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ARTICLE TYPE

p-Aminophenol sensor based on tetra-*β*-[3-(dimethylamine)phenoxy] phthalocyanine cobalt(II)/multiwalled carbon nanotube hybrid

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A high efficient catalyst is a key challenge for the development of electrochemical sensor for *p*-aminophenol (4-AP), which widely exists in environment. In this paper, we describe a feasible synthesis for the hybrid of tetra-*β*-[3-(dimethylamine)phenoxy] phthalocyanine cobalt(II) (aPcCo) and acid-treated multiwalled carbon nanotube (CNT) by strong π-π stacking interaction. The combination of aPcCo and CNT can improve the conductivity of aPcCo and the dispersion of CNT simultaneously, which benefit to form uniform electrodes, provide the unimpeded pathways for matter diffusion, as well as accelerate the charge-transfer kinetics. As a result, the obtained aPcCo/CNT hybrid can serve as an efficient electrochemical catalyst for 4-AP oxidation and sensitive detection. The oxidation current of 4-AP is linear to its concentration from 0.5 μM to 300 μM, 300 μM to 800 μM. The detection limit is as low as 0.3 μM (S/N = 3). This development offers an attractive catalyst material for electrochemical sensor.

1. Introduction

p-Aminophenol (4-AP) is important environmentally because it is commonly used as industrial raw or processed materials in cosmetics, photography and dyes. 4-AP is also widely used in the pharmaceutical industry for the production of paracetamol and clofibrate,[1-2] but it is high toxicity. The maximum content of 4-AP in pharmaceuticals is limited to 50 ppm (0.005%, w/w) by the standard of European, United States, and Chinese Pharmacopoeias.[3-5] So the quick and convenient detection of 4-AP is often a necessity.

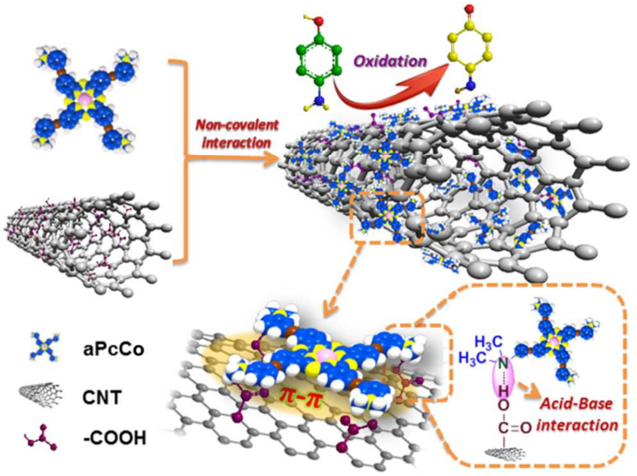
Many attempts, therefore, have been made to develop an efficient and selective way of determining 4-AP, such as liquid chromatography,[6] spectrophotometry,[7] sequential injection analysis,[8] capillary electrophoresis,[9] surface enhanced Raman scattering,[10] micellar electrokinetic chromatography.[11] However, these techniques are expensive, or complicated step, or require time consuming, and even low sensitivity and selectivity in some case, making them unsuitable for a routine detection. In contrast, electrochemical technique, with low cost, simplicity, and high selectivity and sensitivity, is a desired method for 4-AP detection. Commonly, bare electrode often suffers from a fouling effect, which causes rather poor selectivity and sensitivity. An effective way to overcome this abuse is electrode modification, which is capable of reducing the overvoltage and improving the slow kinetics processes.

Phthalocyanine (Pc) complexes, as tetrapyrrole derivatives, have attracted great research interest in photodynamic therapy,[12] microbial fuel cells,[13] nonlinear optical materials,[14] gas sensors,[15] and especially electrochemical sensors,[16-19] because of their large conjugated electronic molecular structures and diversiform central metal ions. However, as far as electrochemical sensors, the pristine Pcs are difficult to attain the satisfactory results. This mainly attributed to their insolubility in water or lower solubility in organic solvent, and poor conductivity. The poor solubility is not conducive to fabricate the uniform electrodes. To improve it, Pc complexes are generally modified by introducing solubility-enhancing substituents at the peripheral of Pc ring and good choice of the right metal ion centre for improving Pc complexes water soluble.[20-23] In addition, in term of the intrinsic characteristic-poor conductivity, the most effective solution is to introduce the conductive agent.[24] Thus, it may easily be conceived, that, if we could design a novel hybrid to overcome these problems synchronously, it could provide good opportunities for the development of electrochemical sensors.

As the conductive agent, carbon nanotubes (CNTs) are receiving much concern, owing to the large specific surface area, high mechanical strength, excellent conductivity and low production cost.[25-27] In particular, its one-dimensional (1D) structure, helical tube of graphitic-carbon sheets, can be employed for the directional transmission electrons, and accelerate of the charge-transfer kinetics.[28] However, the intrinsic Van der Waals interactions between the pristine tubes make CNTs insoluble in routine solvents,[29] thereby reducing the available active sites for electrocatalysis. Recent studies present evidences that Pc complexes modified CNTs show great performance for the determining of ascorbic acid,[22, 30] nitrite,[16] thiocholine,[31] and hydrazine.[32] Evidently, the combination of

Pc complexes and CNTs could cover each other's shortages.

Based on the above design, we synthesized tetra-β-[3-(dimethylamine)phenoxy] phthalocyanine cobalt(II)/multiwalled carbon nanotube hybrid (aPcCo/CNT) by π-π non-covalent interaction (as shown in Scheme 1). Besides π-π force, there is a weak acid-base interaction between aPcCo (base) and acid-treated CNTs (acid).[33, 34] The N, N-dimethylaminephenoxyl group of aPcCo could enhance the dispersion of hybrid, and benefit forming uniform 3D-network electrodes, providing the unimpeded pathways for matter diffusion.[30] Meanwhile, the electrocatalytic current could quick transfer from aPcCo to CNTs via π-π interaction, and the latter promote the orientation transmission of electrons.[22, 16] Thus, the high catalytic activity of aPcCo/CNT hybrid for 4-AP come true through this strategy.



Scheme 1 Schematic illustration of the synthesis procedure for aPcCo/CNT hybrid and its electrocatalytic mechanism.

2. Experimental

2.1. Reagents

Multi-walled carbon nanotubes (MWCNTs, purity > 95%) were purchased from Shenzhen Nanotech Port Co. Ltd. To functionalize them with carboxylic acid, they were chemically oxidized with strong oxidizing with H_2SO_4/HNO_3 mixture (3:1 v/v ratio) for 8 h. After that, the resulting dispersion was diluted in water and filtered. MWCNTs were stirred in the mixture of H_2SO_4 (98 wt%) and H_2O_2 (30 wt%) in ratio 4:1 v/v for 1 h at 70 ^{o}C. The acid-treated MWCNT (CNT) was washed up to neutral pH and the sample was dried in vacuum at 50 ^{o}C overnight. Tetra-β-[3-(dimethylamine)phenoxy] phthalocyanine cobalt (II) was synthesized by template-reaction method at the present of 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) (see details in SI). 4-nitrophthalonitrile (99% purity), DBU (98% purity), and Nafion (5 wt% in low aliphatic alcohols and water) were purchased from Sigma-Aldrich Co. LLC. 3-dimethylaminophenol (97% purity) was purchased from Acros Organics. 0.1 mol L^{-1} phosphate buffer solutions (PBS) of different pH values were prepared from stock solutions of 0.1 mol L^{-1} NaH_2PO_4 and Na_2HPO_4. Milli-Q ultrapure water was used throughout the experiments. All other chemicals were of analytical grade or better quality and used without any further purification.

2.2. Preparation of aPcCo/CNT hybrid

The aPcCo/CNT hybrid in dry DMF was synthesized through the π-π stacking interaction between aPcCo and CNT. Briefly, 10 mg of CNT were added into 5 mL of DMF containing 30 mg of aPcCo by successive ultrasonic for 48 hours. The resultant solution was filtered through a 0.22 μm PTFE-membrane filter. The filter cake was washed with ethanol and tetrahydrofuran, after which the filtrate became colourless, and then dried in a vacuum oven for 3 h at 60 ℃, affording the desired aPcCo/CNT hybrid as black powders.

2.3. Preparation of aPcCo/CNT Modified Glassy Carbon (aPcCo/CNT/GC) Electrode

The glassy carbon electrode (diameter: 3mm) was carefully polished by 1 μm, 0.3 μm, and 0.05 μm alumina, followed by successive sonicate with distilled water and ethanol for 3 min until a mirror like surface was obtained. Then, 5 μL aPcCo/CNT hybrid suspension (1.0 mg mL^{-1}), which was prepared by dispersing aPcCo/CNT in anhydrous ethanol/Nafion mixture with the aid of ultrasonic, was dropped on the clean surface of GC electrode. The solvent was evaporated under an infrared lamp, denoted as aPcCo/CNT/GC electrode. For comparison, the aPcCo/GC and CNT/GC electrodes were also fabricated by the similar procedures.

2.4. Apparatus

UV-vis absorption spectra were recorded with a Lambda 35 UV/VIS spectrometer (Perkin-Elmer, USA). FT-IR spectra were recorded on a Nicolet FT-IR NEXUS spectrometer (Thermo Scientific). Scanning electron microscopy (SEM) images were recorded with a Hitachi S-4800 field emission scanning electron microscope operating at 15 kV. Transmission electron microscopy (TEM) images were performed on a JEM-3010 electron microscope (JEOL, Japan) with an acceleration voltage of 300 kV. X-ray photoelectron spectroscopy (XPS) measures were performed with AXIS UL TRA DLD. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis was carried out by Optima 7000 DV (Perkin-Elmer, USA). The Raman spectra were acquired using a Raman spectrophotometer (HR800, HORIBA Jobin Yvon Company) excited by a laser with 457.9 nm wavelength. Samples for ICP-AES were prepared by ashing 0.0050 g of sample in quartz test-tubes at 800 ^{o}C for 30 min, and then leached out with concentrated acids (HCl:HNO_3 in 3:1 v/v ratio) and volume to 5 mL. Electrochemical measurements were performed on a computer-controlled CHI 660D electrochemical workstation (CH Instrument, Shanghai, China). All the electrochemical measurements were carried out in 0.1 M PBS at room temperature (25 ± 2 ^{o}C) using a conventional three-electrode system with a modified glassy carbon electrode as a working electrode, a platinum foil as an auxiliary electrode, and a saturated calomel electrode (SCE) as a reference electrode. All potentials in this study were reported with respect to SCE. The electrolyte was purged with high purity nitrogen for at least 10 min prior to measurements to remove the dissolved oxygen unless otherwise stated.

3. Results and discussion

3.1. Characterization of aPcCo/CNT hybrid

The as-synthesized aPcCo/CNT hybrid was first examined by electronic absorption spectra, and the compare UV-vis spectra of the aPcCo/CNT, aPcCo and CNT in DMF are shown in Fig. 1A. Two strong absorption peaks, one in UV region at about 327 nm (B-band) and the other in the visible region at 666 nm (Q-band), can be observed in the UV-vis spectrum of pristine aPcCo, indicating that aPcCo is non-aggregated in DMF solution.[35] Meanwhile, it is evident that the characteristic Q-band peak of aPcCo also appears in UV-vis spectrum of aPcCo/CNT hybrid, which occurs slightly red shift relative to that of pristine aPcCo (681 vs 666 nm). The red shift could be attributed to the electron transfer from the phthalocyanine ring to CNT by the strong π-π interaction, which could expand the macrocyclic conjugated structure of aPcCo.[36-38]

Fig. 1B shows the FT-IR spectra of aPcCo/CNT, aPcCo and CNT, respectively. For CNT, the bands at 1718 cm^{-1} and 3431 cm^{-1} are assigned to (υ C=O) and (υ O-H),[39, 40] respectively, implying the existence of large numbers of carboxyl groups, which is further identified by the peaks in the range 1000-1300 cm^{-1} attributed the composite of (υ C-C).[41] In the FT-IR spectrum of aPcCo, the peaks at 1266 cm^{-1} (Ar-O-Ar stretching vibration), 1472 cm^{-1} (υ C-N), 1572 (υ C=C) cm^{-1}, 1605 cm^{-1} (υ C=N), 1720 cm^{-1} (υ C=O), 2927 cm^{-1} (υ_{as} C-H) and 2953 cm^{-1} (υ_{as} CH_3) are the characteristic peaks of pristine aPcCo.[35, 42, 43] These peaks also present the spectrum of aPcCo/CNT, except the slight blue shift due to the electron delocalization of π-π interactions, which is consistent with the result of UV-vis spectra.[15, 22]

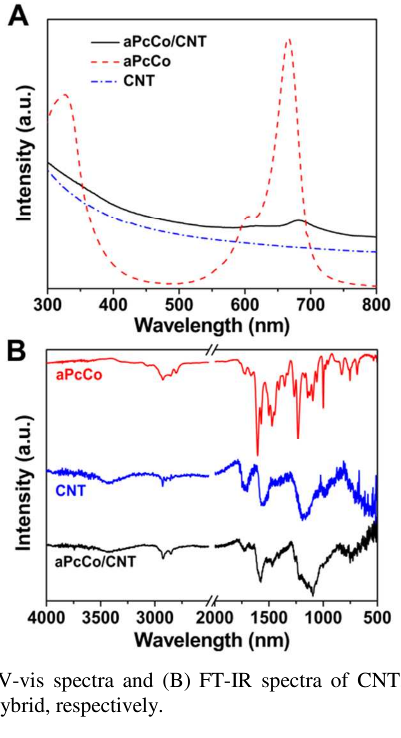


Fig. 1 (A) UV-vis spectra and (B) FT-IR spectra of CNT, aPcCo, and aPcCo/CNT hybrid, respectively.

To further gain insight about the interaction between aPcCo and CNT, Raman spectra of aPcCo/CNT hybrid and CNT were recorded as shown in Fig. 2. The Raman spectra of CNT and aPcCo/CNT hybrid display two apparent bands, 1347.4 cm^{-1} (D band) and 1558.8 cm^{-1} (G band). D band (disordered band) is the breathing mode of sp^3 rings that is related to bond-angle disorder, bond-length disorder, and hybridization.[44, 45] G band is related to the in-plane bond-stretching motion of pairs of sp^2 carbon atoms from the graphitized structure.[46] It is worth noting that, the I_D/I_G value of aPcCo/CNT hybrid is very close to that of CNT (0.52 vs 0.55). The result confirms that the main interaction between CNT and aPcCo is π-π non-covalent, and the modification of CNT with aPcCo does not destroy the surface structure of CNT.[16]

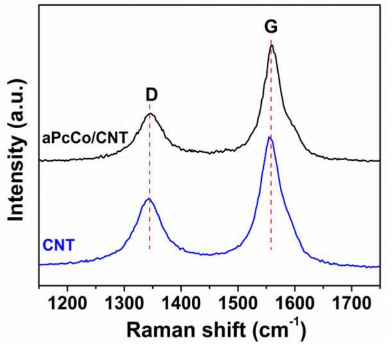


Fig. 2 Raman spectra of aPcCo/CNT hybrid and CNT.

XPS is performed to confirm the surface chemical compositions, chemical state and electronic state of the elements existed in aPcCo/CNT hybrid. As shown in Fig. 3A, only C 1s peak (at 284.60 eV) and O *1s* peak (532.70 eV) present in the XPS spectrum of CNT; whereas two new peaks, N *1s* and Co *2p*, appear in that of aPcCo/CNT hybrid, implying that aPcCo succeeds in anchoring onto the surface of aMWCNT by π-π and acid-base interactions.[22] The Co *2p* peaks of as-obtained aPcCo/CNT could be fitted to four contributors: two strong peaks correspond to $2P_{3/2}$ (780.3 eV) and $2P_{1/2}$ (795.5 eV), respectively accompanied by two relatively weaker satellite features (Fig. 3B). It is the chemical nature of Co^{2+}, which is the mainly valence state in electrchemical catalysis.[18, 47, 48]

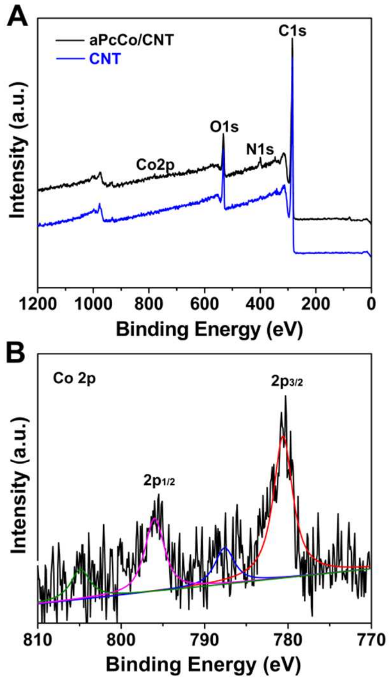


Fig. 3 (A) XPS spectra of aPcCo/CNT hybrid and CNT; (B) the high–resolution Co *2p* XPS spectrum of aPcCo/CNT hybrid.

The surface morphology and structure of the synthesized aPcCo/CNT hybrid was investigated by SEM and TEM. As shown in Fig. 4A and B, the three-dimensional network-like structure of aPcCo/CNT hybrid is more uniform and looser as compared to CNT, corresponding to its good dispersion, which is mainly attributed to the modification of CNT by aPcCo. The obtained loose and interconnected structure, formed by aPcCo/CNT hybrid, simultaneously offers the larger surface area and more active sites for electrocatalysis, the directional confinement for rapid electronic transmission, and the unimpeded pathways for matter diffusion, which is reckoned to be an excellent electrocatalyst.[37, 49, 50] Fig. 4(C-E) shows the typical TEM images of aPcCo/CNT hybrid. CNT presents multiwall structure, and the diameter is in the range 10 to 20 nm. Besides the distinct core and walls of carbon nanotube, the surface of CNT is covered by discontinuous amorphous carbon, further indicating that the combination of aPcCo and CNT via π-π and acid-base interactions. The amount of aPcCo assembled on the surface of CNT is about 6.48 wt% determined by ICP-AES.

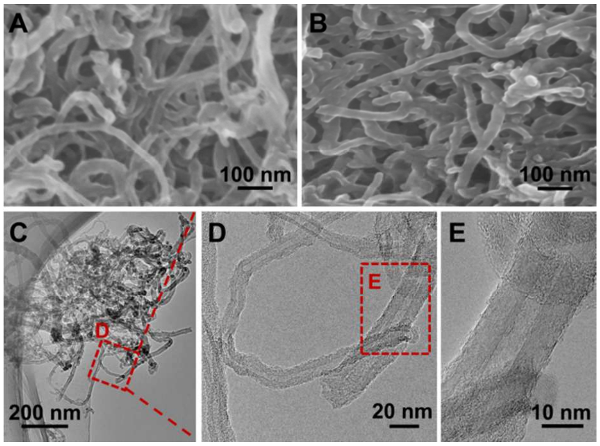
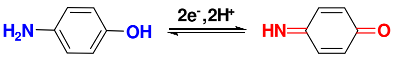


Fig. 4 (A and B) SEM images of CNT and aPcCo/CNT hybrid, respectively; (C-E) TEM images of aPcCo/CNT hybrid.

3.2. Electrocatalytic activity of aPcCo/CNT hybrid to 4-AP

The electrocatalytic activity of aPcCo/CNT/GC electrode towards 4-AP was investigated by cyclic voltammetry (CV) in 0.10 M PBS solution as the supporting electrolyte at pH 5.8. Fig. 5 shows the typical CVs of aPcCo/CNT/GC, CNT/GC, aPcCo/GC, and bare GC electrodes in PBS solution with 50 μM 4-AP at a scan rate of 50 mV s^{-1}. It appears that all electrodes present electrochemical response towards 4-AP, with an anodic peak potential (E_{pa}) of ~ 0.2 V and cathodic peak potential (E_{pc}) of ~ 0.11 V versus SCE, indicating that 4-AP shows quasi-reversible behaviour. In contrast to bare GC, aPcCo/GC, and CNT/GC electrodes, for which the redox peaks ascribed to 4-AP at around 0.2 V are weak, aPcCo/CNT/GC electrode generates an obvious couple of high redox peaks. These mean that the synergic effect between aPcCo and CNT can enhance the electrochemical performance. One hand, compared with CNT, aPcCo on the surface of aPcCo/CNT hybrid offers more efficient interfacial active sites for electrocatalysis. On the other hand, the reaction charge could be quickly transferred to CNT via π-π interaction, and 1D CNT further promotes the orientation transmission of electrons.[16, 30] According to previous reports,[51, 52] the electrocatalytic oxidation of 4-AP on aPcCo/CNT/GC electrode should undergo the following reaction:



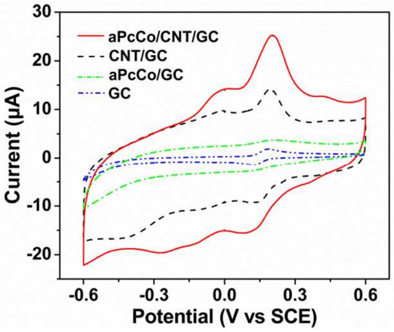


Fig. 5 CVs of aPcCo/CNT/GC, CNT/GC, aPcCo/GC and GC electrodes in 0.1 M PBS (pH = 5.8) solution with 50 μM 4-AP, scan rate: 50 mV · s^{-1}.

Apparently, the electrochemical oxidation of 4-AP is relevant to pH value. To highlight the effect of hydrogen ion concentration on the electrocatalytic activity of 4-AP, CVs at different pH were carried out (Fig. 6). It is obvious that the redox current and potential of 4-AP are sensitive to pH value. With increasing pH from 4.4 to 8.0, the redox current of 4-AP increases maximum, and then decreases. Meanwhile, the redox potential is also negatively shifted, and the linear relationship with the redox process signifies that protons and electron are involved in redox (Fig. 6B and Fig. S2). According to $dE_p/dpH = 2.303\ mRT/nF$, in which F is faraday constant, R is gas constant, m is the number of proton, n is the number of electron,[53] the m/n value of the oxidation process is 1.01 and the reduction process is 1.19, indicating that the number of proton and electron involved in the electrochemical redox process of 4-AP are equal. Taking into account the detection sensitivity, PBS solution at pH 5.8 is selected as the supporting electrolyte solution.

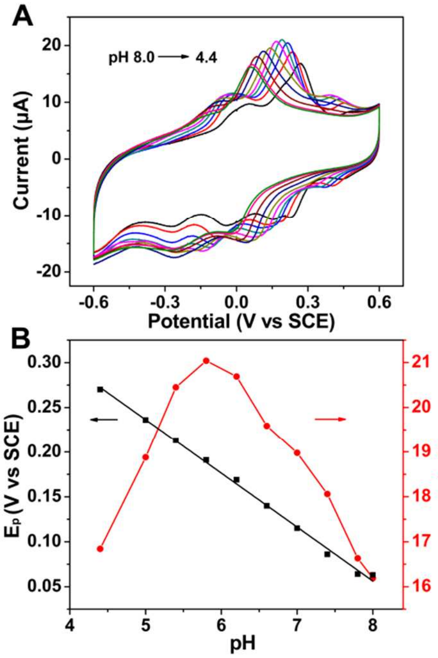


Fig. 6 (A) CVs of aPcCo/CNT/GC electrode in 0.1 M PBS with 50 μM 4-AP at different pH value, scan rate: 50 mV · s^{-1}. (B) The relation between the oxidation peak potentials (black line) and currents (red line) and the pH value, and the linear regression equation is E_{pa} (V) = 0.5366-0.0601× pH (R^2=0.9971), E_{pa} is anodic peak potential.

In order to explore the reaction kinetics of 4-AP oxidation, the CVs of the aPcCo/CNT/GC electrode at different scan rates were investigated. As shown in Fig. 7, both of the redox peak currents increase linearly as the scan rate increases from 10 to 100 mV·s^{-1}, and the linear regression equation is I_{pa} (μA) = 2.5213 + 0.4128 × V (R^2 = 0.9978) and I_{pc} (μA) = -1.9815 - 0.2461 × V (R^2 = 0.9974), respectively. I_{pa}, I_{pc}, and V are anodic, cathodic peak current and scan rate, respectively. It suggests that it is a adsorption-controlled electrochemical process,[52 ,54, 55] which is also consistent with the fast charge propagation in the aPcCo/CNT/GC electrode. CNT seems to support the charge transport within the hybrid. In other words, the unimpeded distribution of charge to 3D matrix is feasible.

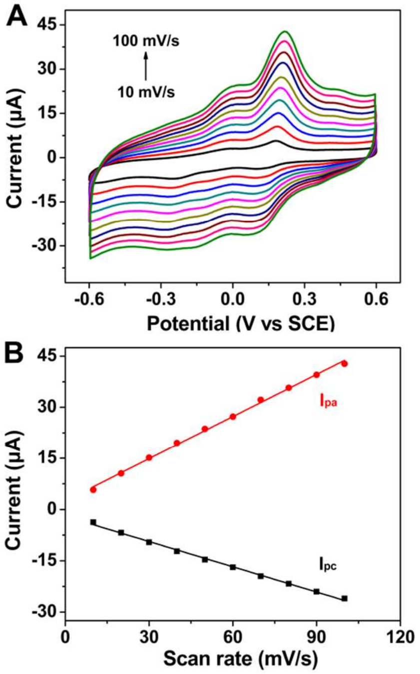


Fig. 7 (A) CVs of aPcCo/CNT/GC electrode in 0.10 M PBS (pH = 5.8) solution with 50 μM 4-AP measured at different scan rates (10 ~ 100 mV·s^{-1}). (B) The calibration plots between the anodic (red line) and cathodic (black line) peak currents and the scan rate.

To evaluate the sensitivity towards 4-AP, a series of differential pulse voltammograms (DPVs) were recorded on aPcCo/CNT/GC electrode with various concentrations of 4-AP. With the increase of 4-AP concentration, the oxidation current at 0.09 V increases (Fig. 8). The increases of the DPV peak currents are proportional to the species concentrations, and the two linear regression equations for 4-AP are expressed as: I (μA) = 0.0579 (μA $μM^{-1}$)×C (μM) + 4.5838 (0.5-300 μM, R^2 = 0.9876), I (μA) = 0.0240 (μA $μM^{-1}$)×C (μM) + 14.325 (300-800 μM, R^2 = 0.9849). The 4-AP sensor has a detection limit as low as 0.3 μM (S/N = 3), derived from the calibration curve. All of the parameters indicate that aPcCo/CNT/GC electrode is very effective as a sensor for determining 4-AP with high activity, which greatly exceeds the linear range of most previously reported 4-AP detection (Table S1).

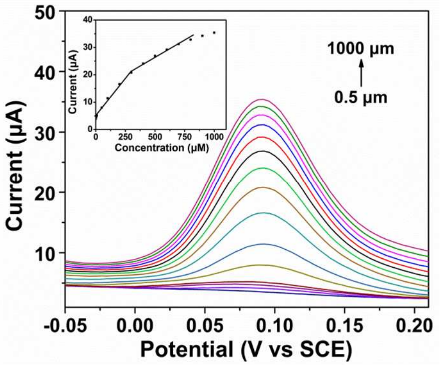


Fig. 8 DPVs response for the different concentrations of 4-AP at aPcCo/CNT/GC electrode in 0.1 M PBS (pH = 5.8) (from bottom to up: 0.5, 1, 5, 10, 50, 100, 200, 300, 400, 500, 600, 700, 800, 900, and 1000 μM, respectively). The inset is the calibration linear relationship of currents *versus* 4-AP concentration.

The stability and repeatability of aPcCo/CNT/GC electrode have also been evaluated by CV measured at different cycle numbers. As shown in Fig. 9A, the current response at the hundredth cycle is almost the same as that at the first cycle. Moreover, the long-term storage stability of aPcCo/CNT/GC electrode was also been evaluated by measuring the electrode responses at intervals of several days. The oxidation peak current slightly decreases after 30 days stored in PBS (pH 5.8) at 4 ℃, and about 91.55% initial current response retains (Fig. 9B). Such high stability and accuracy of aPcCo/CNT/GC electrode is acceptable for most practical applications.

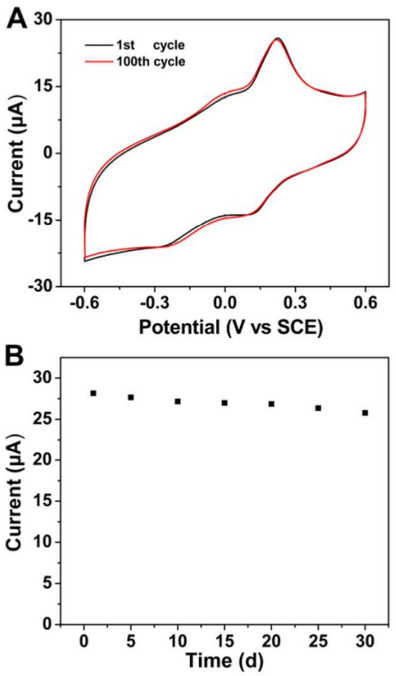


Fig. 9 (A) CVs of aPcCo/CNT/GC electrode in 0.10 M PBS (pH = 5.8) solution with 50 μM 4-AP obtained at the first cycle and hundredth cycle, respectively. (B) Stability experiment of aPcCo/GC electrode to detect 4-AP for 30 days.

In addition, sensitivity and selectivity is also another key property for a sensor, especially in the practical application. The low response potential also indicates that aPcCo/CNT hybrid possess excellent selectivity for 4-AP.[56] As expected, in I–t curve as shown in Fig. 10, the successive addition of interferents in the order 250 μM of paracetamol, KCl, $NaNO_2$, catechol, glucose, anilofos, resorcinol and $MgSO_4$ to a PBS (pH 5.8) solution containing 50 μM of 4-AP gives rise to a negligible current response, while a significant current response is observed after the subsequent addition of 50 μM of 4-AP. The response time was less than 3.2 s, revealing the rapid response of the modified electrode toward 4-AP. Such a fast response may be contributed to the rapid adsorption and activation of 4-AP on the surface of aPcCo/CNT hybrid, and the continuous conducting pathways of electron. Compare the response current of 4-AP after adding interferents with that in the absence of interferents, it is clear that the interferents had no impact on the 4-AP detection performance.

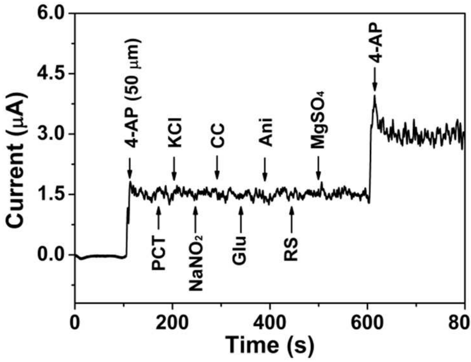


Fig. 10 Amperometric response to the addition of different analytes to 50 mL of 0.10 M PBS (pH = 5.8), PCT = paracetamol, CC = catechol, Glu = glucose, Ani = anilofos, Rs = resorcinol.

In order to verify the performance and feasibility of the proposed method for analysis of 4-AP in environmental samples, the aPcCo/CNT/GC electrode was applied to the determination of 4-AP in tap water. The sample was mixed with PBS (0.1 M, pH 5.8) for 4-AP determination, and the results are summarized in Table S2. A good recovery, between 94 % and 108 %, suggests the practical applicability of the proposed method. Therefore, the proposed method could be effectively used for determination of 4-AP in real samples.

4. Conclusions

In summary, we demonstrated the synthesis of aPcCo/CNT hybrid by the facile π-π stacking interaction. Superior performance of the aPcCo/CNT hybrid was observed in determining 4-AP in comparison pristine aPcCo and CNT. The enhanced effectiveness was ascribed to the interconnected 3D-network structure, and the synergistic effect of aPcCo and CNT, in favour of the large accessible surface area, more active sites and the orientation transmission of electrons, as well as the unimpeded pathways for matter diffusion. 4-AP sensors such as the ones described herein offer tremendous potential for the application in environmental monitoring.

Acknowledgments

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Notes

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