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Fabrication of ternary CNT/PPy/K_xMnO_2 composite nanowires for electrocatalytic applications

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ABSTRACT

CNT/PPy/K_xMnO_2, a novel ternary core–shell nanowires, was successfully prepared by a two-step self-assembly method and utilized as an electrocatalyst for the oxidation of hydrogen peroxide. The as-synthesized products were characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), energy dispersive X-ray (EDX) spectroscopy and Fourier-transform infrared spectra (FTIR) measurements. The results exhibited that the K_xMnO_2 nanosheets were grown on the surface of CNT/PPy core–shell nanotubes. The planes of the K_xMnO_2 nanosheets were more or less perpendicular to the CNT/PPy nanotubes. Cyclic voltammetry (CV) results demonstrated that the CNT/PPy/K_xMnO_2 composite nanowires, as a nonenzyme catalyst, performed well with regards to the oxidation of hydrogen peroxide in 0.1 M phosphate buffer solution (pH 7.0). The composite had a fast response with a linear range of 5.0 μM to 9.7 mM and a relatively low detection limit of 2.4 μM (S/N = 3). The sensitivity of the sensor for H_2O_2 was 114.6 μA mM^{-1} cm^{-2}. These excellent properties might be due to the large surface area of the composite nanowires and the quick electron transfer promoted by the combination of CNT and PPy.

1. Introduction

It has been well established that hydrogen peroxide (H_2O_2) has wide applications in industrial processes as a universal oxidant. Furthermore, it has emerged as a very important intermediate in environmental, biological and medicinal reactions. Therefore, the rapid and accurate detection of H_2O_2 becomes more and more important in the field of environment science and biotechnology. Up to now, many methods have been employed for the determination of H_2O_2, such as titrimetry [1] spectrophotometry [2,3], fluorometric [4,5] and chemiluminescence [6]. Above them, electroanalytical methods are suitable for the determination of H_2O_2 for their simple devices, rapid response time and low detection limits. Specially, as enzymes could accelerate the electron transfer between H_2O_2 and the electrode, electrochemical biosensors based on the immobilized enzymes for H_2O_2 sensing have attracted more and more attention due to their high sensitivity and selectivity [7–10]. However, the enzyme-modified electrodes for the determination of H_2O_2 have many disadvantages, such as difficult immobilization, instability, and high cost of the enzymes, which limit their practical applications. In the past few years, scientists have developed many methods for the electrochemical determination of H_2O_2 without using enzymes [11–13]. For example, we have used the noble metal nanoparticle composites modified electrodes as an electrochemical sensor for the detection of H_2O_2 [14,15].

Since first discovery in 1991 [16], carbon nanotubes (CNTs) have been widely used in the field of electrochemistry for their excellent performance. CNTs can not only achieve large active surface at electrodes but also enhance the electron transfer between the electrode and the analytes. For the detection of H_2O_2, several enzyme or non-enzyme modified electrodes based on the CNTs have been fabricated. For example, Wang et al. reported an electrochemical biosensor based on a CNT/SiO_2 sol–gel architecture, which immobilizes horseradish peroxidase [17]. Salimi et al. reported SWCNTs–manganese complex modified GCE as a non-enzymatic H_2O_2 sensor [18]. Meanwhile, conducting polymers have attracted considerable attentions for their applications in electrochemistry, taking advantages of their high conductivity, easy preparation and good environmental stability. As one of the most promising organic conducting polymers, polypyrrole (PPy) is of great practical interest [19,20]. In particular, composite materials based on the coupling of conducting polymers and CNTs have been widely studied because they might exhibit a novel property different from the individual components due to a synergistic effect [21]. In the past few years, many efforts have been tried to fabricate CNT/conducting polymer nanocomposites. Peng et al. reported the electrochemical co-deposition of CNT with a series of conducting polymers, including polyaniline (PANI), PPy and poly[3,4-ethylenedioxythiophene] (PEDOT), and illustrated the different capacitance changing performances of the films [22]. New PPy/CNT composite nanowires

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have also been fabricated [23]. With the dopant of CNT, it is easy for PPy to grow into the pores of a host membrane involving an electrochemical procedure.

MnO_2 is a good candidate for H_2O_2 sensors because of its excellent catalytic oxidation property. In the past few years, several kinds of MnO_2 nanostructures were prepared and used to construct sensors to detect H_2O_2. Schachl et al. reported the fabrication of MnO_2 modified carbon paste electrode for H_2O_2 sensing in flow injection analysis and a low detection limit was obtained [24]. Lin et al. reported the preparation of a nano-structured cryptomelane-type MnO_2 modified carbon paste electrode for the amperometric determination of H_2O_2 with a low potential [25]. Zhang et al. also fabricated MnO_2 microspheres/Nafion composite modified glass carbon electrode for electrocatalytic of H_2O_2 in phosphate buffer solution (PBS) [26]. These MnO_2 modified electrodes exhibited a good catalytic oxidation of H_2O_2. However, it is still a great challenge to enhance the performance of the electrode, including the sensitivity, the detection limit and the selectivity. In this paper, we have presented a novel functional ternary core–shell nanowire, CNT/PPy/K_xMnO_2, and investigated its electrochemical properties for the determination of H_2O_2. The as-prepared CNT/PPy/K_xMnO_2 composite nanowires have the advantages of strong catalysts of K_xMnO_2 and excellent electron conductor of CNT/PPy. The studies showed that the CNT/PPy/K_xMnO_2 composite nanowires modified electrode exhibited an excellent electrocatalytic oxidation activity for H_2O_2. The sensor possesses a high sensitivity, a low detection limit and a good selectivity.

2. Experimental

2.1. Chemicals and reagents

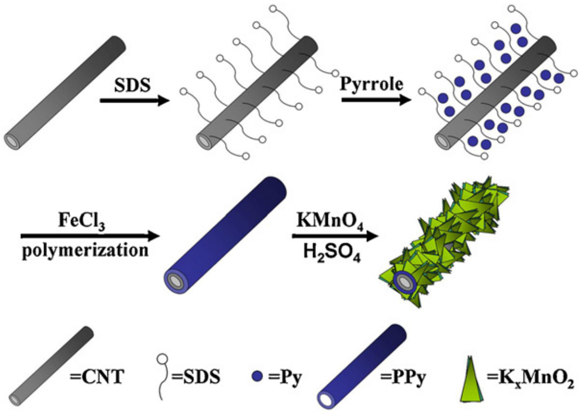
The purity of carbon nanotube (CNT) (Shenzhen Nanotech Port Co., Ltd.) was 95.0%. All the other reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. and used without further purification, including pyrrole (Py) monomer, ferric chloride ($FeCl_3{\cdot}6H_2O$), dodecyl sulfate sodium (SDS), ethanol, potassium permanganate ($KMnO_4$), sulfuric acid (H_2SO_4), hydrogen peroxide (H_2O_2) (30%), sodium nitrate ($NaNO_3$), potassium chloride (KCl), glucose, acetic acid and citric acid. 0.1 M phosphate buffer solution (PBS, pH 7.0) was prepared with 0.1 M Na_2HPO_4 and 0.1 M NaH_2PO_4, both of which contain 0.1 M NaCl. H_2O_2 aqueous solution was prepared freshly with 30% H_2O_2 just before use.

2.2. Preparation of core–shell CNT/PPy nanostructures

In a typical procedure, 0.015 g SDS and 0.075 g CNT were dispersed into 150 mL of deionized water with ultrasonication. The slurry was vigorously stirred for 2 h at room temperature. Then, 0.15 g Py monomer was added into the above solution. The prepared solution was stored in refrigerator for 10 min so that it could cool down to 0 °C. To begin the polymerization, 15 mL of 0.15 M $FeCl_3{\cdot}6H_2O$ was added dropwise into the mixture. The reaction was on with ultrasonication for about 10 min and then stirred for another 2 h. The black products were obtained through filtering, water washing and were then dried in vacuum at 40 °C overnight.

2.3. Preparation of ternary CNT/PPy/K_xMnO_2 composite nanowires

To prepare the ternary core–shell–shell CNT/PPy/K_xMnO_2 nanowires, 0.008 g CNT/PPy was dispersed into 9 mL of 2 M H_2SO_4 and the mixture was heated to 90 °C. After the addition of 0.04 g $KMnO_4$, the reaction was on at the same temperature for 10 min. The products were filtered and washed by water and ethanol for several times. Finally, they were dried in vacuum at 40 °C overnight.



Scheme 1. Schematic of the preparation of CNT/PPy/K_xMnO_2 composite nanowires.

2.4. Preparation of the modified electrodes

Prior to modification, the bare glassy carbon disk electrode (GCE) was polished with emery papers and slurries of alumina polishing powder to a mirror finish. After each polishing, the electrode was sonicated in ethanol and distilled water for 0.5 min, respectively, in order to remove any adhesive substances on the electrode surface. To modify the electrode, 4.5 μL CNT/PPy/K_xMnO_2 hybrid nanowires dispersion solution (1 mg/mL in ethanol) was mixed with 0.5 μL 5% Nafion (in ethanol). Then the mixture was sonicated about 10 min. Finally, the suspension was dropped on GCE surface and dried under ambient atmosphere.

2.5. Apparatus

Transmission electron microscopy (TEM) measurements were performed on a Hitachi H-8100 electron microscope with an acceleration voltage of 100 kV. X-ray diffraction patterns (XRD) were obtained with a Siemens D5005 diffractometer using Cu Ka radiation. Energy Dispersive X-ray analysis (EDX) was done using a SEM (SHIMADZU SSX-550 microscope) coupled to an X-ray detector for EDX analysis. Fourier-transform infrared (FTIR) spectra of KBr powder-pressed pellets measurements were recorded on a BRUKER VECTOR 22 spectrometer. The electrochemical performance of nanocomposites was investigated by using CV with a CHI660B Electrochemical Station (Shanghai CHENHUA instrument Co. Ltd.). In a three-electrode system, a modified GCE (Φ3.0 mm), a platinum wire and a saturated calomel electrode (SCE) were used as the working electrode, the counter electrode and the reference electrode, respectively.

3. Results and discussion

3.1. Formation and morphology of the ternary CNT/PPy/K_xMnO_2 composite nanowires

The process for fabricating the ternary CNT/PPy/K_xMnO_2 composite nanowires involves two main steps, which is shown in Scheme 1. Firstly, the core–shell structured CNT/PPy composite nanotubes are fabricated through a chemical oxidation polymerization in the presence of SDS. Then K_xMnO_2 nanosheets are deposited on the surface of CNT/PPy composite nanotubes via the following reaction:

$$4MnO_4^- + 4H^+ \rightarrow 4MnO_2 + 3O_2 + 2H_2O$$

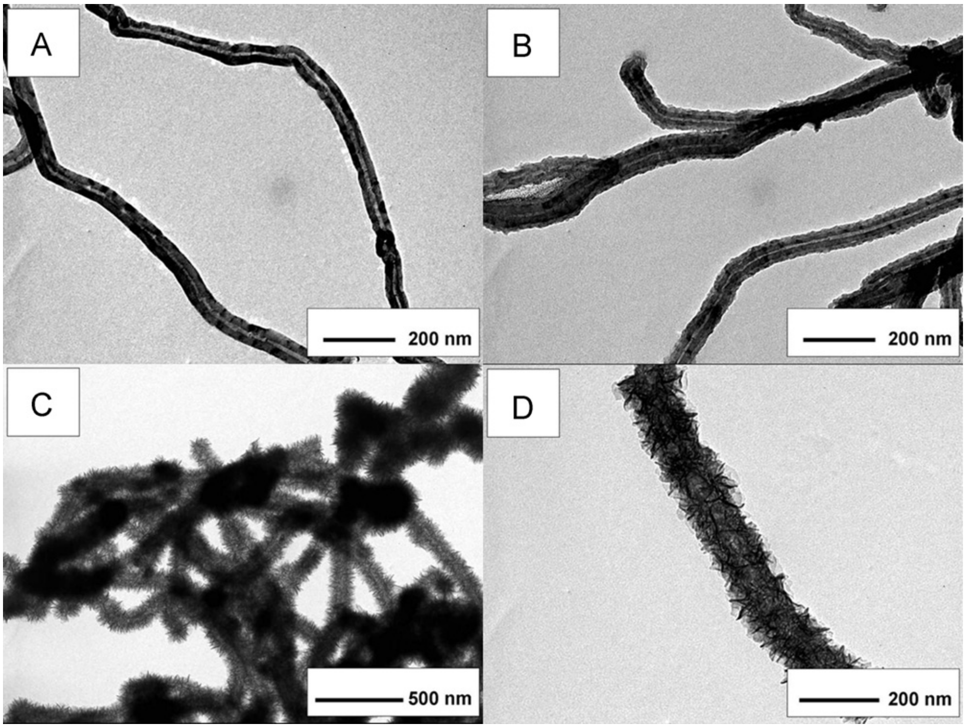


Fig. 1. TEM images of (A) CNTs, (B) CNT/PPy nanocomposites and (C and D) CNT/PPy/K_xMnO_2 nanowires at different magnification.

During the reaction, the cation of K^+ could be intercalated between the layered structure of MnO_2 to form K_xMnO_2. Detailed structures of CNT, CNT/PPy and CNT/PPy/K_xMnO_2 have been displayed by TEM, as shown in Fig. 1. Generously, the diameters of CNTs used range from 40 to 60 nm (Fig. 1A). With the oxidation of polymerization of pyrrole by $FeCl_3$, a PPy shell with uniform thickness about 10 nm was obtained (Fig. 1B). Fig. 1C and D show the images of the finally achieved ternary CNT/PPy/K_xMnO_2 composite nanowires. It is observed that the surface of CNT/PPy/K_xMnO_2 hierarchical nanostructures becomes rough compared with that of the obtained CNT/PPy composite nanotubes. The K_xMnO_2 nanosheets are aligned with their planes more or less perpendicular to the CNT/PPy nanotubes. It has been clearly shown that the obtained CNT/PPy/K_xMnO_2 hierarchical composite nanowires exhibited core–shell morphology, with CNT/PPy nanotubes in the core and K_xMnO_2 nanosheets coated on the surface. The TEM images also confirm that the surface of the CNT/PPy nanotubes was fully covered by the K_xMnO_2 nanosheets. The average edge length of the CNT/PPy/K_xMnO_2 nanowires is 150 nm (Fig. 1D). Taking their small sizes and two dimensional morphologies into consideration, it is expected that those ternary CNT/PPy/K_xMnO_2 composite nanowires with relatively high surface areas could display excellent performances in electrochemical catalytic applications.

3.2. Characterization of the ternary CNT/PPy/K_xMnO_2 composite nanowires

The chemical structure of the obtained ternary CNT/PPy/K_xMnO_2 composite nanowires has been characterized by XRD, EDX and FTIR measurements. Fig. 2 shows XRD patterns of the CNT/PPy nanostructures before and after the coating by K_xMnO_2 nanosheets. In curve A, the sharp peak at the position of 25.9° belongs to CNTs, which could be hardly observed after the formation of CNT/PPy/K_xMnO_2 hierarchical nanostructures. This could be due to the thick layer of K_xMnO_2 shell and its good crystallinity. In curve B, two diffraction peaks at 36.8° and 65.9° for K_xMnO_2 nanostructures are observed. These two peaks correspond to (006) and (119) Bragg reflection of MnO_2, respectively, which are in agreement with the XRD patterns of birnessite-type MnO_2. These results proved that the core–shell CNT/PPy nanotubes had been coated by K_xMnO_2 after the reaction. Fig. 3 shows the EDX spectrum of the CNT/PPy/K_xMnO_2 sample. At 0.34 keV, N element has a peak, part of which is overlapped by the peak of O element. In addition, significant peaks of the elements of Mn, C and K also appear in the EDX spectrum. Both the XRD and EDX results confirm the formation of the CNT/PPy/K_xMnO_2 composite nanowires.

Fig. 4 displays the typical FTIR spectra of the CNT/PPy nanotubes and the ternary CNT/PPy/K_xMnO_2 composite nanowires, respectively. It shows that the characteristic bands of the CNT/PPy nanostructures are the pyrrole ring fundamental vibrations, which are at 1561 cm^{-1} (C=C stretching), 1463 cm^{-1} (C—C stretching),

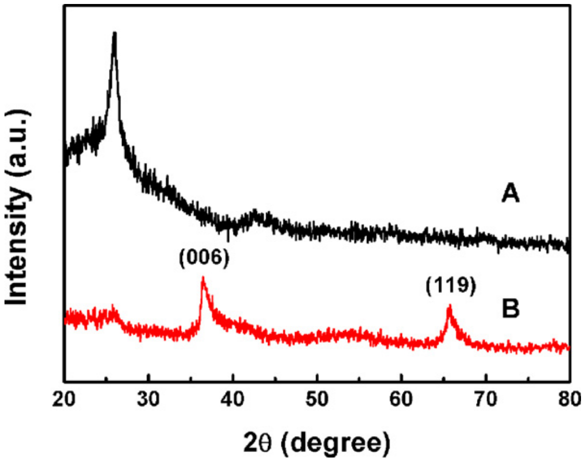


Fig. 2. X-ray diffraction patterns of (A) CNT/PPy nanocomposites and (B) CNT/PPy/K_xMnO_2 nanowires.

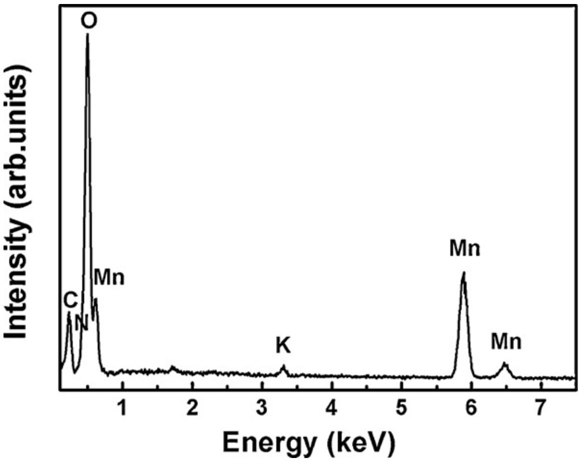


Fig. 3. EDX spectrum of CNT/PPy/K_xMnO_2 composite nanowires.

1020 cm^{-1} (C—H deformation vibration), 664 cm^{-1} (C—H out of plane vibration) and 3443 cm^{-1} (N—H stretching mode). The peak at 1634 cm^{-1} refers to C—C vibration in CNTs. Compared to the CNT/PPy nanotubes, an extra peak is found in FTIR spectrum of the ternary CNT/PPy/K_xMnO_2 composite nanowires at 541 cm^{-1}, which is corresponding to the Mn—O bond, indicating the formation of the K_xMnO_2 nanosheets.

3.3. Electrochemical performances of the ternary CNT/PPy/K_xMnO_2 composite nanowires modified electrode for hydrogen peroxide sensing

3.3.1. Cyclic voltammetric detection of H_2O_2

Fig. 5A shows the cyclic voltammograms (CV) of H_2O_2 at bare GCE and CNT/PPy/K_xMnO_2 modified GCE. At bare GCE, little response to 0.8 mM H_2O_2 in PBS (0.1 M, pH 7.0) within the applied potential is observed, which interprets that H_2O_2 oxidation could not be achieved at bare GCE (curve a and b). For modified GCE, an obvious peak in 0.7 V appears, attributing to oxidation of H_2O_2 with K_xMnO_2 reduced to Mn^{2+} or Mn^{3+}. The oxidation peak current is much larger than that of bare GCE, indicating the good performance of the prepared nanomaterials. CVs of CNT/PPy/K_xMnO_2 modified GCE for the oxidation of H_2O_2 with different concentrations ranging from 0 to 0.8 mM are shown in Fig. 5B. With the addition of H_2O_2, the oxidation current increases generously, from −6.8 to −20.5 μA. The peak current has a good linear relationship with the concentrations of H_2O_2, with the regression coefficient of 0.9994. Fig. 5C shows the relationship of the peak current and scan rate, in the presence of 0.5 mM H_2O_2. The peak current increases linearly with the scan rate in the range of 20–180 mV/s, indicating that a surface-controlled process has involved in the oxidation of H_2O_2.

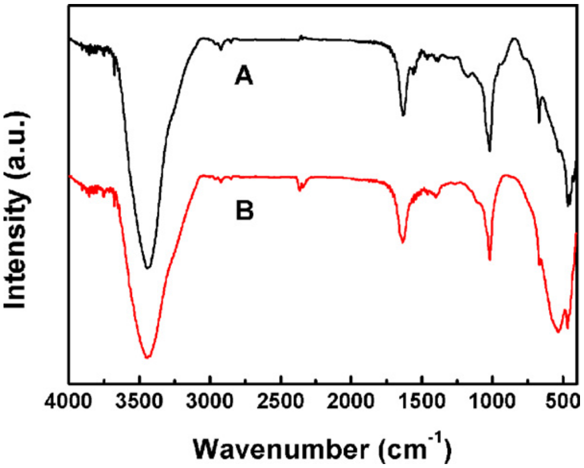


Fig. 4. FTIR spectra of (A) CNT/PPy nanocomposites and (B) CNT/PPy/K_xMnO_2 nanowires.

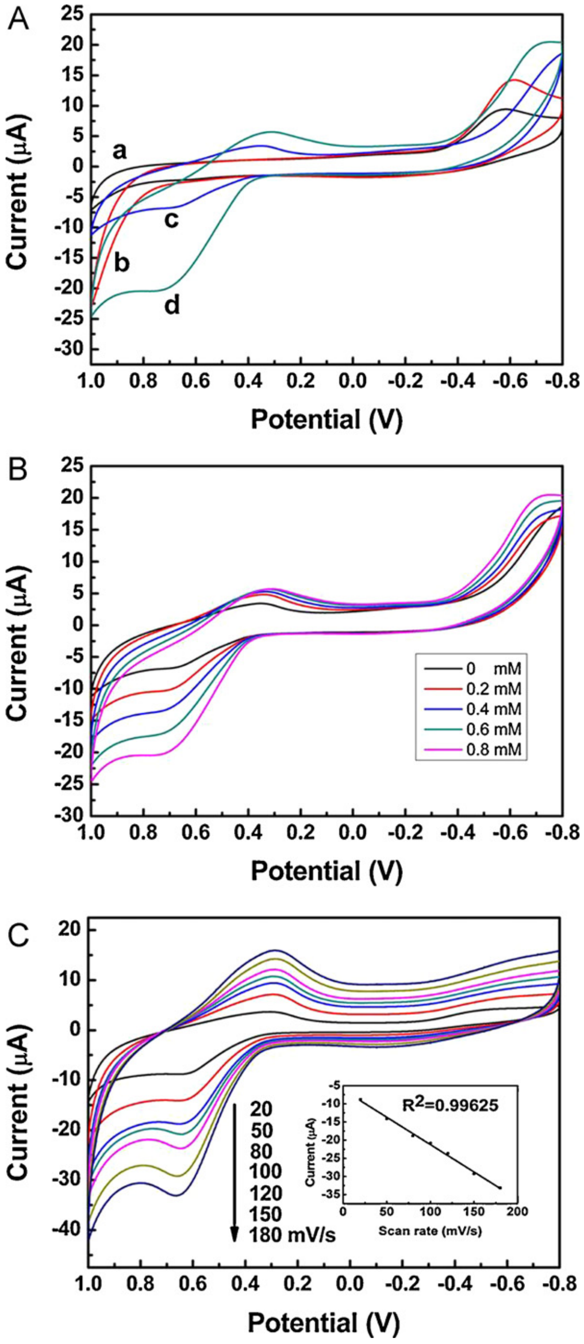


Fig. 5. (A) CVs of H_2O_2 oxidation at the bare GCE (a and b) and GCE modified by CNT/PPy/K_xMnO_2 nanowires (c and d) in a 0.1 M PBS in the absence (a and c) and presence of 0.8 mM H_2O_2 (b and d). The scan rate is 100 mV/s. (B) CVs of modified GCE in 0.1 M PBS (pH 7.0) in the presence of H_2O_2 with different concentrations. Scan rate: 100 mV/s. (C) CVs of modified GCE in 0.1 M PBS (pH 7.0) in the presence of 0.5 mM H_2O_2 with different scan rates. The inset shows the calibration plot of oxidation peak current of H_2O_2 verse scan rate.

3.3.2. Amperometric detection of H_2O_2 and the pertinent calibration curve

The amperometric response of the modified electrode has been investigated in 0.7 V by successively adding a certain amount

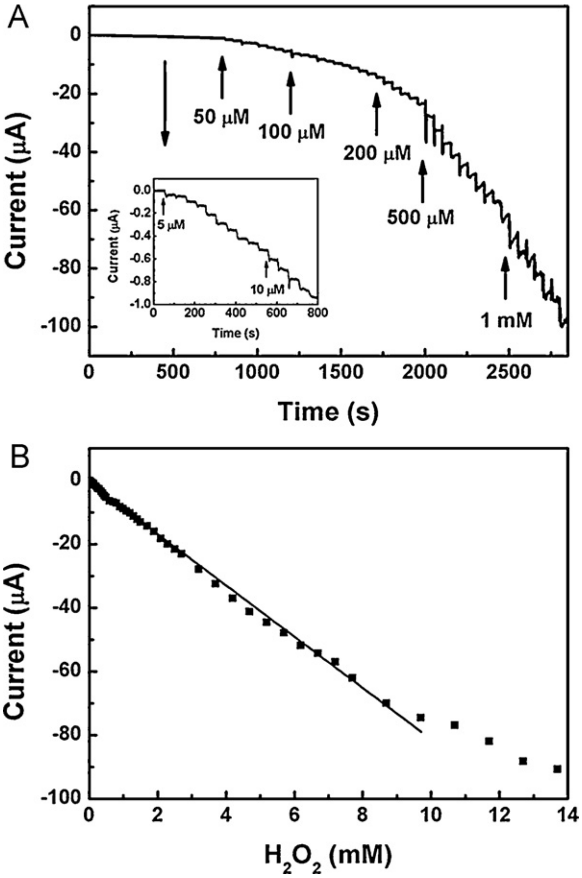


Fig. 6. (A) Amperometric *i*–*t* curves of modified GCE at the constant potential of 0.7 V in 0.1 M PBS (pH 7.0) with successive injection of H_2O_2. The inset shows amperometric *i*–*t* curve in the beginning. (B) The calibration curve of electrocatalytic current of H_2O_2 verses its concentrations.

of H_2O_2 to a continuous stirring PBS solution. Fig. 6A is the presentation of the typical *i*–*t* curve for the modified electrode. It has been seen that the amperometric sensor possesses a quick response to the changes of substrate's concentrations. The calibration curve (Fig. 6B) shows a linear response to H_2O_2 concentration in the range of 5.0 μM to 9.7 mM ($R^2 = 0.9973$). The sensitivity is calculated to be 114.6 μA mM^{-1} cm^{-2} and the detection limit is 2.4 μM based on a signal-to-noise ratio (S/N) of 3. The CNT/PPy/K_xMnO_2 nanowires modified electrode has a relative high sensitivity and a much wider linear range than certain MnO_2-based sensors [26–29]. The electrocatalytic performance of the prepared ternary core–shell nanostructure sensor is better than others using MnO_2 nanomaterials as electrode in one or more categories. This may be related to the higher specific surface area of the obtained CNT/PPy/K_xMnO_2 composite nanowires and the efficient electron transfer between K_xMnO_2 nanosheets and the electrode, which is similar to that of CNT/PPy/metal composite sensors.

3.3.3. Anti-interference property of the ternary CNT/PPy/K_xMnO_2 composite nanowires modified electrode and real sample measurement

It is known that some typical electroactive species may affect the response of the H_2O_2 during the electrochemical measurements. The most common interfering species including glucose, acetic acid, and citric acid were evaluated. It was found that the current responses almost did not change after addition of the same concentration of glucose, acetic acid and citric acid to H_2O_2 (Fig. 7). Also, the sensor has good anti-interference properties to NaCl and KCl, the commonest inorganic salts in human body fluids. As we measured, the currents changed 2.54% and 1.49% as the concentrations of NaCl and KCl were 1000-fold higher than that of H_2O_2, respectively. These results indicated that the ternary CNT/PPy/K_xMnO_2 composite nanowires modified electrode shows a good selectivity.

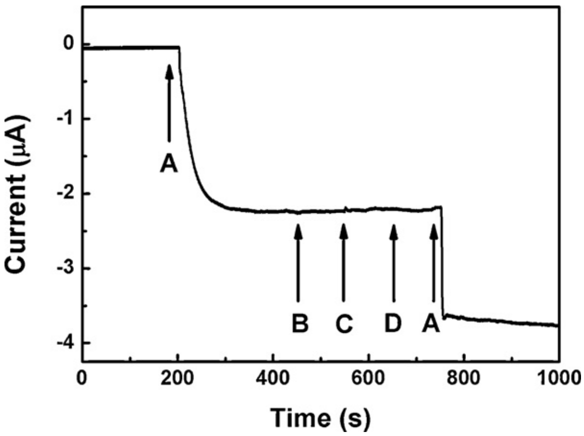


Fig. 7. Amperometric response of CNT/PPy/K_xMnO_2 nanowires modified GCE to (A) 0.2 mM H_2O_2 and different interferences, (B) 0.2 mM glucose, (C) 0.2 mM acetic acid, (D) 0.2 mM citric acid in a stirring 0.1 M PBS. The working potential is 0.7 V.

For practical application, we utilized the sensor to determine H_2O_2 in sterilized milk. 10 μL milk sample was added to 10.0 mL PBS, and the current response was recorded at +0.7 V. The recovery of H_2O_2 was determined by standard addition method. The initial concentration of H_2O_2 in the sample was 5.0 mM measured by the classical $KMnO_4$ titration method and 5.1 mM measured by our sensor. As we added 10 mM H_2O_2 into the milk, the current changed immediately. The recovery was about 92.6% and the relative standard deviation calculated from three separate experiments was 4.4%. The data are well accepted by practical use, which indicates that the ternary CNT/PPy/K_xMnO_2 composite nanowires modified electrode is promising for the determination of H_2O_2.

4. Conclusions

In summary, a novel ternary core–shell CNT/PPy/K_xMnO_2 composite nanowires has been fabricated by simply deposition of K_xMnO_2 nanosheets on the surface of CNT/PPy nanotubes. The ternary core–shell CNT/PPy/K_xMnO_2 composite nanowires modified electrodes show excellent electrocatalytic activity as an amperometric responder for the oxidation of H_2O_2. A low detection limit, a high sensitivity, a wide linear range and good anti-interference properties are obtained in our sensors for their high specific surface area and the efficient electron transfer between K_xMnO_2 nanosheets and the electrode by introducing the CNT and PPy. This kind of materials gives a new strategy for fabricating sensor materials and is promised to wide applications in nonenzymatic electrochemical sensors.

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References

[1] N.V. Klassen, D. Marchington, H.C.E. McGowan, Anal. Chem. 66 (1994) 2921–2925.
[2] R.C. Matos, E.O. Coelho, C.F. De Souza, F.A. Guedes, M.A.C. Matos, Talanta 69 (2006) 1208–1214.
[3] P.A. Tanner, A.Y.S. Wong, Anal. Chim. Acta 370 (1998) 279–287.
[4] T. Taniai, A. Sakuragawa, T. Okutani, Anal. Sci. 15 (1999) 1077–1082.
[5] I. Mori, K. Takasaki, Y. Fujita, T. Matsuo, Talanta 47 (1998) 631–637.
[6] J.C. Yuan, A.M. Shiller, Anal. Chem. 71 (1999) 1975–1980.
[7] Y.H. Song, L. Wang, C.B. Ren, G.Y. Zhu, Z. Li, Sens. Actuators B 114 (2006) 1001–1006.
[8] Q. Lu, X.C. Dong, L.J. Li, X. Hu, Talanta 82 (2010) 1344–1348.
[9] A. Salimi, E. Sharifi, A. Noorbakhsh, S. Soltanian, Electrochem. Commun. 8 (2006) 1499–1508.
[10] A. Salimi, E. Sharifi, A. Noorbakhsh, S. Soltanian, Biophys. Chem. 125 (2007) 540–548.
[11] E. Jin, X.F. Lu, L.L. Cui, D.M. Chao, C. Wang, Electrochim. Acta 55 (2010) 7230–7234.
[12] T.T. Zhang, R. Yuan, Y.Q. Chai, W.J. Li, S.J. Ling, Sensors 8 (2008) 5141–5152.
[13] Z.X. Zhang, H. Zhu, X.L. Wang, X.R. Yang, Microchim. Acta 174 (2011) 183–189.
[14] X.J. Bian, X.F. Lu, E. Jin, L.R. Kong, W.J. Zhang, C. Wang, Talanta 81 (2010) 813–818.
[15] L.R. Kong, X.F. Lu, X.J. Bian, W.J. Zhang, C. Wang, J. Solid State Chem. 183 (2010) 2421–2425.
[16] S. Iijima, Nature 354 (1991) 56–58.
[17] J.W. Wang, M. Gu, J.W. Di, Y.S. Gao, Y. Wu, Y.F. Tu, Bioprocess. Biosyst. Eng. 30 (2007) 289–296.
[18] A. Salimi, M. Mahdioun, A. Noorbakhsh, A. Abdolmaleki, R. Ghavami, Electrochim. Acta 56 (2011) 3387–3394.
[19] K. Maksymiuk, Electroanalysis 18 (2006) 1537–1551.
[20] R. Akinyeye, I. Michira, M. Sekota, A. Al-Ahmed, P. Baker, E. Iwuoha, Electroanalysis 18 (2006) 2441–2450.
[21] M. Hughes, G.Z. Chen, M.S.P. Shaffer, D.J. Fray, A.H. Windle, Chem. Mater. 14 (2002) 1610–1613.
[22] C. Peng, J. Jin, G.Z. Chen, Electrochim. Acta 53 (2007) 525–537.
[23] J. Wang, J.H. Dai, T. Yarlagadda, Langmuir 21 (2005) 9–12.
[24] K. Schachl, H. Alemu, K. Kalcher, J. Jezkova, I. Svancara, K. Vytras, Analyst 122 (1997) 985–989.
[25] Y.H. Lin, X.L. Cui, L.Y. Li, Electrochem. Commun. 7 (2005) 166–172.
[26] L. Zhang, Z. Fang, Y.H. Ni, G.C. Zhao, Int. J. Electrochem. Soc. 4 (2009) 407–413.
[27] S.J. Yao, J.H. Xu, Y. Wang, X.X. Chen, Y.X. Xu, S.S. Hu, Anal. Chim. Acta 557 (2006) 78–84.
[28] S.J. Yao, S. Yuan, J.H. Xu, Y. Wang, J.L. Luo, S.S. Hu, Appl. Clay Sci. 33 (2006) 35–42.
[29] S.B. Hocevar, B. Ogoreve, K. Schachl, K. Kalcher, Electroanalysis 16 (2004) 1711–1716.