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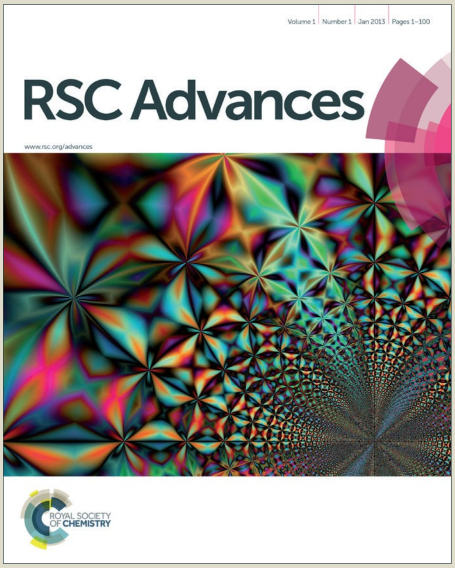

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Copper Phthalocyanine modified SiO_2/C electrode as a Biomimetic Electrocatalyst for 4-amionophenol in the Development of an Amperometric Sensor

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Abstract

A selective, simple, and low cost method for 4-aminophenol (4-APh) determination was developed using the mesoporous carbon ceramic SiO_2/50 wt% C (S_{BET} = 170 m^2 g^{-1}), composite was prepared by the sol‑gel method. The material was fabricated to use as matrix to support copper phthalocyanine (CuPc), prepared *in situ* on their surface, to assure homogeneous dispersion of the electrocatalyst complex in the pores of the matrix. The pressed disk electrodes made of SiO_2/C/CuPc was tested as amperometric sensors for 4-APh. Under the optimized conditions, at −75 mV vs SCE in 0.06 mol dm^{-3} Britton‑Robinson buffer (BRB) solution (pH 7.0) containing 250 μmol dm^{-3} of H_2O_2, a linear response range for 4APh from 5 up to 230 μmol dm^{-3} was obtained with a sensitivity of 123 nA dm^{-3} μmol^{-1} cm^{-2} and the limit of detection LOD was 2 (± 0.002) nmol dm^{-3}. The prepared sensors present a stable response during successive determinations. The repeatability, evaluated in terms of relative standard deviation of 3% for n = 10 and μmol dm^{-3} 4-APh. The response time was 1 s and life time 12 months. Finally, the sensor was tested to determine 4-APh in the sample, and gives very good results for its determination. The presence of other phenols like 2-aminophenol, hydroquinone, catechol, cysteine and resorcinol did not show any interference in the detection of 4-APh on this electrode, even in the same concentration with the 4-APh.

Keywords: Amperometric sensor, Copper Phthalocyanine, biomimetic catalyst, 4-aminophenol.

1. Introduction

The contamination of environmental resources by the ever-increasing number of organic toxic compounds being detected in human environment has upraised our attention in recent years. Among various toxic compounds, phenols are extensively present and tenacious in the environment, especially in waters.[1] In this context, it give an undesirable taste and odor to drinking water, even in very low concentrations. Thus, the determination of phenols in the environmental samples is of high interest due to their toxic effects on human, animals, and plants. Furthermore, many of these compounds have potential to aggravate carcinogenesis and mutagenesis in a grade that are considered to be hazardous wastes and priority toxic pollutants by U.S. Environmental Protection Agency (EPA).[2]

4-APh is the primary hydrolytic degradation product of the paracetamol and has been identified in various pharmaceutical preparations as a synthetic intermediate or a degradation product of paracetamol. 4-APh may be dangerous, which can cause teratogenic effect and nephrotoxicity.[3] In addition, 4-APh is also broadly used in production of dyestuff, chemical inhibitor, developer and petroleum additives. As a result, large amounts of 4-APh may be unavoidably released into the environment as a pollutant. Therefore, it is of great importance to develop a simple, sensitive and accurate analytical method for the 4-APh determination.[4,5,6] Hence, the interest in its determination in environmental samples has lead to the development of several quantification methods, like spectrometry,[7, 8] HPLC,[9-11] Capillary electrophoresis [12] and Electrochemical methods.[13-16] Among these, electrochemical technique provide the best opportunity for the development of portable, economic, sensitive and rapid methodologies for the detection of 4-APh.[17,18.]

The carbon ceramic electrodes (CCE) have important feature of physical rigidity and tunable porosity that lead to significant advantages in the development and design of electrochemical sensors.[19, 20] In terms of electrode fabrication, sol-gel approach distinguishes from other methods especially by its ease and flexibility, for example, either external surface or bulk-modified CCE can be prepared in different dimensions and geometrical configurations (like rods, disks, monolithic, micro electrodes). Moreover, the active section area of a bulk-modified electrode can be refreshed by a simple polishing step extending the useful life of the electrode.[21-23]

The silica backbone, itself is electrochemically inactive, not only provides rigidity to the material, but the electroactive species can attach through physical entrapment or covalent and non-covalent binding, wherein the charge transfer occurs preferably by electron hopping.[24,25]
Nowadays, the biomimetic catalyst has more common use in the field of electroanalytical chemistry to mimic the natural enzyme. It is the most efficacious substitute that make the electron transfer easier[26] which try to mimic the natural enzymes with the same selectivity and effectiveness.

This principle has been used to construct the amperometric sensors with higher sensitivities and stabilities.[22] In these biomimetic sensors, a simple redox substance is immobilized on the electrode surface to act as the active center of an enzyme and catalyze the substrate reaction in the same way. This concept has been investigated in our laboratory[22] and remains an interesting field to be exploited. In this context, the structural similarity of metallophthalocyanines and metalloporphyrins with the prosthetic groups of the heme enzymes has led to the development of synthetic models capable of mimicking the enzymatic reactions. Many systems have been reported for reactions involving cytochrome P-450 monooxygenases [27, 28] and peroxidases.[29, 30]

In this study a novel CCE based on SiO_2/C-graphite was used as an electrically conductive support to the *in situ* synthesis of copper(II) phthalocyanine (CuPc) in the porous matrix of SiO_2/C. The material obtained, SiO_2/C/CuPc was pressed in a disk format to fabricate an electrode, whose potential usefulness was evaluated by the electrochemical oxidation of 4-APh.

2. Experimental Section

2.1. Reagents

All the reagents having the analytical grade purity were used as received: tetraethyl orthosilicate, TEOS (Sigma–Aldrich, 98%), HF (Vetec, 48%), graphite powder < 150 µm (Aldrich, 99.99%), HNO_3 (Nuclear, 70%), dopamine (Sigma), resorcinol (Acros, 98%), catechol (Acros, 99%),2-aminophenol (Sigma-Aldrich ≥99%), H_3PO_4 (Nuclear, 85%), H_3BO_3 (Merck, 99.8%),Cysteine (Aldrich, 99.99%) acetic acid (Nuclear, 99.9%), KCl (Vetec, 99%), 4-aminophenol (Sigma-Aldrich ≥99%). Other used reagents were: ethanol (99.9%) and HCl (37%, Synth).

2.2. Preparation of material

2.2.1. Preparation of the SiO_2/C by the sol–gel method

The material SiO_2/C was prepared according to a procedure described in literature reported by our group.[31] The sol gel method was used to prepare SiO_2/C containing 1:1 of SiO_2 and C. For desire synthesis, the tetraethylorthosilicate (TEOS) was pre-hydrolyzed in the ethanol solution catalyzed by HNO_3 at 70 ^{0}C for 3 h. After that, graphite (Aldrich), deionized water and HF (Vetec) catalyst were added to the pre-hydrolyzed TEOS solution. The mixture was sonicated until gelation of the material occoured and then allowed to rest. The xerogel obtained was dried at room temperature and then ground to fine powder and washed thoroughly, initially with deionized water and then with ethanol in soxhlet extractor for 3 h. Finally the product was dried under vacuum at 393 K for 4 h.

2.2.2. *In situ* synthesis of Cu(II) phthalocyanine in the pores of the SiO_2/C matrix

The CuPc was synthesized *in situ* on the SiO_2/50 wt% C powder matrix as described elsewhere.[23] In brief, 1.0 g of SiO_2/C was immersed in 10 mL of 0.01 mol dm^{-3} copper acetate $Cu(OAc)_2$ followed by heating in a water bath at 343 K until complete evaporation of the solvent take place. The obtained dry solid, now represented as SiO_2/C/Cu(II), was mixed with 0.22 g of phthalonitrile and heated in an ampoule at 493 K for 3 h to form the CuPc complex. Copper phthalocyanine not cramped in the matrix pores and therefore unreacted phthalonitrile were removed from the solid surface in a Soxhlet extractor with absolute ethanol. Furthermore the resultant solid was heated at 398 K under vacuum to evaporate all solvents.

2.3. Instrumentation for material characterization

a) Specific surface area (S_{BET}) was determined by the BET multipoint technique and the average pore diameters were obtained from the sorption-desorption isotherms by the BJH method. The measurements were carried out with an Autosorb 1 Quantachrome instrument with the materials previously degassed at 423 K for 19 h, before analysis.

b) The electronic spectrum of CuPc prepared *in situ* on the SiO_2/C matrix was obtained using the diffuse reflectance technique on a UV–vis DRS CARY 5G UV/vis spectrophotometer. Barium sulphate was used as the white reference sample. The Kubelka–Munk function was used for the analysis of diffuse reflectance spectrum.

c) X-ray photoelectron spectra (XPS) were obtained from powdered samples pressed into a thin film pellet and fixed on a stainless steel holder with conducting double-faced adhesive tape. A VSW HA 100 hemispherical electron analyzer and an Al anode X-ray source were used to record the spectra. The analyzer was used in the fixed transmission mode with 44 eV pass energy and the X-ray source was operated at 12 keV and 15 mA. The binding energies were referenced to the Si2p line from silica, set at 103.4 eV. Prior to decomposing the spectra using Gaussian, a Shirley background was subtracted. [32]

d) The electrical resistance (R) of the samples was obtained using the four points probe method on a National Instruments NI PXI-1033 equipment. Measurements were performed for a disk of finely powdered SiO_2/C with 0.5 cm diameter and approximately 0.01 cm thickness (w) pressed under a pressure of 4.5 tons. The conductivities (s) were calculated by applying the Equation 1.

$$\sigma = \frac{1}{R w F_2 F_4} \qquad \text{(Eq.1)}$$

where R is the electrical resistance, w is the thickness of the disk, and F_2 and F_4 are correction factors taken from the literature as 0.50 and 0.98, respectively.[33]

e) Scanning electron micrograph (SEM) images were obtained using secondary back scattered electrons on a JEOL JSM 6360LV microscope operating at 20 kV, equipped with an energy dispersive (EDS) X-ray attachment from NORAN Instruments. The samples (~1 mg) were fixed onto double-faced carbon tape (3 M Electrical Division, Brazil) adhered to an aluminum support and coated with a gold layer using a Bal-Tec MD20 metallizing system

2.4. Electrode fabrication and electrochemical measurements

The working electrode was fabricated by pressing 25 mg of SiO_2/C/CuPc under a pressure of 3 ton, at normal atmospheric conditions. The resultant disk of geometric area (0.20 cm^2) was immersed in pure melted paraffin at 343 K under vacuum (0.13 Pa), until all adsorbed gas in the matrix pores was completely eliminated. The resulting self-supported disk was polished with emery paper to remove the paraffin from the disk surface, and then glued with cyanoacrylate ester glue to the end of a glass tube (external area of 0.20 cm^2 and 15 cm length). A copper wire linked to the disk by graphite powder inserted inside the tube made the electrical contact.

Electrochemical measurements were carried out with a PGSTAT-20 (Autolab) potentiostat–galvanostat using an electrochemical cell with three electrodes system at room temperature. A saturated calomel electrode (SCE) and Pt wire were used as reference and auxiliary electrode, respectively. The pressed disk of SiO_2/C/CuPc was used as a working electrode. The measurements were carried out using the electrochemical cell containing 25 mL of BRB solution containing 1 mol dm^{-3} KCl. Adjustment of the pH of the electrolyte solution was carried out with 0.06 mol dm^{-3} BRB of pH 7.0. The experiments to find the optimum operational conditions for the biomimetic sensor were carried out using 4-APh. An adequate potential was applied in this system and the current was continuously monitored until reach the steady state. Then, hydrogen peroxide solution was added to the buffer solution monitoring the current for several seconds (until reach the steady state). After that, successive additions of standard solutions of the 4-APh were done every 40 s.

3. Results and Discussion

3.1. Characterization of the SiO_2/C-Graphite Matrix

From the N_2 adsorption-desorption isotherm of the matrix SiO_2/C (data not shown) exhibit the presence of hysteresis, typical of mesoporous materials. The material demonstrates a mesopore distribution region (supplementary Figure) with maximum at 15.8 nm diameter, according to the IUPAC classification.[34] The specific surface area, S_{BET}, and the pore volume, pv, obtained from the isotherms of the material used to fabricate the electrode are: S_{BET} 170 m^2 g^{-1} and pv 0.90 cm^3g^{-1}.

The conductivity obtained for SiO_2/C was 0.4 S cm^{-1}. The good conductivity of the matrix is due to the well dispersed and interconnected graphite particles in the silica network. It is an important parameter for electroanalytical applications.

3.2. *In Situ* Synthesis of Copper Phthalocyanine (CuPc)

The *in situ* generation of CuPc can be described by two steps reaction. In the first step (Eq. (2)) Cu(II) is adsorbed on the silica surface by a reaction with formation of a Si-O-Cu bond:

$$\equiv\text{Si-OH} + \text{Cu(AcO)}_2 \rightarrow (\equiv\text{SiO})_2\text{Cu} + 2\text{HOAc} \qquad \text{(Eq. 2)}$$

$$(\equiv\text{SiO})_2\text{Cu} + \text{phthalonitrile} \rightarrow 2\ \text{SiOH/CuPc} \qquad \text{(Eq. 3)}$$

where -OH represents the Brϕnsted acid groups present on the matrix surface. In the second step the adsorbed Cu(II) served as the template for phthalocyanine complex formation inside the silica

pores. The adsorbed Cu(II) on the matrix surface, in the presence of phthalonitrile at 473 K, forms CuPc through the reaction described by Eq. (3).

UV-vis diffuse reflectance spectrum of the immobilized CuPc on SiO_2/C material, shows two electronic transition peaks observed at 589 and 689 nm (Figure 1) and for standard CuPc at 560 and 689 nm. These two transitions are assigned as Q bands for Cu(II) under D_{4h} symmetry, slightly distorted in the CuPc confined in the pores of the matrix.[34]

SEM and EDS images are shown in Figure 2. Within the applied magnification (2000X) it can be noticed that there are no segregated phases of SiO_2 and graphite particles (Figure. 2a). While the surface EDS image (Figure. 2b), shows that copper are homogeneously dispersed throughout the matrix surface of the sample. Table 1 also shows the quantitative results obtained of the EDS spectrum and the amount of copper (in weight and atom %) are 3.25 and 1.32 respectively, this amount is sufficient for electrocatalysis.

Conductivity acquired for SiO_2/C was 0.4 S cm^{-1}.The good conductivity of the matrix is owing to the good amount, well dispersed and interconnected graphite particles in the silica network. It is an important parameter for electroanalytical applications.

The XPS spectra for Cu and N for the material SiO_2/ C/CuPc are shown in Figures 3a and 3b, respectively. In SiO_2/C/CuPc, the Cu $2p_{3/2}$ and $2p_{1/2}$ BE peaks are shown in 932.9 and 652.6 eV, respectively.[35] Other peaks, centered at 396.6 and 400.4 eV with the N 1 s BE, assigned to the pyrrolic and meso-nitrogen atoms in CuPc.[36, 37] Table 2 shows the peak intensities and the atoms % obtained by XPS for SiO_2/C/CuPc. In particular the peak of interest, $Cu2p_{3/2}$ BE, allowed to estimate the amount of 0.1 Cu atom % at the depth probed by the technique.

3.3. Electrochemical study

A pressed disk of SiO_2/C/CuPc was used to fabricate the electrode to test the potential application in the determination of 4-APh.

3.3.1. Hydrogen Peroxide Influence

Figure 4 shows the results obtained in the experiments conducted in the presence and the absence of hydrogen peroxide. In the absence of H_2O_2 (curve a), no oxidation signal for 4-APh was observed, while in the presence of H_2O_2 (curve b), a good response for 4-APh was observed, suggesting that the peroxide is very important in the sensor mechanism, which could be attributed to the inefficacy of the SiO_2/C/CuPc to directly oxidize the 4-APh. On the other hand, good cathodic current after adding peroxide and 4-APh is observed (curve b in Figure 4), viewing that peroxide plays an important role in the catalytic process. A good sensitivity was attained for H_2O_2 concentration of 250 μmol dm^{-3} in Figure 5. This concentration was established for further experiments, based both on these results and on the fact that higher concentrations result in lower stability of peroxidase systems as well as electrodes.

A possible mechanism to explain the behavior of the CuPc complex as a biomimetic catalyst in the construction of an amperometric sensor was proposed as schematized in Figure 6. This mechanism is similar to those proposed for determinations of phenolic compounds with biomimetic catalysts of dopamine β-monooxigenase, peroxidase and tyrosinase enzymes, [22] where the most important stage for phenolic quantification is the electrochemical reduction of quinone species on the electrode surface, recycling the substrate, and consequently resulting in signal amplification and reduction of the detection potential of the phenolic compound. Figure 7 shows the prior addition of H_2O_2 to the solution before adding 4-APh and shows a very good sensitivity of the electrode. It confirms the proposed mechanism as depicted in Figure 6.

3.3.2. Optimization of the parameters for the amperometric detection of 4-aminophenol

Sensor response was influenced by the applied potential, as shown in Figure 8. The maximum sensor response was obtained at −75 mV vs. SCE. This value is similar to the reduction potential of 1,2-quinone to catechol,[38] which also strengthens the idea that the phenolic compound was electrochemically regenerated and produced a pseudo-bioelectrocatalytic amplification cycle,[39] as shown schematically in Figure 6.

The effect of pH on the sensor response was observed during experiments carried out in 0.06 mol dm^{-3} BRB solution, with the pH varying from 3.0 to 11.0. The best result was obtained at pH 7.0 as shown in Figure 9.

Four different 0.01 mol dm^{-3} buffer solutions (phosphate, TRIS, HCl-KOH and BRB) were tested, with best response (data not shown) obtained using the BRB buffer. Further experiments were conducted in an optimized BRB concentration of 0.06 mol dm^{-3}.

3.3.3 Sensor characteristics

Under optimized conditions, the proposed sensor showed a good linear response for 4-APh concentration, varying from 5 up to 230 µmol dm^{-3} with a sensitivity of 123 nA dm^{-3} μmol^{-1} cm^{-2} (Figure 10), represented by the following equation:

$\Delta j/\mu A = (4.8)(\pm 0.075) + (123)(\pm 0.06)[4APh] \backslash \mu mol\ dm^{-3}$, with a correlation coefficient of 0.9997 for n = 20

A limit of detection (3 times standard deviation of the blank divided by the slope of calibration curve) was calculated in triplicate, LOD = 2 (± 0.002) nmol dm^{-3} was found. In addition, the response time of the sensor required to reach 100% signal, was approximately 1s. Compared with other sensors and biosensors for phenol described in the literature,[18, 39-41] the proposed sensor provided a lower detection limit, with higher sensitivity and linear range.

The repeatability in the measurements was evaluated through ten successive experiments carried out with 30 µmol dm^{-3} 4-APh in BRB solution (pH 7.0). The repeatability was evaluated as the relative standard deviation (RSD) resulting in a value lower than 3%. The lifetime of the sensor was more than 12 months, stored at room temperature and there is no significant decrease in the sensitivity of the sensor was observed (data not shown).

Repeatability, in the construction of sensors was assessed, fabricating six sensors individually from the very beginning and determined the sensitivity obtained for each one. The repeatability expressed as RSD was 4%. This result shows an optimum repeatability in the sensor construction and it was possible due to the ability in the membrane preparation, containing the copper (II) complex. This sensor can be kept at room temperature and used without loss of sensitivity, after several months just polishing with emery paper. However, the sensor presents good sensitivity until approximately one hundred successive determinations, and the stability of the sensor was due to the strongly bonding of the copper within the complex.

3.3.4. Selectivity of the biomimetic sensor

To confirm that the sensor was selective to 4-APh, the sensor was tested using phenolic compounds having analogous structures, as potential interferents. The reduction current increased sharply after adding 10 µmol dm^{-3} 4-APh (Figure 11). Further successive additions of 10 µmol dm^{-3} 2-aminophenol, hydroquinone, catechol, resorcinol and Cysteine into the electrolyte did not show any response in the amperogram. A further addition of 10 µmol dm^{-3} 4-APh sharply increased the reduction current again.

Moreover, at concentrations tested, the interferents did not affect the steady state current of 4-APh. The high selectivity of the sensor is due to the specific recognition sites, which reflect the template in terms of size, shape and arrangement of the functional group.

3.3.5. Application of the sensor

In order to evaluate the practical usefulness of the method, 4-APh was determined in the tap water and river water samples. Prior to the analyses, the river water samples were filtered under vacuum through 0.45 µm cellulose acetate membranes to remove the suspended solid substance. The accuracy of the method was evaluated by performing recovery tests after spiking the samples, as shown in Table 3. All the measurements were conducted in triplicate, the recovery values were obtained in the range of 98‑106 %, which reveals the viability in using the SiO_2/C/CuPc electrode as a highly selective amperometric sensor for 4-APh in these matrices.

5. Conclusions

The proposed biomimetic sensor SiO_2/C/CuPc, showed a wide response range (5 up to 230 µmol dm^{-3}), high sensitivity of 123 nA dm^{-3} µmol^{-1} cm^{-2} and with a detection limit of 2 nmol dm^{-3} of 4-APh. This sensor showed a long life time of 12 months, great stability, repeatability and short response time of (1s) for determination of 4-APh. The sensor was highly selective and the preparation procedure was facile, fast and reproducible. Compared to peroxidase-based biosensors, the amperometric electrode SiO_2/C/CuPc is more selective and stable showing a great potential for practical use. These characteristics can be assigned to the conductivity of the material and the environment of the copper complex in the porous material keeping the great reactivity after activating it with hydrogen peroxide. The proposed sensor is highly selective for 4-APh determination; it does not show any interference with other phenolic compound. Indeed this sensor was successfully employed for determination of 4-aminophemol in real sample. A

CuPc was used as an active catalytic site to mimic peroxidase enzymes for the determination of 4-APh showing a great potential for practical use.

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Figures and Tables captions

Graphical Abstract: SiO_2/C/CuPc sensor response for 4-aminophenol oxidation

Figure 1: UV_Vis diffuse reflectance spectra of SiO2/C/CuPc, expressed in Kubelka-Munk units

Figure 2: SEM image (a) and EDS mapping of Cu (b) for SiO_2/C/CuPc.

Figure 3: XPS spectra for Manganese (a) and N (b).

Figure 4: Signals obtained with the proposed sensor using SiO_2/C/CuPc: (a) in absence and (b) presence of 250 µmol dm^{-3} H_2O_2. Each step corresponds to the increment of 30 µmol dm^{-3} 4-APh. Applied potential −75 mV vs SCE in 0.06 mol dm^{-3} BRB at pH 7.0, containing 1 mol dm^{-3} KCl.

Figure 5: Influence of the H_2O_2 concentration on the sensor response. Measurements carried out in 0.06 mol dm^{-3} BRB at pH 7.0, containing 1 mol dm^{-3} KCl, and 30 µmol dm^{-3} of 4-APh.

Figure 6: Proposed mechanism for the sensor SiO_2/C/CuPc response for 4-APh. Copper phtalocyanine is represented by $CuPc_{red}$, $CuPc_{ox}$ is oxidized CuPc, and $4\text{-}APh_{red}$ and $4\text{-}APh_{ox}$ are the reduced and oxidized 4-APh species, respectively.

Figure 7: Amperometric response for the biomimetic sensor for 4-APh. Each step corresponds to the increment of 30 µmol dm^{-3} 4-APh and containing 250 µmol dm^{-3}. The inset figure shows the analytical curve. Applied potential −75 mV vs SCE in 0.06 mol dm^{-3} BRB at pH 7.0, containing 1 mol dm^{-3} KCl.

Figure 8: Influence of the applied potential on the current density Δj. Measurements carried out in 0.06 mol dm^{-3} BRB at pH 7.0, containing 1 mol dm^{-3} KCl, and 30 µmol dm^{-3} of 4-APh and 250 µmol dm^{-3} of H_2O_2.

Figure 9: Influence of the pH on the current density Δj. Measurements carried out in 0.06 mol dm^{-3} BRB containing 1 mol dm^{-3} KCl, and 30 µmol dm^{-3} of 4-APh and 250 µmol dm^{-3} of H_2O_2.

Figure 10: A typical profile of the sensor response using the optimized conditions. Applied potential of −75 mV vs SCE, in 0.06 mol dm^{-3} BRB at pH 7.0 containing 1 mol dm^{-3} KCl, and 250 µmol dm^{-3} of H_2O_2.

Figure 11: Current density j vs. time for the addition of 10 µmol dm^{-3} each (a) 4-aminophenol (b) 2- aminophenol (c) hydroquinone, (d) catechol (e) resorcinol (f) Cysteine and (g) 4-

aminophenol into the electrochemical cell in sequence at 50, 75, 100, 125, 150, 175 and 200 s. Applied potential of −75 mV vs. SCE, in 0.06 mol dm^{-3} BRB at pH 7.0 containing 250 µmol dm^{-3} H_2O_2 and 1 mol dm^{-3} KCl.

Table 1: Quantitative result of the EDS spectrum

Table 2. Peak intensities and atoms % for SiO_2/C/CuPc calculated from XPS data.

Table 3: 4-Amiophenol recovery data for water samples using the proposed sensor

Supplementary Figure 1. N_2 adsorption-desorption isotherms for SiO_2/50 wt% C. Pore size distribution curve (Inset).

Figure 1

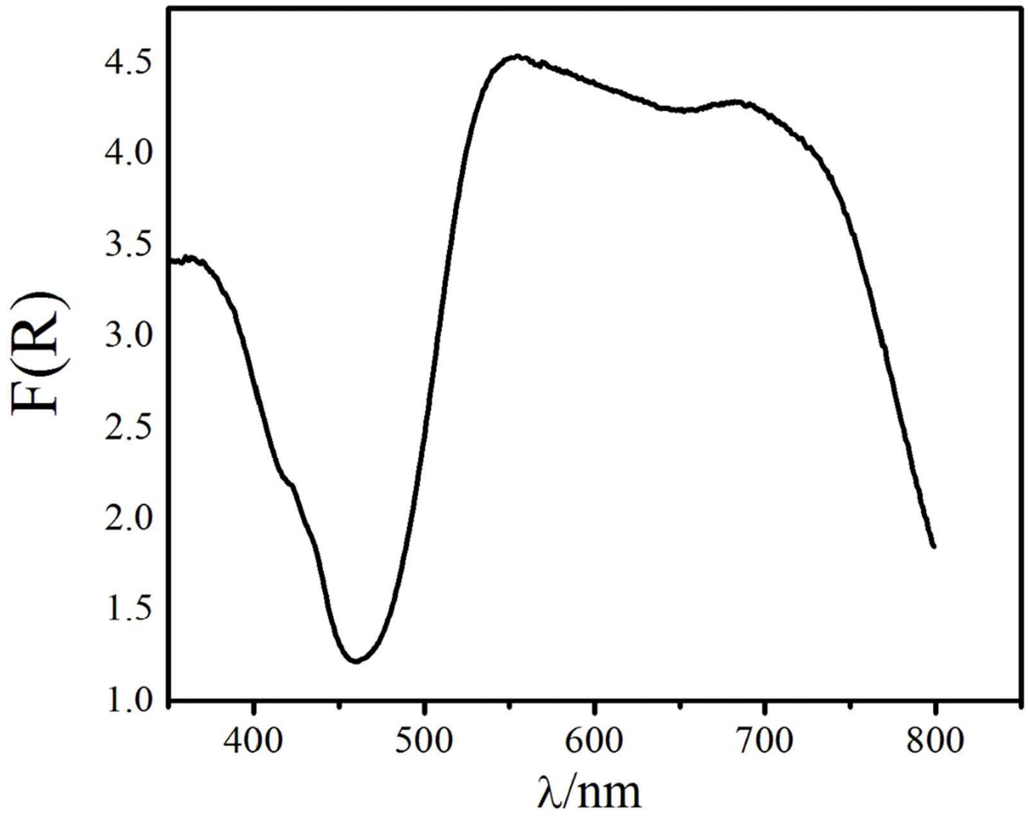


Figure 2

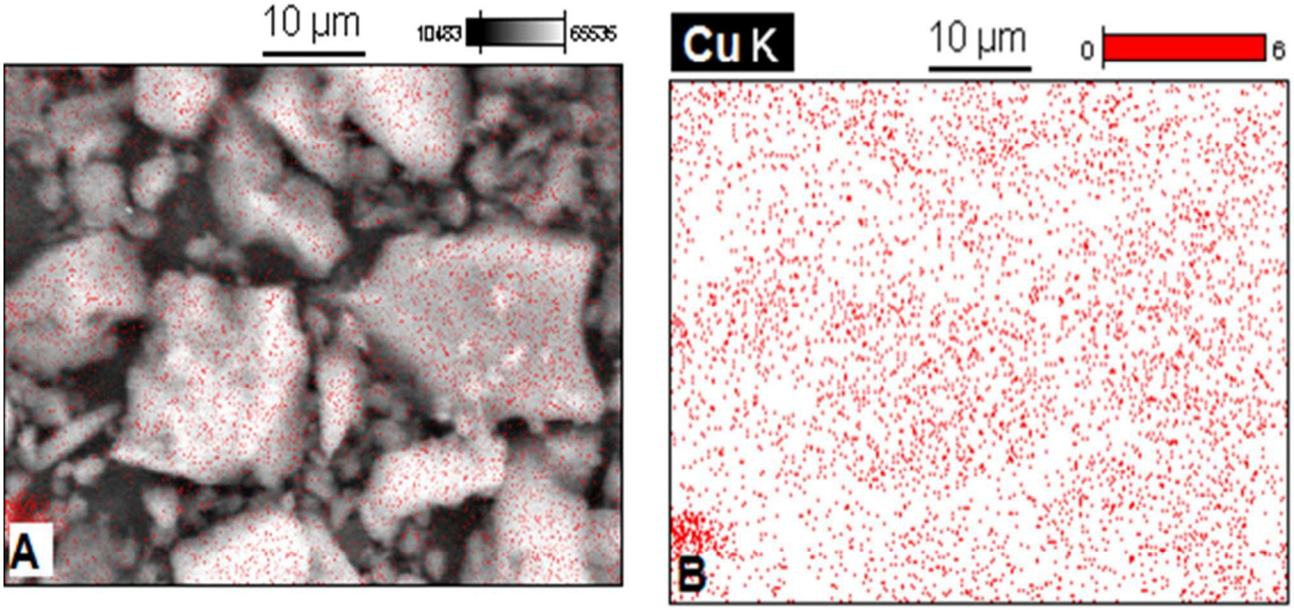


Figure 3A

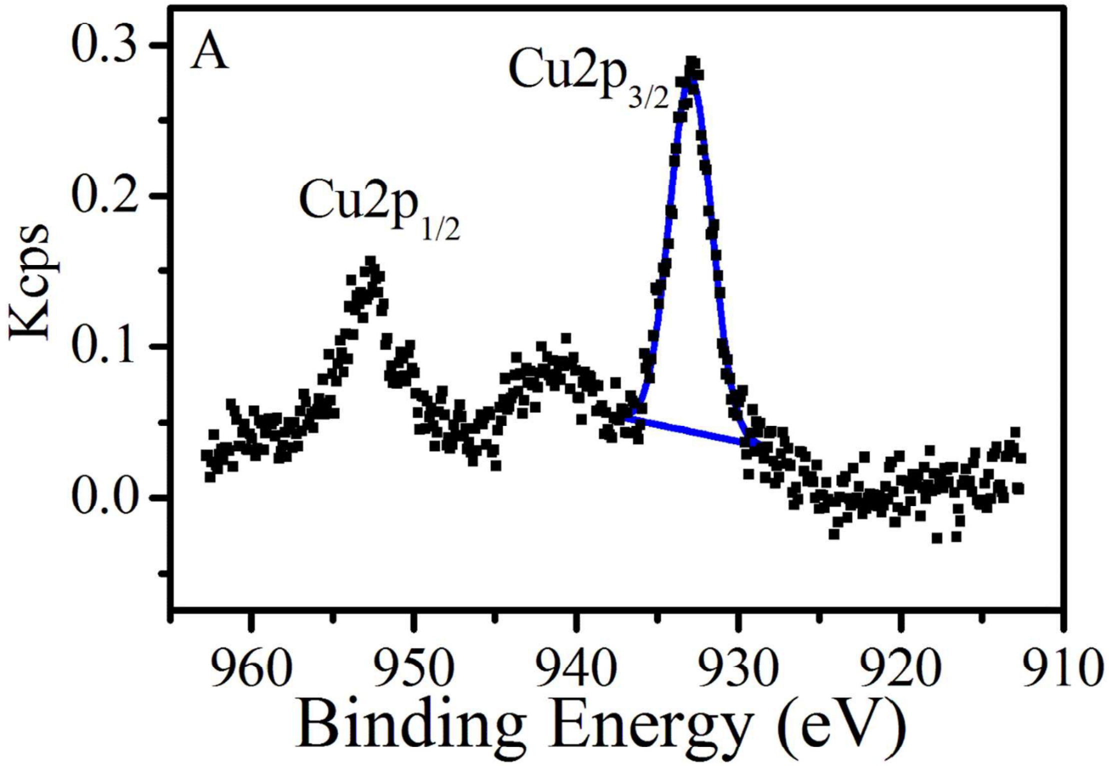

A
Cu2p$_{3/2}$
Cu2p$_{1/2}$
Kcps
0.3
0.2
0.1
0.0
960
950
940
930
920
910
Binding Energy (eV)

Figure 3B

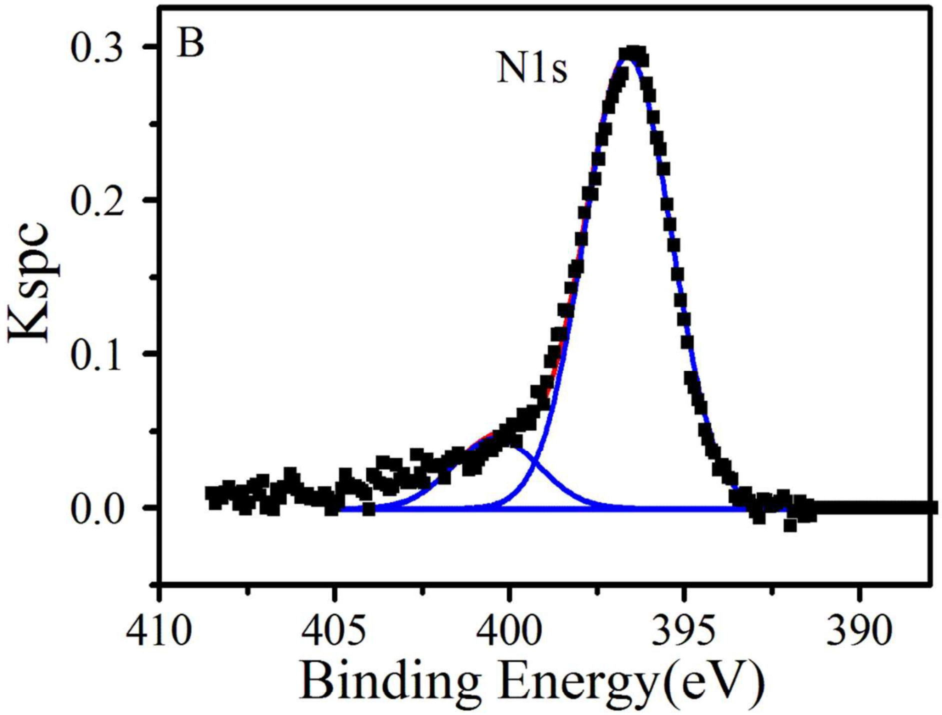


Figure 4

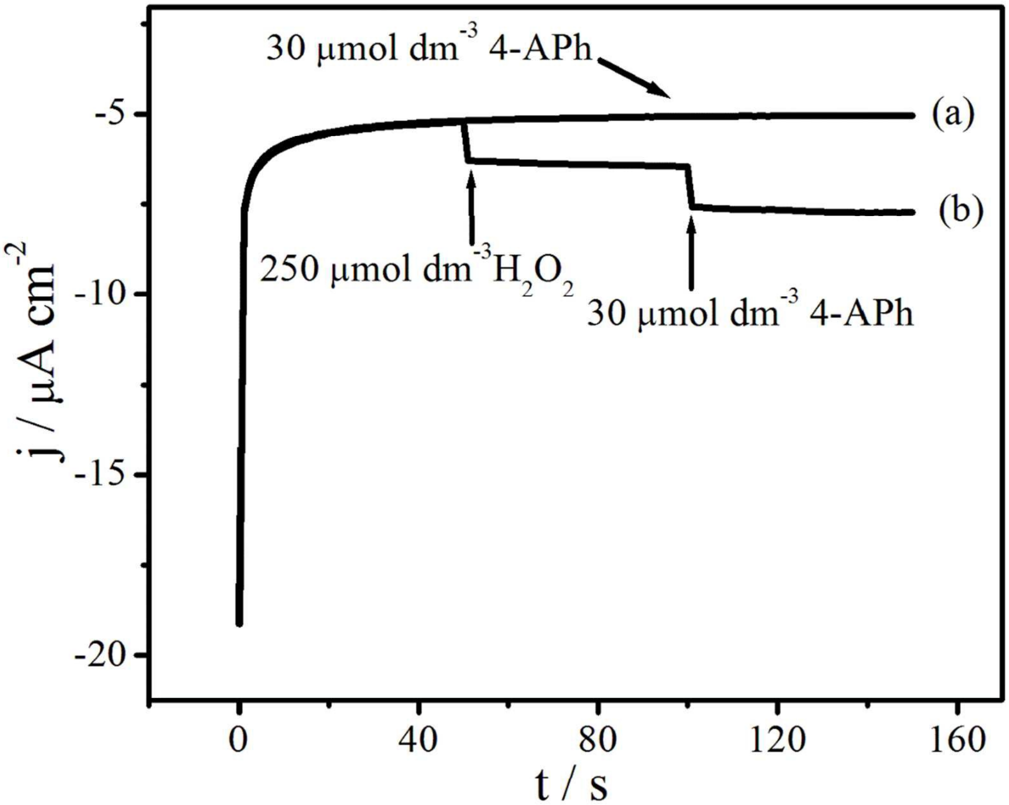

30 μmol dm^{-3} 4-APh
250 μmol dm^{-3} H_2O_2
30 μmol dm^{-3} 4-APh
(a)
(b)
-5
-10
-15
-20
j / μA cm^{-2}
0
40
80
120
160
t / s

Figure 5

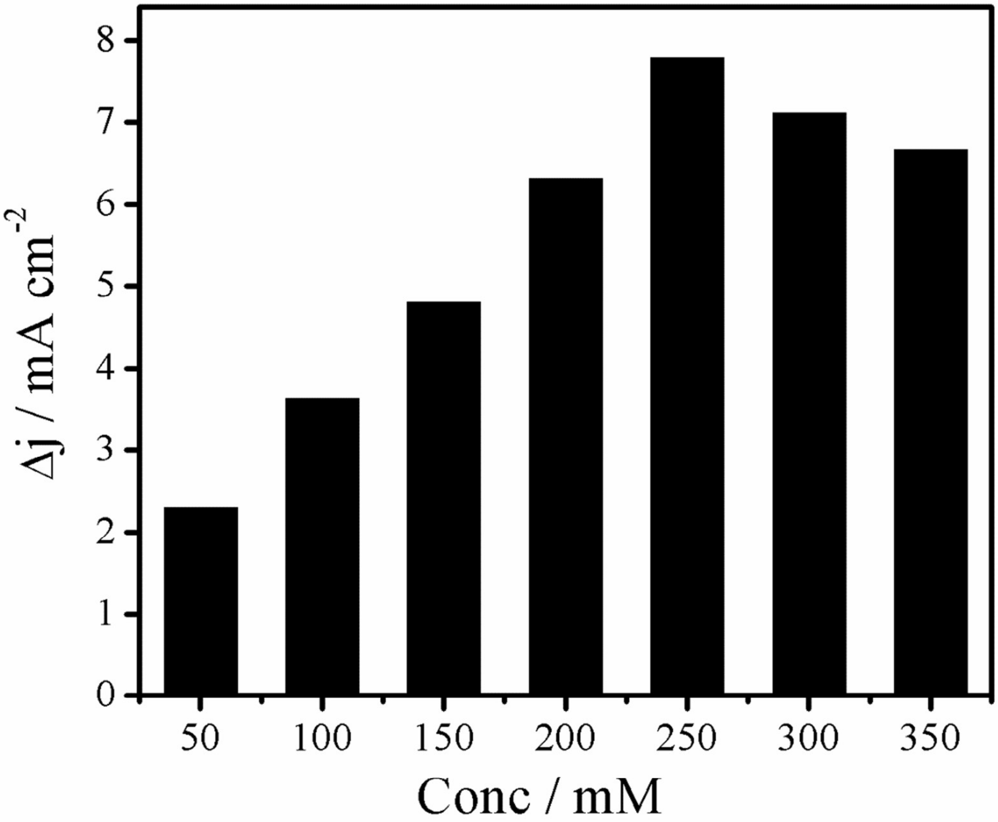


Figure 6

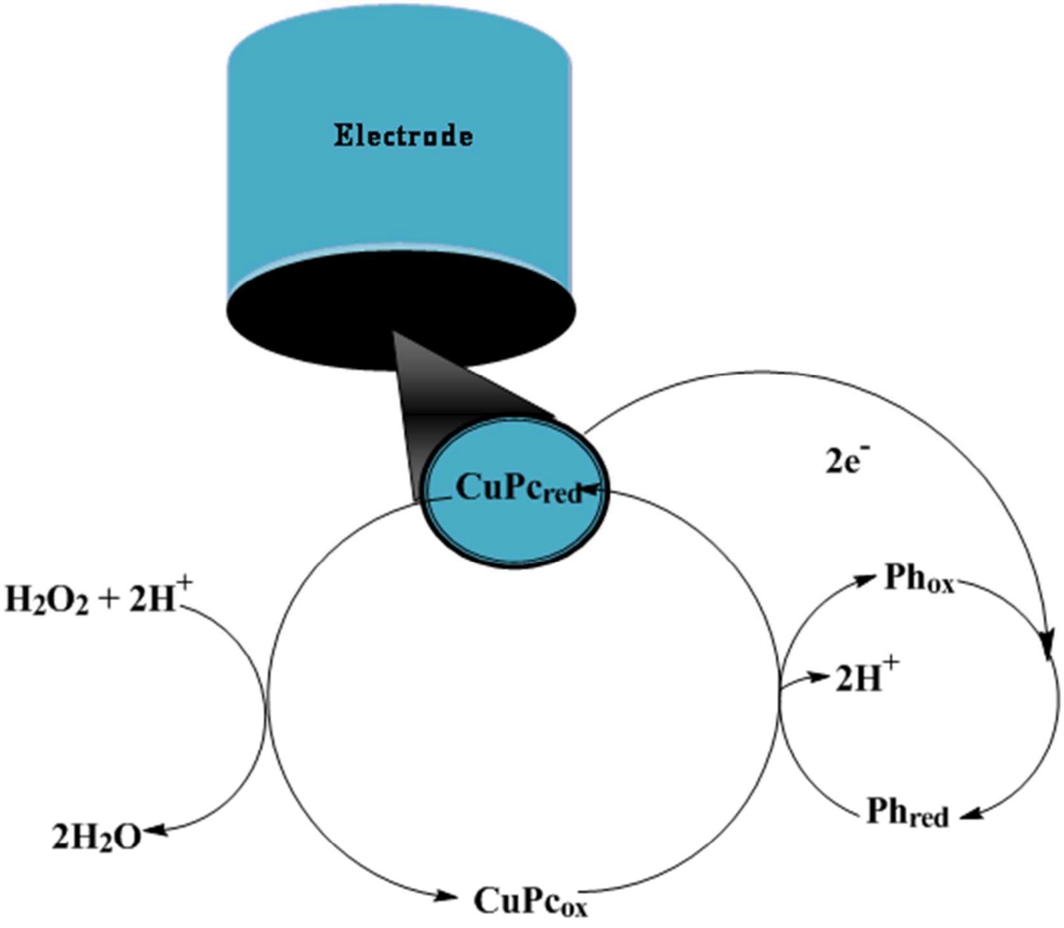


Figure 7

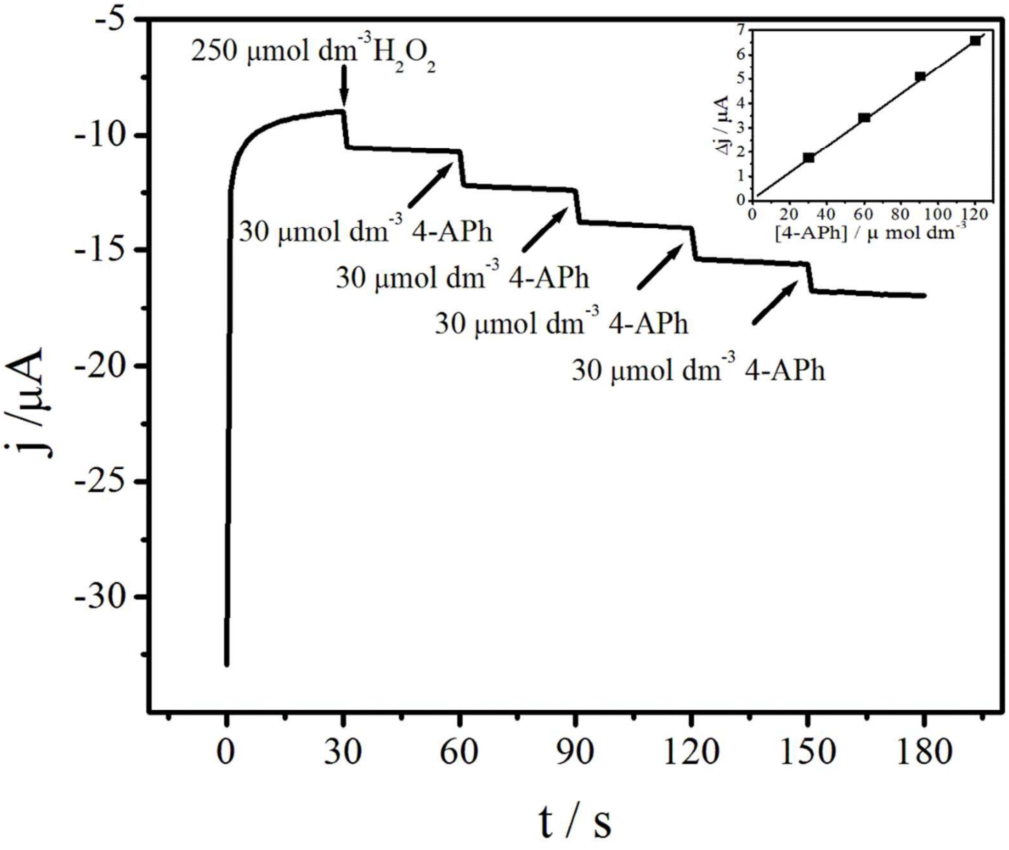

250 µmol dm^{-3} H$_2$O$_2$
30 µmol dm^{-3} 4-APh
30 µmol dm^{-3} 4-APh
30 µmol dm^{-3} 4-APh
30 µmol dm^{-3} 4-APh
j /µA
-5
-10
-15
-20
-25
-30
t / s
0
30
60
90
120
150
180
Δj / µA
0
1
2
3
4
5
6
7
[4-APh] / µ mol dm^{-3}
0
20
40
60
80
100
120

Figure 8

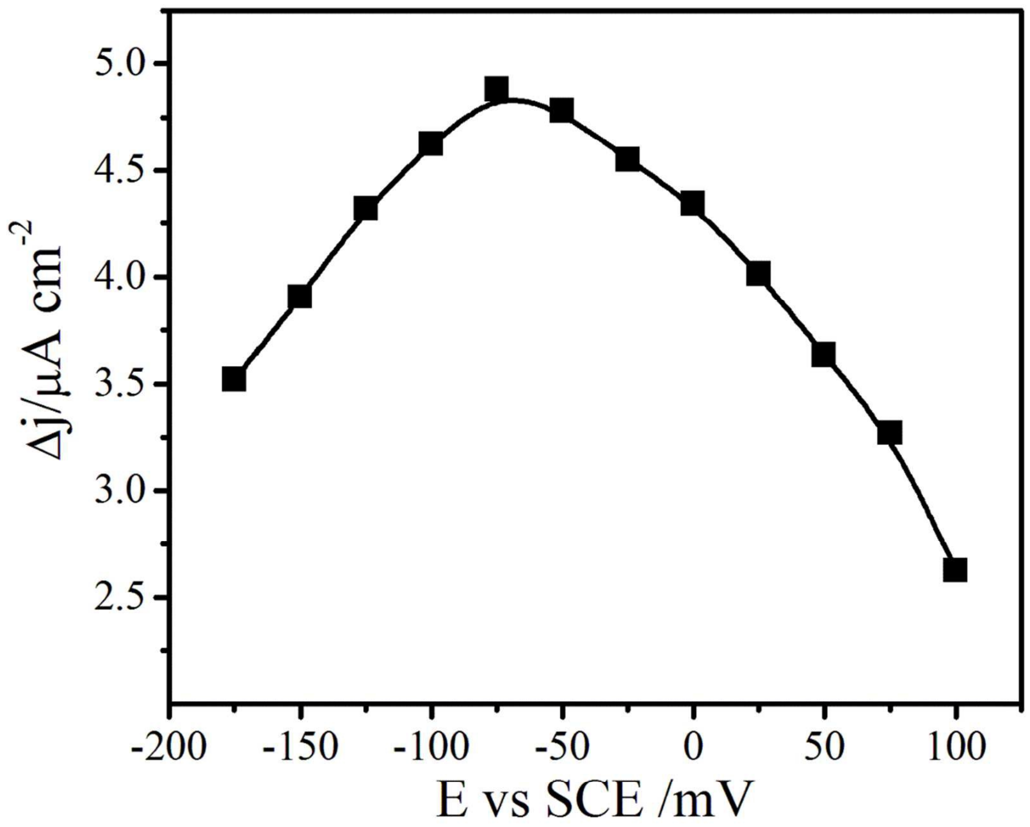


Figure 9

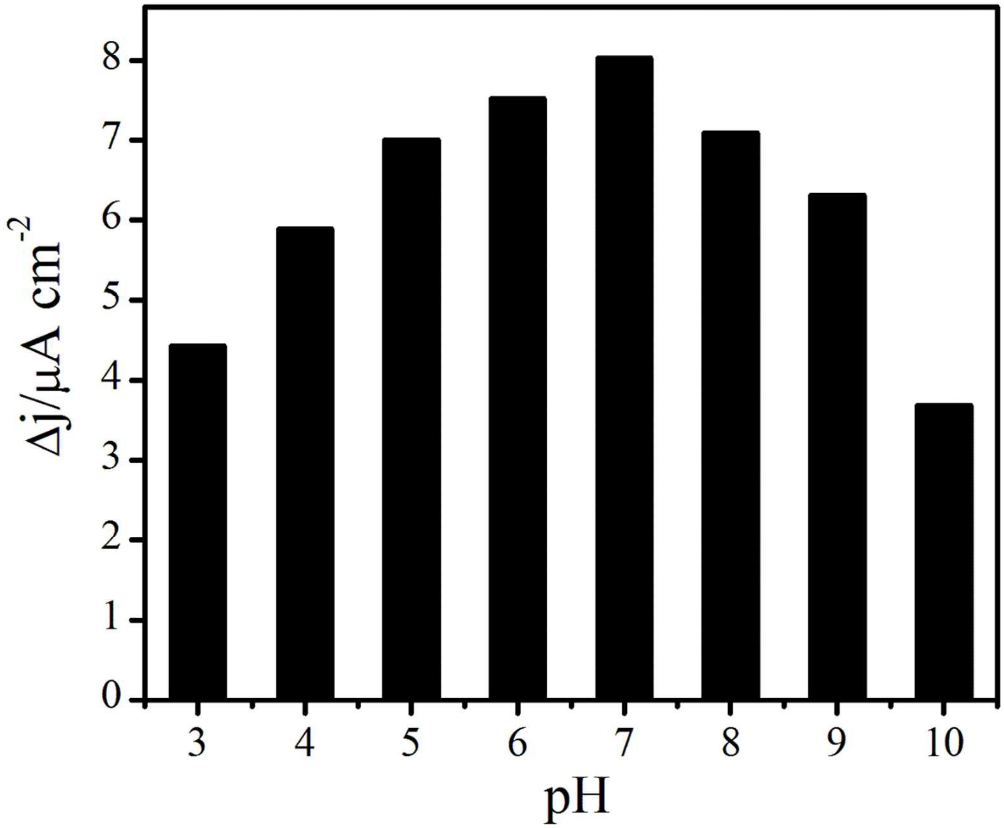


Figure 10

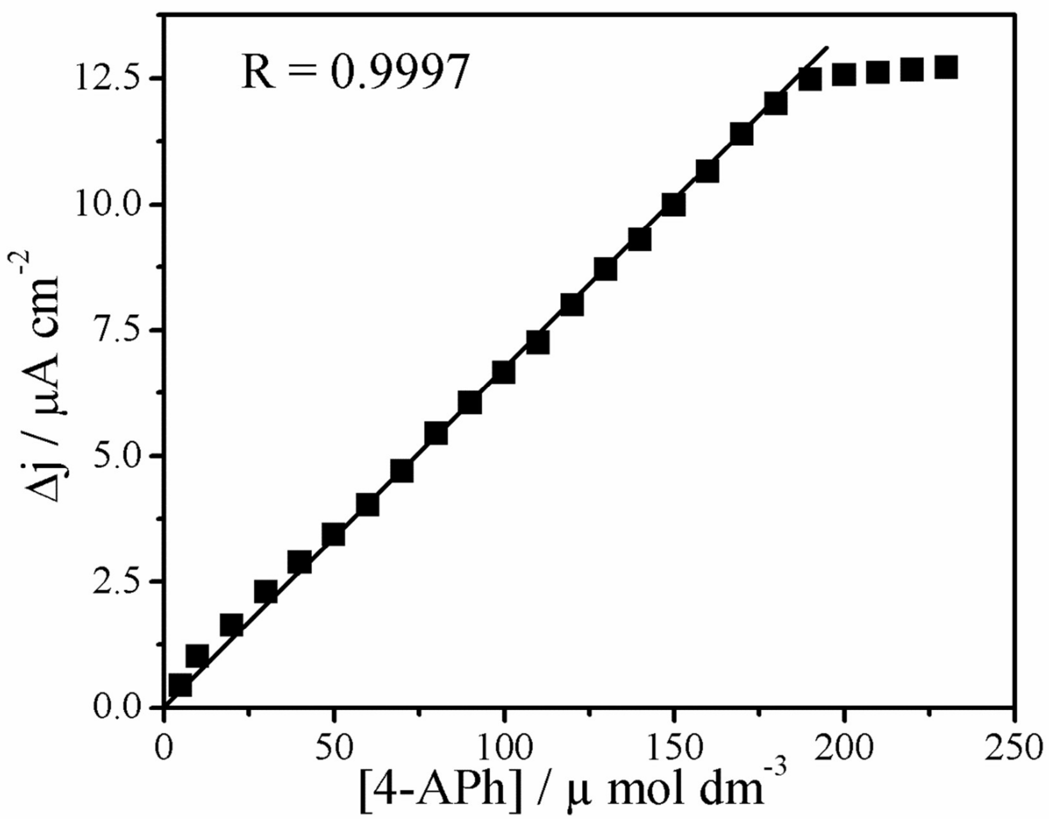
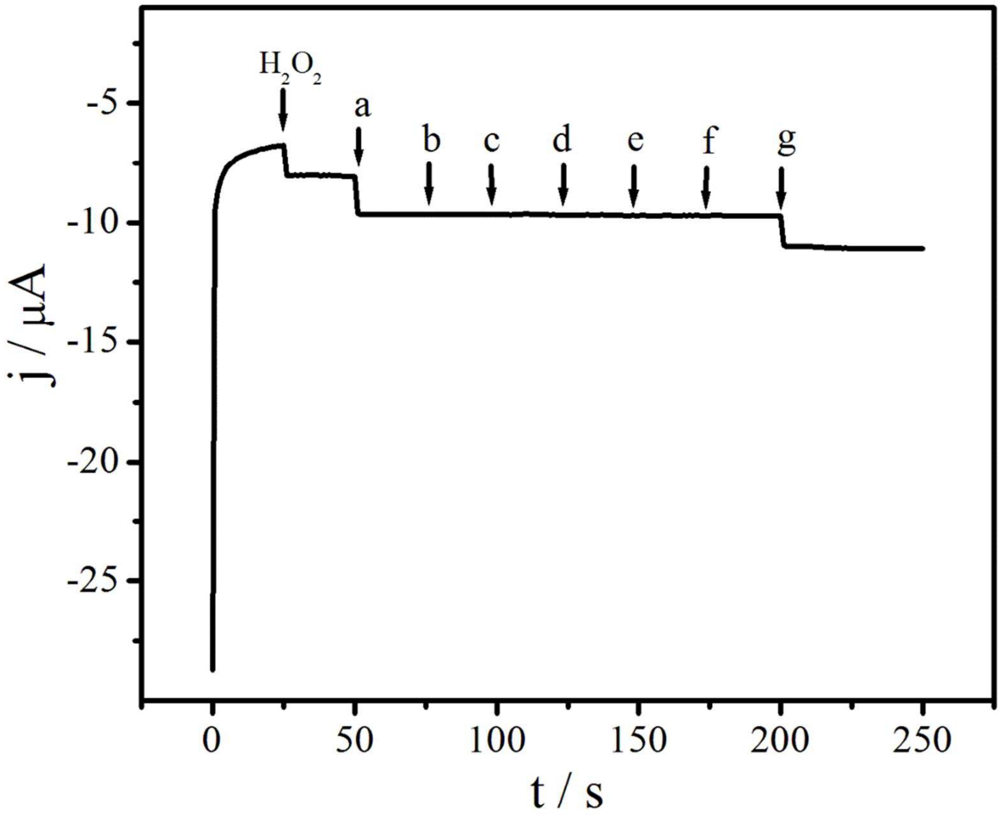

R = 0.9997
12.5
10.0
7.5
5.0
2.5
0.0
Δj / µA cm^{-2}
0
50
100
150
200
250
[4-APh] / µ mol dm^{-3}

Figure 11



Element	Weight %	Atom %
C	15.25	24.45
Si	38.25	24.62
O	43.25	49.61
Cu	3.25	1.32

Table 1:

SiO_2/C/CuPc	Peak Intensity	Atomic %
Cu2$p_{3/2}$	0.23	0.1
C1s	70.65	34.6
N1s	3.51	1.7
O1s	73.97	36.2
Si2p	55.98	27.4

Quantitative results of the EDS spectrum

Table 2. Peak intensities and atoms % for SiO_2/C/CuPc calculated from XPS data

Samples	4-APh added (µmol dm^{-3})	4-APh found (µmol dm^{-3})	Recovery [b] (%)
River water	-	<QL	-
1	10.0	10.4 (±0.03)	104 (±4)
2	12.0	11.8 (±0.06)	98.33 (±3)
Tap water	-	<QL	-
1	10.0	9.8 (±0.07)	98 (±5)
2	12.0	12.7 (±0.05)	105.83 (±6)

Table 3: 4-aminophenol recovery data for water samples using the proposed sensor

[a] The results are expressed as mean value ±SD based on 3 replicates. Confidence interval of 95%. LQ, limit of quantification.

[b] Recovery obtained from spiked samples.

Supplementary Figure