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# Electrochemical impedance determination of polychlorinated biphenyl using a pyrenecyclodextrin-decorated single-walled carbon nanotube hybrid†

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**This work reports the first detailed study on an electrochemical impedance sensor for determination of polychlorinated biphenyl (PCB), such as 3,3′,4,4′-tetrachlorobiphenyl (PCB-77), based on a single-walled carbon nanotube/pyrenecyclodextrin (SWCNT/PyCD) hybrid.**

Polychlorinated biphenyls (PCBs) are persistent and ubiquitous pollutants existing in the environment. These chemicals enter the environment in various ways, and cause several adverse toxic effects in humans, such as genotoxicity, immunosuppression, tumor promotion and oxidative stress.[1,2] Due to the toxicity of PCBs, it is significant to develop efficient and economical methods to detect and quantify them. The conventional methods for PCBs detection include GC (gas chromatography)/MS (mass spectrometry)[3,4] and LC (liquid chromatography)/MS,[5] phosphorimetry method,[6,7] and chromatographic analysis,[8] *etc.* Although these methods have excellent determination limits and can effectively identify and quantify PCBs, they require sophisticated instruments and are time consuming.

Most recently, a series of excellent results on PCB detection have been obtained by Meng *et al.*[9–12] The authors found that the surface photovoltage of the porous ZnO sensor could be remarkably reduced after PCB-29 and PCB-101 adsorption under visible light illumination.[10] In another work, they found that Ag dendritic nanostructures and Ag-capped Au nanopillar arrays could be used as a surface-enhanced Raman scattering effect substrate for detection of PCB-77 and PCB-20, respectively.[9,11] In the mean time, they found that the membrane of fluorophore phenyl isothiocyanate immobilized porous anodic aluminium oxide exhibits a dynamic fluorescence detection of PCB-101.[12]

Electrochemical methods offer advantages in terms of high sensitivity, easy-use, and low cost and power requirements. In particular, electrochemical impedance spectroscopy (EIS) is a very sensitive technique, and EIS analysis of the system response contains information about the interface, its structure and reactions taking place there.[13–16] However, to the best of our knowledge, studies on direct electrochemical detection of PCBs were not found owing to their insulating properties and hydrophobicity.

The current study presents the first ever electrochemical determination of polychlorinated biphenyl, such as 3,3′,4,4′-tetrachlorobiphenyl (PCB-77), at a single-walled carbon nanotube (SWCNT)/pyrenecyclodextrin (PyCD) modified glassy carbon (GC) electrode using an electrochemical impedance spectrum. Cyclodextrins (CDs) are well-known molecular hosts capable of including small hydrophobic molecules inside their cavities in aqueous media. Furthermore, with the aid of a pyrenyl group, CD could tightly attach to the sidewall of CNTs by means of π–π stacking interactions.[17,18] CNT was chosen here considering that it can enhance the electrode conductivity and facilitate the electron transfer.[19,20] The electrochemical impedance sensing interface is based on PyCD self-assembled onto SWCNT, as illustrated in Fig. S1, ESI.† Characterization of SWCNT/PyCD is performed by SEM (Fig. S2, ESI†), TEM (Fig. S3, ESI†) and FTIR (Fig. S4, ESI†). The determination mechanism mainly involves a change of electrochemical impedance originated from the electron-transfer resistance ($R_{et}$). If guest molecules are captured by the cavities of the PyCD hosts, the formation of guest–host complexes could create a barrier for the electrochemical process, thereby hindering the access of the redox probe ($Fe(CN)_6^{3-/4-}$) to the electrode surface, resulting in an increase in the electron-transfer resistance. The magnitude of the increase in electron-transfer resistance is related to the number of guest molecules captured by the hosts.

Fig. 1a shows representative Nyquist diagrams of the electrochemical impedance spectra of a bare GCE, SWCNT/PyCD

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† Electronic supplementary information (ESI) available: Description of experiments; schematic diagram of the sensing interface; SEM, TEM and FTIR of SWCNT/PyCD; equivalent circuit analysis; optimization of experimental conditions. See DOI: 10.1039/c1cc11267h

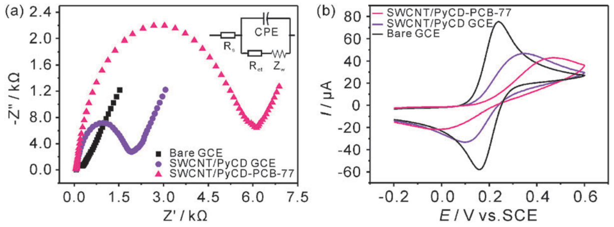

**Fig. 1** Nyquist diagram of electrochemical impedance spectra (a) and cyclic voltammograms (b) of a bare GCE, SWCNT/PyCD GCE and SWCNT/PyCD after preconcentration of 10 μM PCB-77 in the solution of 5 mM $Fe(CN)_6^{3-/4-}$ and 0.1 M KCl. The inset in panel (a) is an equivalent circuit of the SWCNT/PyCD electrochemical impedance measurement system (see ESI† for details). In panel (b), scan rate is 50 mV $s^{-1}$.

GCE and SWCNT/PyCD after preconcentration of 10 μM PCB-77. There is almost a very small semicircle domain of the bare glassy carbon electrode, implying a very low electron-transfer resistance of the redox probe. The slightly bigger $R_{et}$ for the SWCNT/PyCD system indicates that the SWCNT/PyCD hybrids layer obstructed electron-transfer of the electrochemical probe. And it also indicates that SWCNT/PyCD hybrids had been electrically attached to the GCE surface. After preconcentration by PCB-77, the $R_{et}$ increases greatly. This could be explained by the fact that the pyrenecyclodextrin molecules can act as hosts and recognize guest molecules. Ignoring the influence of pyrene units on the volume of cavities of the cyclodextrin, the volume of PyCD's cavities could be thought the same as the cyclodextrin's (262 Å$^3$; the volume of molecules was obtained from ISP sales offices).[21] And when the PCB-77 as hydrophobic guest molecules was included in the cavities of the pyrenecyclodextrin hosts, insulating layer on the modified electrode surface became thicker, which hindered the diffusion of the electrochemical probe toward the electrode surface. Further confirmation that the electron-transfer behaviour is caused by the guest–host complexes can also be found by looking at the cyclic voltammograms of $Fe(CN)_6^{3-/4-}$ (Fig. 1b, see ESI† for details).

Fig. 2a shows the Nyquist diagrams at the SWCNT/PyCD electrode hybridized with different concentrations of PCB-77, ranging from 2.0 to 10 μM. Clearly, as the concentration is increased, the $R_{et}$ increases as well. This could be due to that more PCB-77 molecules were included in the cavities of the pyrenecyclodextrin hosts in higher concentrations, which act as a definite kinetic barrier for the electron-transfer. As shown in Fig. 2b, a linear relation between $\Delta R_{et}$ and the logarithmic value of PCB-77 concentrations was observed in a range from 2 to 10 μM. The linear regression equation is $\Delta R_{et}$ (kΩ) = −1.2 + 5.73 log $C_{PCB}$ (μM) with a correlation coefficient 0.998. The lowest determination limit of PCB-77 concentration was 1 nM. According to the linear equation, we could detect PCB-77 concentration quantitatively. In the equation, $\Delta R_{et}$ is calculated by the following equation:

$$\Delta R_{et} = R_{et}(\text{SWCNT/PyCD-PCB-77}) - R_{et}(\text{SWCNT/PyCD}) \qquad (1)$$

where $R_{et}$(SWCNT/PyCD) and $R_{et}$(SWCNT/PyCD-PCB-77) represent the electron-transfer resistance of SWCNT/PyCD electrode before and after preconcentrated with PCB-77, respectively. As can be seen, $\Delta R_{et}$ increases with increasing PCB-77 concentrations within the determination range. So this SWCNT/PyCD modified electrode could be for the determination of polychlorinated biphenyl by using the EIS technique.

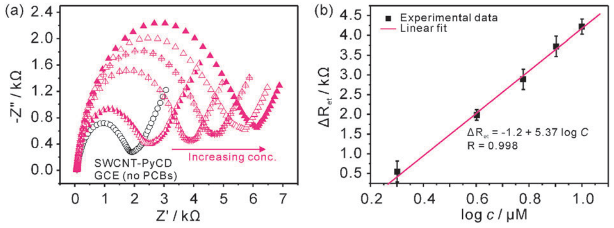

**Fig. 2** (a) Nyquist diagram of electrochemical impedance spectra of a SWCNT/PyCD GCE before and after preconcentration of a range of concentrations (2, 4, 6, 8 and 10 μM) of PCB-77. (b) Plot of $\Delta R_{et}$ as a function of logarithmic value of PCB-77 concentrations shown in panel (a).

Having established that the SWCNT/PyCD network film modified electrode exhibited excellent electrochemical impedance to additions of PCB-77, we attempted to optimize the ratio of SWCNT to PyCD in the film. The optimal composition ratios are listed in Table S1 (see ESI† for details). Several points concerning these results merit some comment. The first thing to notice is that, when the mass of PyCD was fixed, an increase in the value of $R_{et}$ is obtained with the addition of SWCNT, suggesting that the electron-transfer could be blocked by the SWCNT network. However, the largest $\Delta R_{et}$ (3900 Ω) was obtained in the ratio of 1 : 2. On the other hand, although increasing the mass of modified PyCD results in an obvious increase of $R_{et}$, no significant increase in the relative $R_{et}$ response, $\Delta R_{et}$ (1200 Ω), to target guest molecule was found. Therefore, unless otherwise stated, this composition ratio of 1 : 2 (v/v, PyCD/SWCNT) was used throughout. Considering the time consumed and that short time could be used to avoid damaging the electrode surface, an optimized preconcentration time of 3 h was used throughout (Fig. S5, ESI†).

Next we studied the behavior of using single-SWCNT and single-PyCD modified GCE, as shown in Fig. S6, ESI.† It is found that the $R_{et}$ of the single-SWCNT modified electrode remains almost unchanged before and after binding with guest PCB-77 molecules (Fig. S6a, ESI†), suggesting no guest–host complex was formed. In Fig. S6b (ESI†), the PyCD modified electrode reveals a bigger semicircle domain than the SWCNT electrode, implying a very high electron-transfer resistance of the redox probe. After the hybrids were bind with PCB-77, the $R_{et}$ increased by a small margin, showing that fewer guest PCB-77 molecules were included in the cavities of the pyrenecyclodextrin hosts compared with the SWCNT/PyCD electrode. This might tentatively be attributed to reduced PyCD cavities that appeared outside without the support of SWCNT. Together with Fig. S6a (ESI†), these results suggest that the sensing sites of the SWCNT/PyCD electrode are the open cavities of the PyCD. The SWCNT was used as a three-dimensional substrate ensuring that more cavities appeared outside, which will increase the response of the sensors. Finally, considering the CD's water-solubility, the stability of the sensors is greatly improved by the SWCNT support.

Using these optimal conditions, attention now turns to study another important parameter, reproducibility, of the SWCNT/PyCD PCB-77 sensor. Firstly, the reproducibility of three independently fabricated SWCNT/PyCD electrodes shows a satisfactory value of 1.9% (Relative Standard Deviation). And the intraassay precision of the SWCNT/PyCD electrode was evaluated by assaying one PCB-77 level for reduplicate measurements, in which the SWCNT/PyCD electrode can be regenerated by soaking it in an ethanol saturated solution of sodium acetate for 1 h with magnetic stirring after included by PCB. It may be that the self-aggregation behavior of PCB was promoted by sodium acetate. Only 3.2% loss of $\Delta R_{et}$ was found from 10 μM PCB-77 in the intraassay precision measurements (Fig. S7a, ESI†), suggesting satisfactory precision and reproducibility. Furthermore, the $\Delta R_{et}$ towards guest PCB-77 molecules almost remains unchanged despite the modified electrode being stored in air for more than one week. In addition, after continuously scanning for 200 cycles, only 5.74% (at 0.388 V) for the current densities of the peaks in the same potential region was observed. These results provide evidence that the SWCNT/PyCD electrode exhibits a high stability and could be perfectly renewed in sodium acetate solutions. Secondly, for a control, the same intraassay precision measurements were carried out with the SWCNT/CD (without pyrenyl group) electrode. The $R_{et}$ was shown to be significantly reduced by almost 71% after transferring the electrode to an ethanol saturated solution of sodium acetate (Fig. S7b, ESI†), suggesting that without the pyrene units the CWCNT/CD has poor reproducibility, some CD molecules were peeled off with magnetic stirring.

Nine persistent organic pollutants with different sizes, namely, 1,3,5-trichlorobenzene (1,3,5-TCB), 1,2,3,4-tetrachlorobenzene (1,2,3,4-TeCB), dipterex, imidacloprid, acephate, omethoate, acetofenate, fenpropathrin and cypermethrin (the structures are shown in Fig. S8, ESI†), were chosen as suitable guests for interference studies since they are found in many groundwater sources. As shown in Fig. 3, no obvious impedance spectra, $\Delta R_{et}$, were changed for 100 μM 1,3,5-TCB and 1,2,3,4-TeCB, respectively. And for 1 μM dipterex, imidacloprid, acephate, omethoate, fenpropathrin and cypermethrin the deviation of the impedance spectra determination is within 3.5%. The reason may be that 1,3,5-TCB, 1,2,3,4-TeCB, dipterex, imidacloprid, acephate and omethoate are smaller ($<200$ Å$^3$), but fenpropathrin and cypermethrin are bigger ($>300$ Å$^3$) compared with the cavity of PyCD. They do not favor the formation of cyclodextrin complexes, and thus produce similar electron-transfer resistance in respect to the response on the bare SWCNT/PyCD modified electrode. However, acetofenate shows slight interference with the determination of PCB-77, which is due to that acetofenate is comparable to the PCB-77 not only with respect to volume but also with respect to the hydrophobic property.

In summary, we have demonstrated an electrochemical impedance sensor for determination of polychlorinated biphenyl, such as PCB-77, based on the concept of host–guest molecular recognition with an SWCNT/PyCD modified electrode. This system is highly sensitive and selective to PCB-77 without any interference. Also, the SWCNT/PyCD electrode exhibits a high stability and could be perfectly renewed in sodium acetate solutions. The method offers considerable simplicity and economy of determination of polychlorinated biphenyl as compared to the redox reaction-based electrochemical methods.

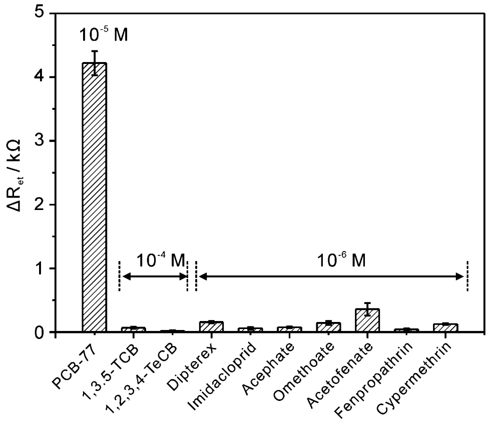

**Fig. 3** Interference studies of a SWCNT/PyCD system. Nine organic compounds were employed as the guests for the sensing test.

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## Notes and references

1 M. Machala, L. Blaha, H. J. Lehmler, M. Pliskova, Z. Majkova, P. Kapplova, I. Sovadinova, J. Vondracek, T. Malmberg and L. W. Robertson, *Chem. Res. Toxicol.*, 2004, **17**, 340.
2 J. Matthews and T. Zacharewski, *Toxicol. Sci.*, 2000, **53**, 326.
3 S. Ozcan, A. Tor and M. E. Aydin, *Anal. Chim. Acta*, 2009, **647**, 182.
4 D. A. Lambropoulou, I. K. Konstantinou and T. A. Albanis, *J. Chromatogr., A*, 2006, **1124**, 97.
5 J. F. Focant, J. W. Cochran, J. M. D. Dimandja, E. DePauw, A. Sjodin, W. E. Turner and D. G. Patterson, *Analyst*, 2004, **129**, 331.
6 R. Belfatmi, M. Lamotte, S. Ait-Lyazidi and P. F. de Violet, *Chemosphere*, 2005, **61**, 761.
7 A. F. Arruda, H. C. Goicoechea, M. Santos, A. D. Campiglia and A. C. Olivieri, *Environ. Sci. Technol.*, 2003, **37**, 1385.
8 V. Schurig and S. Reich, *Chirality*, 1998, **10**, 316.
9 Z. L. Huang, G. W. Meng, Q. Huang, Y. J. Yang, C. H. Zhu and C. L. Tang, *Adv. Mater.*, 2010, **22**, 4136.
10 M. T. Li, G. W. Meng, Q. Huang, Z. J. Yin, M. Z. Wu, Z. Zhang and M. G. Kong, *Langmuir*, 2010, **26**, 13703–13706.
11 Y. J. Yang and G. W. Meng, *J. Appl. Phys.*, 2010, **107**, 044315.
12 M. L. Wang, G. W. Meng, Q. Huang, M. T. Li, Z. B. Li and C. L. Tang, *Analyst*, 2011, **136**, 278.
13 X. J. Chen, Y. Y. Wang, J. J. Zhou, W. Yan, X. H. Li and J. J. Zhu, *Anal. Chem.*, 2008, **80**, 2133.
14 C. M. Ruan, L. J. Yang and Y. B. Li, *Anal. Chem.*, 2002, **74**, 4814.
15 L. J. Yang, Y. B. Li and G. F. Erf, *Anal. Chem.*, 2004, **76**, 1107.
16 H. R. Gu, X. D. Su and K. P. Loh, *J. Phys. Chem. B*, 2005, **109**, 13611.
17 Y. L. Zhao, L. B. Hu, J. F. Stoddart and G. Gruner, *Adv. Mater.*, 2008, **20**, 1910.
18 R. J. Chen, Y. G. Zhang, D. W. Wang and H. J. Dai, *J. Am. Chem. Soc.*, 2001, **123**, 3838.
19 H. Khani, M. K. Rofouei, P. Arab, V. K. Gupta and Z. Vafaei, *J. Hazard. Mater.*, 2010, **183**, 402.
20 R. N. Goyal, V. K. Gupta and S. Chatterjee, *Sens. Actuators, B*, 2010, **149**, 252.
21 CAVAMAX Native Cyclodextrins. http://isppharmaceuticals.com/.