

# Platinum nanoparticles-doped sol–gel/carbon nanotubes composite electrochemical sensors and biosensors

Minghui Yang, Yunhui Yang, Yanli Liu, Guoli Shen\*, Ruqin Yu

*Chemistry and Chemical Engineering College, State Key Laboratory of Chemo/Biosensing and Chemometrics, Hunan University, Hunan, Changsha 410082, PR China*

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## Abstract

Platinum nanoparticle-doped sol–gel solution is prepared and used as a binder for multi-walled carbon nanotubes (CNT) for the fabrication of electrochemical sensors. Amine group containing sol–gel solution is selected to utilize the affinity of  $-\text{NH}_2$  groups toward metal nanoparticles for stabilization the nanoparticles in solution. The resulting CNT-silicate material brings new capabilities for electrochemical devices by using the synergistic action of the electrocatalytic activity of Pt nanoparticles and CNT. The combined electrocatalytic activity permits low-potential detection of hydrogen peroxide with remarkably improved sensitivity. With the incorporation of glucose oxidase within the Pt-CNT-silicate matrix, a Pt-CNT paste-based biosensor has been constructed that responds more sensitively to glucose than CNT-based biosensor. The influences of the composite of the sol–gel solution, the quantity of the solution and the Pt nanoparticles loading are examined. In pH 6.98 phosphate buffer, almost interference free determination of glucose is realized at 0.1 V versus SCE with a linear range from 1 to 25 mM, a response time  $<15$  s, and the sensitivity is  $0.98 \mu\text{A mM}^{-1} \text{cm}^{-2}$ . The sensitivity of the Pt-CNT paste-based biosensor is almost four times larger than that of the CNT-based biosensor ( $0.27 \mu\text{A mM}^{-1} \text{cm}^{-2}$  at 0.1 V). The improved electrocatalytic activity and surface renewability made the Pt-CNT-silicate system a potential platform to immobilize different enzymes for other bioelectrochemical applications.

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**Keywords:** Biosensors; Carbon nanotube; Enzymes; Platinum nanoparticle; Synergistic action

## 1. Introduction

Nanoparticles have been used extensively in the fields of physical, chemical and material sciences in the past few years (Brown et al., 1996; Bao et al., 2003; Ma et al., 2004; Kidambi et al., 2004). Carbon nanotube (CNT) represents an important group of nanomaterials which are receiving considerable research interest (Rubianes and Rivas, 2003; Moore et al., 2004; Chen et al., 2003). Carbon nanotube-modified electrodes have shown excellent electrocatalytic activity toward hydrogen peroxide and NADH due to the fast electron transfer ability of CNT. A dramatic decrease in the overvoltage of hydrogen peroxide and NADH was observed with improved sensitivity, which makes the carbon nanotube-modified electrodes of great promise for dehydrogenase and oxidase-based

amperometric biosensors. Wang and Musameh (2003) have evaluated a CNT paste electrode using Teflon as a binder, observing a substantial decrease of overvoltage in the detection of glucose and ethanol with enzyme glucose oxidase and alcohol dehydrogenase, respectively, as compared to conventional carbon paste electrode. Zhang et al. (2004) have reported an investigation of solubilization of pristine CNT in aqueous solutions of chitosan. When the CNT-chitosan film was cast onto the glassy carbon electrode surface, the oxidation potential of NADH decreased greatly. Furthermore, the enzyme glucose dehydrogenase was immobilized onto the electrode surface with amino groups of chitosan through cross-linking with glutaric dialdehyde. The resulting biosensor was shown with high sensitivity and good operational stability.

Nanosized dispersions of metals have gained considerable attention because of their size-dependent electrical, chemical and optical properties and the effective utilization of ex-

\* Corresponding author. Tel.: +86 731 8821355; fax: +86 731 8821848.  
E-mail address: [gshen@hnu.net.cn](mailto:gshen@hnu.net.cn) (G. Shen).

pensive metals. The catalytic and electrochemical activity of highly dispersed metal nanoparticles is of keen interest in the fabrication of amperometric biosensors (You et al., 2003; Park and Cheon, 2001; Genies et al., 1998). However, aggregation of nanoparticles often prohibits the application of the particles. To circumvent this problem, many successful methods have been reported for the stabilization of metal nanoparticles based on capping by polyelectrolytes, or ligands, or stabilized in silicate-based matrix (Bharathi et al., 1999; Li and El-Sayed, 2001).

The sol–gel technique has been widely used for the incorporation of different reagents in the development of biosensors. Since the first report of sol–gel derived ceramic-carbon composite electrode by Lev's group (CCE) (Tsionsky et al., 1994; Sampath and Lev, 1996; Tian and Zhu, 2003; Del Mar Cordero-Rando et al., 2002), it has triggered active research because of high conductivity of carbon sol–gel silicate composite, as well as the wide operational voltage window, the renewability of the sensor surface and easy in fabrication at room temperature.

In this paper, we tried to combine the electrocatalytic activity of Pt nanoparticles and CNT together in a simple and robust way to produce composite material with high-performance of heterogeneous catalytic activity. As CNT is insoluble in most solvents, Pt nanoparticles could not be easily attached to CNT and physically adsorbed particles can be easily removed. In the present work, sol–gel solution with highly dispersed Pt nanoparticles is used as a binder for multi-walled carbon nanotubes for fabrication of electrochemical sensors. Amine group containing sol–gel solution is selected for the affinity and stabilizing effect of  $-\text{NH}_2$  toward metal nanoparticles. The resulting Pt-CNT-silicate electrode shows significantly improved sensitivity to hydrogen peroxide compared to its counterpart CNT-silicate electrode without Pt nanoparticles. The attractive performance of the new electrode is used to incorporate glucose oxidase for the fabrication of glucose biosensors. This is the first report of an electrochemical enzyme biosensor with carbon nanotubes using sol–gel as a binder, the resulting CNT-silicate material brings new capabilities for electrochemical devices by combining the advantages of CNT, Pt nanoparticles and “bulk” composite electrode.

## 2. Experimental

### 2.1. Apparatus and reagents

Multiwalled carbon nanotubes (MWCNTs, with ~95% purity) were obtained from Shenzhen Nanotech Port Co., Ltd. (Shenzhen, China). *N*-[3-(Trimethoxysilyl) propyl] ethylenediamine (EDAS), methyltrimethoxysilane (MTMOS) and hydrogen hexachloroplatinate (IV) hydrate ( $\text{H}_2\text{PtCl}_6$ ) were purchased from Aldrich. Glucose oxidase (GOx, from *Aspergillus niger*; EC 1.1.3.4, type VII-S; 196,000 unit  $\text{g}^{-1}$ ) was from Sigma. All other reagents were of analytical grade.

Phosphate buffer (1/15 M, pH 6.98) was used as supporting electrolyte in all measurements and double distilled water was used throughout.

Cyclic voltammetric and amperometric measurements were carried out on PAR 283 potentiostat/galvanostat and model 270 software (EG&G Princeton Applied Research, Princeton, NJ, USA). The resistance experiment was carried out in phosphate buffer solution containing 1 mM  $\text{K}_3[\text{Fe}(\text{CN})_6]$ , 5 mM  $\text{K}_4[\text{Fe}(\text{CN})_6]$  and 0.1 M KCl. A frequency range of 50,000–1 Hz was utilized with a potential amplitude of 10 mV rms. Hitachi H-800 transmission electron microscope (TEM; Hitachi, Tokyo, Japan) was used for obtaining TEM image of the Pt-silicate sol. A three-electrode cell (10 mL) with the fabricated paste electrode as working electrode, a saturated calomel reference electrode (SCE) and a platinum foil counter electrode was used. All potentials were measured and reported versus the SCE and all experiments were carried out at room temperature.

### 2.2. Preparation of silicate sol and Pt-silicate sol

A homogeneous stock sol–gel solution was prepared by dissolving 0.4 ml of EDAS and 0.6 ml of MTMOS in 0.8 ml of water, 0.02 ml of 0.1 M HCl was added and the solution was stirred until a transparent solution was obtained.

The Pt-silicate sol was prepared according to literature report with some minor revisions (Bharathi et al., 1999): 0.4 ml of EDAS and 0.6 ml of MTMOS were dissolved in 0.8 ml of water, followed by the addition of 0.2 ml of 0.01 M  $\text{H}_2\text{PtCl}_6$ , the solution was then sonicated for 10 min. A volume of 0.02 ml of 0.1 M HCl was added to this clear solution which was stirred regularly. The  $\text{Pt}^{\text{IV}}$  was then reduced using 0.05 ml of freshly prepared 5%  $\text{NaBH}_4$ . Complete reduction was verified by UV–vis adsorption spectroscopy (Perkin-Elmer, Lambda 900) with disappearance of the UV–vis absorption peak of  $\text{PtCl}_6^{2-}$ .

### 2.3. Electrode preparation

The MWCNTs were first purified as reported previously (Gong et al., 2004; Valentini et al., 2003). Briefly, 100 mg of MECNTs were oxidized at 400 °C for 30 min to remove amorphous carbon particles. To eliminate metal oxide catalyst, the oxidized carbon nanotubes were dispersed in 60 ml of 6.0 M HCl for 4 h under ultrasonic agitation, and washed until the pH of the solution was neutral, then dried.

The carbon paste electrode (CPE) was prepared by mixing 600 mg of graphite powder with 1 ml of stock sol–gel solution thoroughly in a mortar to form a homogeneous paste. This paste was then packed into one end of a Teflon tube (6 mm inner diameter and 5 mm deep) and pressed tightly. A copper wire was inserted through the opposite end to establish an electrical contact. The CNT paste electrode (CNTPE) was constructed in a similar manner, with the CNT replacing the graphite powder. The Pt-CPE and Pt-CNTPE electrodes were

prepared with the Pt-silicate sol replacing the stock sol–gel solution.

The glucose biosensors were fabricated with the addition of glucose oxidase (GOx) to the paste. For this purpose, GOx was mixed first with the stock sol–gel and Pt-silicate sol solution to reach a concentration of 20 mg/ml, followed by the addition of CNT.

The composite surface was smoothed on a weighing paper and rinsed with water carefully prior to experiment.

### 3. Results and discussion

#### 3.1. Transmission electron microscopy

Fig. 1 shows typical TEM micrograph of Pt-silicate sol prepared according to method in the experimental section. The sol constitutes predominantly of highly dispersed spherical particles. Some rodlike particles are observed, which seem to be formed by coalescence of two or three spherical particles (Bharathi et al., 1999). The minimal size of the particles observed is around 2–3 nm, and the largest ones about 40 nm, with 60% of the particles are around the size of 20 nm. Repeating the preparation procedure with only MTMOS resulted in precipitation of dark metallic particles immediately after the addition of NaBH<sub>4</sub>. This observation proves the role played by –NH<sub>2</sub> groups in stabilization of the nanoparticles in the sol–gel solution. The stability of the sol was very high, and no visible aggregation was noticed after 2 months when the sol was stored dark at 4 °C.

#### 3.2. Electrochemical characterization of the composite electrodes

Cyclic voltammetry of ferrocyanide system is a valuable and convenient tool to monitor the characteristic of the surface of modified electrode. Cyclic voltammetry was conducted in 20 mM Fe(CN)<sub>6</sub><sup>4–</sup> and 0.2 M KCl at 20 mV s<sup>–1</sup>

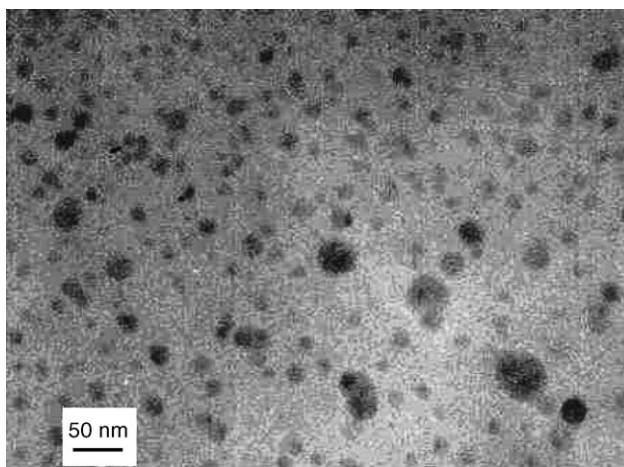


Fig. 1. TEM micrograph of the Pt-silicate sol. The scale bar is 50 nm.

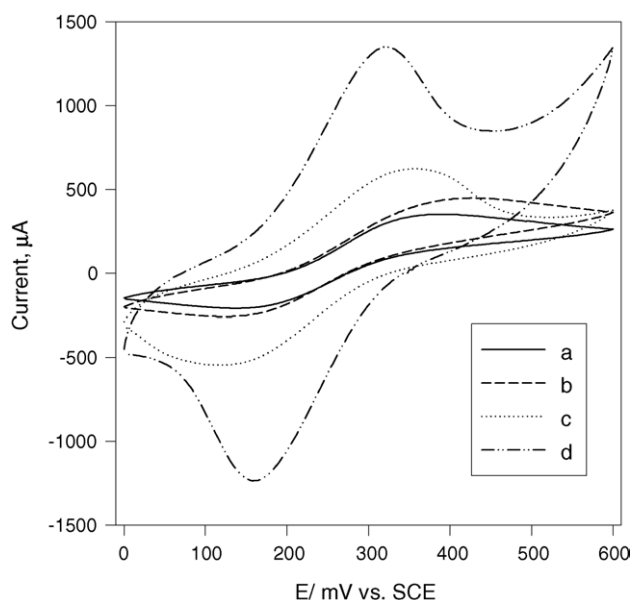


Fig. 2. Cyclic voltammograms in 20 mM Fe(CN)<sub>6</sub><sup>4–</sup> and 0.2 M KCl at 20 mV s<sup>–1</sup> for four kinds of electrodes: (a) CPE, (b) CNTPE, (c) Pt-CPE, and (d) Pt-CNTPE.

for four different types of electrodes: CPE, CNTPE, Pt-CPE, Pt-CNTPE. As shown in Fig. 2, small redox peaks were observed at the CPE and CNTPE, while for the Pt-CPE and Pt-CNTPE, well-defined CVs, characteristic of the Fe<sup>2+/3+</sup> redox couple were observed at 0.17 and 0.32 V. The small peak current of CNTPE may be due to the semiconducting properties of CNT and the increased peak current of Pt-CPE and Pt-CNTPE were because of large geometry and surface area according to Randles–Sevcik equation (Bard and Faulkner, 2002; Hrapovic et al., 2004),

$$I_p = 2.69 \times 10^5 AD^{1/2}n^{3/2}\gamma^{1/2}C$$

where  $A$  represents the area of the electrode (cm<sup>2</sup>),  $n$  is the number of electrons participating in the reaction and is equal to 1,  $D$  is the diffusion coefficient of the molecule in solution and is  $(6.70 \pm 0.02) \times 10^{-6}$  cm<sup>2</sup> s<sup>–1</sup>,  $C$  is the concentration of the probe molecule in the solution and is 20 mM, and  $\gamma$  is the scan rate (V s<sup>–1</sup>). The Pt-CNT electrodes exhibit the highest electroactive surface area, the average value of the electroactive surface area for the optimized Pt-CNT electrode (600 mg CNT added into 1 ml of Pt-silicate sol) was  $(1.18 \pm 0.1)$  cm<sup>2</sup> ( $n = 6$ ) compared to  $(0.50 \pm 0.2)$  cm<sup>2</sup> for the Pt-CPE.

The advantages of the new composite CNT electrode were first illustrated in connection with the detection of hydrogen peroxide. The excellent electrocatalytic activity of the electrode toward H<sub>2</sub>O<sub>2</sub> means that the electrode can provide a signal transduction in the fabrication of biosensors as H<sub>2</sub>O<sub>2</sub> is a product of a number of oxidase-based enzyme reactions. Fig. 3 displays typical hydrodynamic voltammograms for 2 mM H<sub>2</sub>O<sub>2</sub> at the CPE, Pt-CPE, CNTPE and Pt-CNTPE composite electrodes over the potential range 0.0–1.0 V. For the CPE electrode, no current response was observed with

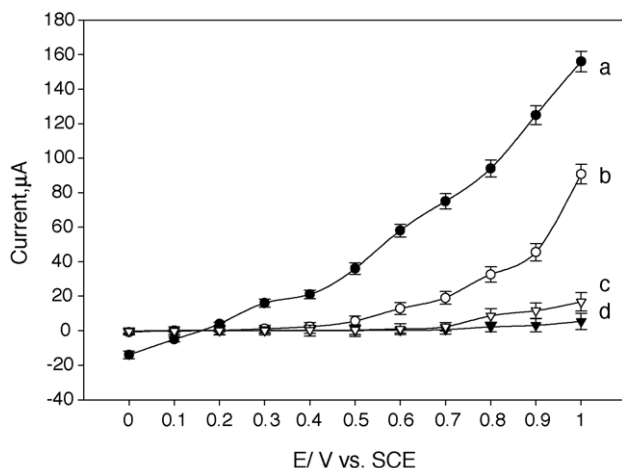


Fig. 3. Hydrodynamic voltammograms for 2 mM hydrogen peroxide at the (a) Pt-CNTPE, (b) CNTPE, (c) Pt-CPE, (d) CPE electrodes. Error bars =  $\pm$ S.D. and  $n = 4$ .

potentials lower than 0.6 V, with the increasing of potential, a small gradual increase of the response was observed. Similar results were observed at the Pt-CPE electrode with a slight increase of the signal due to the introduction of Pt nanoparticles. The CNTPE displayed a significantly larger response over the entire potential range, starting from around 0.1 V. While for the Pt-CNTPE, the current response was further increased. This was because the electrode combined the electrocatalytic activity of both CNT and Pt nanoparticles toward hydrogen peroxide.

The combination of CNT and Pt nanoparticles facilitated low-potential amperometric detection of hydrogen peroxide

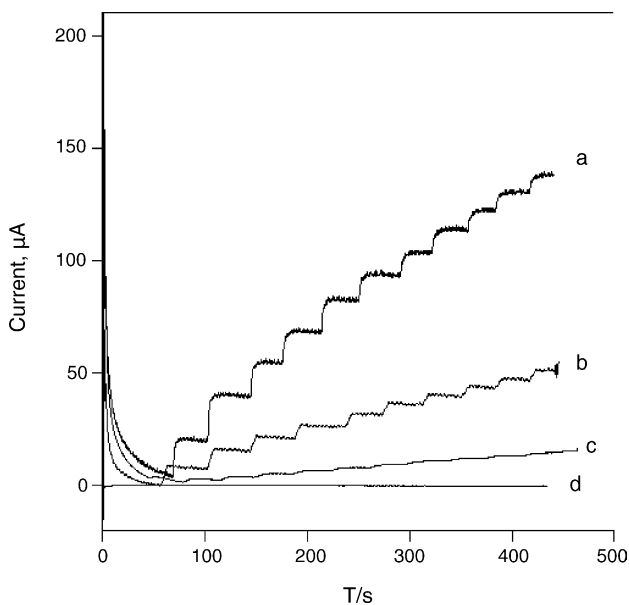


Fig. 4. Current-time recordings for successive addition of 2 mM hydrogen peroxide at the (a) Pt-CNTPE, (b) CNTPE, (c) Pt-CPE, and (d) CPE electrodes. Operating potential, +0.4 V.

with a relatively high sensitivity and wide dynamic range. Fig. 4 compares the response to increasing levels of hydrogen peroxide in 2 mM steps at the CPE, Pt-CPE, CNTPE and Pt-CNTPE electrodes at potential of 0.4 V. As expected from the voltammetric curve, the CPE gives no response signal to the addition of hydrogen peroxide at this low detection potential, and for the Pt-CPE electrode, a slight increase of the response signal was observed. In contrast, the CNTPE and Pt-CNTPE respond rapidly to the changes of the concentration, reaching a steady-state signal within 5 s, and the Pt-CNTPE electrode displays a higher sensitivity than CNTPE, which could also be expected from the voltammetric data. As seen from Fig. 4, a similar noise level is observed for CNTPE as compared to Pt-CNTPE and also for CPE as compared to Pt-CPE. Repeated use of the Pt-CNTPE electrode did not affect its performance with good reproducibility obtained. For example, 1 mM hydrogen peroxide was measured ten times, and a relative standard deviation (R.S.D.) of 4.8% was obtained. Excellent reproducibility seems to mean that no CNT and Pt nanoparticles were leaked out from the electrode surface which indicates the stability advantage of the sol-gel binder.

The effect of the ratio of EDAS to MTMOS (v/v) on the Pt-CNTPE electrode performance was tested and a sol-gel composition of 40% EDAS and 60% MTMOS showed good stability and low background currents and was used in all experiments.

The effect of Pt nanoparticle loading was also investigated. Different Pt nanoparticle loadings were made by further dilution of the original  $\text{H}_2\text{PtCl}_6$  solution. The nanoparticle loading was found to have a significant effect on the response of the Pt-CNTPE toward hydrogen peroxide. As seen from Fig. 5(A), dilution of the original  $\text{H}_2\text{PtCl}_6$  solution concentration resulted in a slight decrease of the current signal at first, and then a sharp decrease is observed with further dilution, which might be due to the decrease of the nanoparticle concentration and as a result the synergistic effect alleviated. Therefore, 0.01 M of  $\text{H}_2\text{PtCl}_6$  solution was used for the preparing of the Pt-silicate sol.

The influence of the CNT content was also examined. The sol-gel composite had poor mechanical stability and the CNT leaked easily from the electrode surface for composite containing higher than 70 wt.% CNT. As the content of the sol was steadily increased, the response of the electrode to hydrogen peroxide improved steadily (Fig. 5B). Composite containing less than 25 wt.% of CNT resulted in a large background current.

The influence of the CNT content was also examined using cyclic voltammetry and resistance experiments. The CV ferrocyanide cathodic and anodic peaks increased with the increasing of the CNT content from 25 to 60 wt.%. Nearly identical peak separations of 0.15 V were observed (Fig. 2d). When the CNT content was higher than 60 wt.%, a larger peak separation was observed. Fig. 6 displays the influence of the CNT loading upon the resistance of the composite electrode. As expected, high content of silicate sol in the composite (containing less than 15 wt.% CNT) resulted in



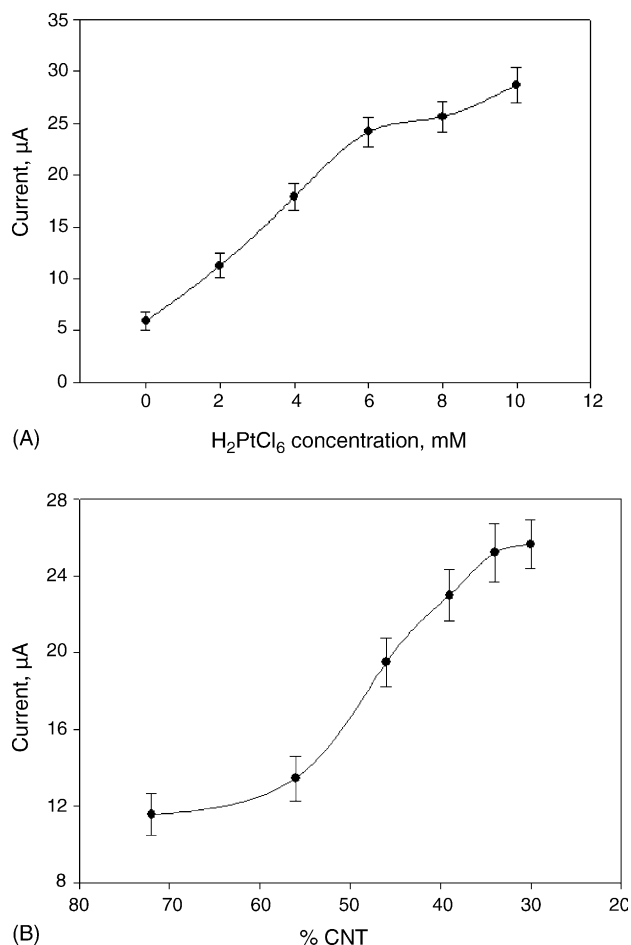


Fig. 5. Optimization of the H<sub>2</sub>PtCl<sub>6</sub> solution concentration (A) and CNT content in the sol-gel composite matrix with respect to amperometric response of 2 mM hydrogen peroxide at 0.4 V vs. SCE. Error bars =  $\pm$ S.D. and  $n = 4$ .

high resistance. Decrease the sol content would cause the resistance decrease. Thus composite containing 35 wt.% CNT and 65 wt.% of Pt-silicate sol was used for the fabrication of electrodes.

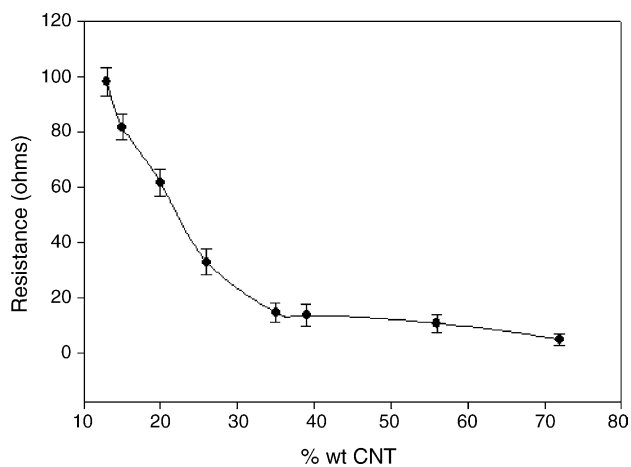


Fig. 6. Effect of the CNT loading upon the electrode resistance. Error bars =  $\pm$ S.D. and  $n = 4$ .

### 3.3. Electrochemical performance of the glucose biosensor

The excellent performance of the new composite electrode toward detection of hydrogen peroxide makes it attractive for the fabrication of oxidase based biosensors. Glucose oxidase was selected as a model enzyme, and the CNTPE and Pt-CNTPE electrodes were used to incorporate the enzymes based on the above investigations. The influence of the GOx loading upon the response to glucose was tested. Increasing the enzyme loading in silicate sol solution from 5 to 25 mg/ml enhanced the linear range and, hence, the sensitivity of the biosensor (Lawrence et al., 2004). When the enzyme concentration was 5 mg/ml, a linear range up to 10 mM glucose was observed at 0.1 V, with the concentration increased to 25 mg/ml, the linear range was observed increased up to 25 mM at 0.1 V. While too high an enzyme concentration will result in the leakage of the enzyme from the sensor surface and affect the stability of the sensor, 25 mg/ml of enzyme concentration was selected.

Fig. 7 shows the amperometric response at the CNTPE/GOx and Pt-CNTPE/GOx biosensors to successive addition of 2 mM glucose using detection potential of 0.6 V (A) and 0.1 V (B), along with the resulting calibration plots (insets). At 0.6 V, both of the two biosensors response rapidly to the addition of glucose ( $t_{95\%} < 10$  s), yet the Pt-CNT-based biosensor displays substantially larger signals. The difference is even more obvious at the potential of 0.1 V, where the current signal of the CNT biosensor decrease greatly, while the Pt-CNT biosensor still maintained strong response ( $t_{95\%} < 15$  s). Note that the two biosensors have similar CNT content and enzyme loading, indicating that the substantial higher sensitivity and wider linear range were due to the combinational effect of Pt nanoparticles and CNT, which result in improved electrocatalytic activity. The detection at 0.6 V is coupled to good linearity from 0.1 to 35 mM for the Pt-CNTPE/GOx biosensors (correlation coefficient of 0.998), and for the CNTPE/GOx biosensors a linear range from 0.1 to 35 mM can also be observed with a slight curvature at high levels (correlation coefficient of 0.991), while at 0.1 V good linearity ranging from 1 to 25 mM was also observed for the Pt-CNTPE/GOx biosensors, however, for the CNTPE/GOx biosensors, a narrow response from 1 to 10 mM glucose was found.

One advantage of the new composite biosensor, like the conventional carbon paste biosensor, is its renewability. In a successive 10 measurements with 2 and 20 mM glucose at 0.1 V, each measurement performed on a freshly polished surface, an excellent R.S.D. of 5.1% and 6.4% were obtained, respectively. Six biosensors were prepared in the same batch of composite paste, and a R.S.D. of 6.5% was observed.

The interferences from electroactive compounds commonly present in physiological samples of glucose such as ascorbic acid, uric acid and acetaminophen used to cause problems in the accurate determination of glucose. The potential interference was examined in detail. At 0.6 V, the response

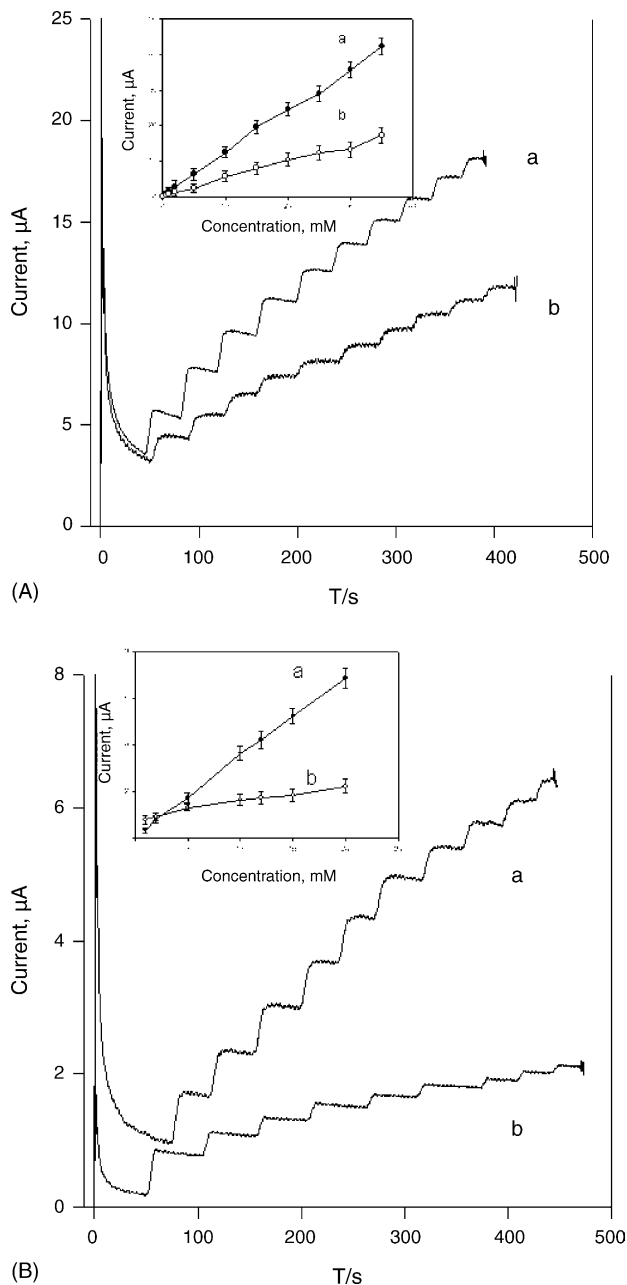


Fig. 7. Current–time recordings for successive addition of 2 mM glucose at the (a) Pt-CNTPE-GOx and (b) CNTPE-GOx biosensors measured at (A) 0.6 and (B) 0.1 V vs. SCE. Insert is the calibration curve. Error bars =  $\pm$ S.D. and  $n = 4$ .

of the Pt-CNT glucose biosensor was affected by the addition of 0.1 mM ascorbic acid, uric acid and acetaminophen, respectively, as these species also yielded response current at the electrode surface. The response signals of uric acid and acetaminophen were nearly eliminated at the potential of 0.1 V, while the addition of 0.1 mM ascorbic acid still resulted in oxidation current. However, high sensitivity of the biosensor towards glucose made the interference of ascorbic acid negligible. The interference-free determination of glucose was demonstrated by an independent recovery test.

The recovery test was carried out at 0.1 V in 10 ml phosphate buffer containing real physiological samples (0.5 ml serum). By using standard addition method, aliquots of standard glucose solution (8 mM) were added to the assay solution. The assays were performed ten times with the results in the range of 103–108%, which illustrated the reliability of the results of the biosensor.

The storage stability of the Pt-CNT glucose biosensor was also studied. When not in use, the biosensor was stored dry at 4 °C, the response to 1 mM glucose was studied intermittently. In the first 3 days, the response decreased to about 90% of its initial value, the strong response decrease maybe due to the leakage of those enzymes not stably incorporated within the sol–gel matrix, after which a steady current signal was obtained. One month later, the biosensor could still maintain 80% of the sensitivity, which was in good agreement with the former report of high stability of enzymes in silicate-based composites (Kumar et al., 2000).

#### 4. Conclusions

In this paper, we have demonstrated a new CNT composite biosensor with Pt nanoparticles doped sol–gel serves as the electrode binder. The sol–gel matrix was chosen with both Si–OH and the  $-\text{NH}_2$  groups capable to stabilize the metal nanoparticles from aggregation. Through this procedure, the electrocatalytic activity of Pt nanoparticles and CNT toward hydrogen peroxide could be combined together easily to gain a synergistic effect, and the performance of the resulting electrode improved greatly with a dramatic decrease in the over-voltage of hydrogen peroxide and an increase of sensitivity. The proposed modified electrode system is especially valuable when used in conjugation with an enzyme, which has been experimentally illustrated with glucose oxidase. The Pt-CNT glucose biosensor is characterized with high sensitivity, fast response and low interferences.

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