (right) electrode for electrochemical application, and TEM (B) and SEM (C, D) images of CNTs grown on CP. The inset of C is the SEM image of CP.



**Fig. 2.** (A) Nyquist plots of CNTs/CP and CP. Inset is the used equivalent circuit; (B) CVs of 100  $\mu\text{M}$  catechol at CNTs/CP at varied scan rates, and the inset is the plots of peak current densities versus scan rates; (C) CVs of, a) 100  $\mu\text{M}$  catechol and b) 100  $\mu\text{M}$  catechol + 100  $\mu\text{M}$  hydroquinone at CNTs/CP, and c) 100  $\mu\text{M}$  catechol + 100  $\mu\text{M}$  hydroquinone at CP. Scan rate: 10 mV/s; (D) DPVs of 100  $\mu\text{M}$  catechol + 100  $\mu\text{M}$  hydroquinone at CP and CNTs/CP respectively; (E) DPVs results for the interferents tests, the concentrations of catechol, ascorbic acid, uric acid and  $\text{H}_2\text{O}_2$  are all 100  $\mu\text{M}$ ; (F) DPVs of catechol in varied concentrations at CNTs/CP with the presence of 100  $\mu\text{M}$  hydroquinone, and the inset is the calibration plot.

catechol was obtained, confirming the accuracy and repeatability of the CNTs/CP-based sensing platform. Additionally, 94% of the initial current response is retained after 4 weeks of storage at room

temperature, indicating a good stability of the CNTs/CP-based sensing platform. Comparatively, the bare CP exhibits a linear relationship in the range of 5  $\mu\text{M}$  to 100  $\mu\text{M}$  with a detection limit of 1.52  $\mu\text{M}$  (data

**Table 1**  
Comparison of different electrochemical sensors for the determination of catechol.

| Electrode  | Technique | Detection limit ( $\mu\text{M}$ ) | Linear range ( $\mu\text{M}$ ) | Real sample            | Reference |
|--|-----------|-----------------------------------|--------------------------------|------------------------|-----------|
| GCE/Pt–MnO <sub>2</sub>                            | DPV       | /                                 | 15–447                         | tap water              | [15]      |
| AuNP/TiO <sub>2</sub> /ITO                         | DPV       | 0.05                              | 0.1–500                        | tea                    | [16]      |
| MWCNT/GCE  | DPV       | 0.6                               | 2–100                          | tap water              | [17]      |
| MWNTs/GCE  | DPV       | 0.2                               | 0.6–100                        | tap water              | [18]      |
| AuNPs/MWCNTs/SPE                                   | DPV       | 0.26                              | 2–730                          | tap water, river water | [19]      |
| SiO <sub>2</sub> /C/Nb <sub>2</sub> O <sub>5</sub> | DPV       | 0.8                               | 39.8–1250                      | tap water              | [20]      |
| SWNTs/GCE  | DPV       | 0.26                              | 0.4–10, 40–100                 | sewage                 | [21]      |
| CNTs/CP  | DPV       | 0.29                              | 1–100                          | tea                    | this work |

**Table 2**  
Determination of catechol in tea samples. Samples A–D is traditional green tea named Xihu-Longjing, Laoshan-Green Tea, Huangshan-Maofeng and Biluochun, respectively. Each sample was tested for three times.

| Sample | By HPLC ( $\text{g g}^{-1}$ ) | By this method ( $\text{g g}^{-1}$ ) | RSD (%) |
|--------|-------------------------------|--------------------------------------|---------|
| A      | 0.00893                       | 0.00915                              | 3.2     |
| B      | 0.01273                       | 0.01329                              | 3.2     |
| C      | 0.01282                       | 0.01271                              | 3.4     |
| D      | 0.01073                       | 0.01093                              | 4.5     |

not shown). The detailed features of our method and the comparisons with previous reports are shown in Table 1. Although some sensors show a little better linear range and detection limit [16,19], sophisticated modification processes and noble metal nanoparticles were normally involved. Thus, our simple and inexpensive method is very promising in the determination of trace catechol.

To verify the application feasibility of the CNTs/CP-based sensing platform in real samples, catechol in 4 tea samples were determined by using the calibration curve presented in Fig. 2F. The results by the electrochemical method are well agreement with the HPLC results, and the RSDs are 3.2%–4.5% (Table 2), confirming that the proposed voltammetric sensor is reliable and practical for the simple and rapid determination of catechol in tea samples.

#### 4. Conclusion

In summary, the CNTs/CP composite was prepared and explored as an electrochemical sensing platform towards sensitively detecting catechol,

which shows a wide linear concentration ranges (1–100  $\mu\text{M}$ ), a low detection limit (0.29  $\mu\text{M}$ ), and excellent reproducibility and stability. Considering that the large-scale fabrication of CNTs/CP by CVD method can be easily and inexpensively realized, and the usage of CNTs/CP as sensing platform was straightforward, this novel sensor could potentially be produced as a disposable test strip electrode, which provides a promising alternative for detecting catechol and other electroactive substrates.

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