

Fabrication of Gold Nanoparticles Modified Carbon Nanofibers/Polyaniline Electrode for H₂O₂ Determination

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Herein, a facile route to fabrication of carbon nanofibers/polyaniline/Au nanofibers (CPANFs) with tunable densities of gold nanoparticles (AuNPs) was proposed, and the potential application of the CPANFs as efficient electrochemical detector of H_2O_2 was demonstrated. First, carbon nanofibers (CNFs) were successfully obtained through the carbonization procedure using electrospun polyacrylonitrile (PAN) nanofibers as a precursor. Then, polyaniline (PANI) nanorods were coated on the CNFs by an in situ polymerization of aniline, in which AuNPs were homogenously distributed via gold-thiol binding interactions. Finally, an aqueous nafion solution was used to attach HRP-modified CPANFs to the pretreated glassy carbon electrode (GCE) for H_2O_2 detection. The fabricated electrochemical detectors for H_2O_2 exhibited a high sensitivity for detection of H_2O_2 with a detection limit of 0.18 μ M at signal-to-noise ratio of 3.

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Nanoelectrode-based biosensors have been researched widely in recent years, since nanoelectrodes possess considerable advantages over conventional electrodes, such as higher spatial resolution, lower background noise, and voltammetric time scales. Due to these advantages, biosensors based on nanoelectrodes have gradually been incorporated into target detection for various fields. Hydrogen peroxide (H₂O₂) is of particular interest because, as a strong oxidant and an industrial waste product, excess amounts of H₂O₂ in rain and groundwater could negatively impact the environment.^{1–3}

As reported in the literature, sensors are often composed of two functional materials to achieve the recognition and transduction processes. Therefore, the majority of recent research on biosensors has focused on the development of modified electrode materials with high sensitivity and transduction. As a type of conducting polymer, PANI has become an attractive class of materials for a variety of advanced properties similar to metal materials, while retaining the flexibility and processability of conventional polymers. Typically, the use of individual materials has intrinsic defects,^{4–6} so to improve upon electronic transduction, scientists combine PANI with carbon materials to form nanocomposites with superior performance.^{7–13} CNFs are one of the most promising materials for fabrication of nanoelectrodes because of their chemical stability, high surface area, electrical conductivity, and relatively low cost.

AuNPs are known to exhibit excellent optical and electronic properties in addition to their pronounced biocompatibility, which have been introduced onto the surface of conducting polymers for gene delivery^{14,15} and development of biosensors.¹⁶ Furthermore, AuNPs have been extensively used in electrochemical sensors due to their unique physicochemical properties.^{17–22} With regards to small, welldispersed AuNPs grafted onto substrate materials, the fabrication of biosensors with low detection limits and a wide dynamic range for H₂O₂ has become an intractable challenge for scientists.^{23,24}

In this work, CNFs were successfully obtained from the electrospun PAN nanofibers through a carbonization process. PANI nanorods were then doped with perchloric acid (HClO₄) and wrapped onto the surface of CNFs under nitrogen. PANI nanorods have been recently recognized as substrates of a new kind of 1-D support for the growth of metal nanoparticles.^{25–27} Various morphologies of PANI/Au nanostructures have been synthesized for the detection of ascorbic acid, glucose oxidase and glucose. In our work, the functional –SH groups allowed for AuNP loading through the chelating effect.^{28–30} In addition, they stabilize the small, uniform, well-dispersed AuNPs. The CPANFs with AuNPs homogeneously decorated on PANI nanorods wrapped by CNFs were developed. Combined the electrical/mechanical properties of CNFs/PANI nanostructure and biorelated functions of Au nanoparticles together, the resultant nanofibers are more biocompatible and they offer an advantageous microenvironment for facilitating direct electron transfer between H_2O_2 and the CPANF-modified GCE nanoelectrode.

Experimental

Materials.— Polyacrylonitrile (PAN), perchloric acid (HClO₄), aniline (PANI), dimethyl formamide (DMF), horseradish peroxidise (HRP), hydroquinone (HQ), phosphate buffer (PB) and thioglycolic acid (TA) were all purchased from Aladdin Chemistry Co., Ltd. Ammonium persulfate (APS) and chloroauric acid (HAuCl₄•4H₂O, 99.9%) were purchased from Shanghai Civi Chemical Technology Co., Ltd. All of the reagents were used without further purification. Deionized water (DIW, 18.2 M Ω) was used for all solution preparations.

Methods.—Synthesis of the carbon nanofibers (CNFs).—PAN nanofibers were obtained by electrospinning at an applied voltage of 12-15 kV. The PAN solution was fed at a speed of 0.6 mL/h with a distance of 20 cm between the tips of the needles with collection plate. CNFs were successfully obtained from PAN through carbonization by muffle furnace. The process that converts the PAN nanofibers to carbon nanofibers has two steps: pre-oxidation and high-temperature carbonization.³¹ In our work, the temperature of pre-oxidation and carbonization were controlled at 280°C and 1000°C, respectively under Ar. Meanwhile, the heating rate was set at 2°C/min.

Synthesis of the CNFs/PANI nanofibers (CPNFs).—CPNFs were achieved by in situ polymerization of aniline in the presence of CNFs. In a typical procedure, 50 mg CNFs was mixed with a 0.01 M aniline solution with moderate stirring. 4 mL HClO₄ was added into the suspension before polymerization. 20 min later, 1 mL ethyl alcohol was added dropwise into the three flasks with stirring. Then 40 mL 0.04 M APS was dropwise added to start the polymerization. An ice bath was used to keep the temperature at 0°C during the polymerization. The solution was left to react for 5 hours with mild stirring under low temperature. The as-prepared CPNFs were initially washed with deionized water and then alcohol three times, respectively. The precipitate was dried at 50°C for 36 hours.

Synthesis of the CNFs/PANI/Au nanofibers (CPANFs).—The CPANFs were obtained by in situ attachment of AuNPs. In a typical procedure, 0.5 g as-prepared CPNFs were immersed into 1 M NH₃.H₂O solution for dedoping. The treated CPNFs were then washed with deionized

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water for three times. Next, 0.6 g TA was added into the mixed solution containing 0.2 g as-prepared CPNFs, followed by vigorous stirring for 1 hour. The nanofibers were then filtered and washed with water and alcohol several times and redispersed in deionized water. 8.0 mL of 10 mM HAuCl₄ solution was added dropwise into the beaker and the solution reacted for 24 h under slightly stirring. Finally, the resulting black solution was filtered and the as-prepared CPANFs were washed by deionized water and then alcohol several times. The precipitate was dried at 50°C for 24 hours.

Electrochemical detection experiments.—The feasibility of electrocatalytic activity of CPANF-modified electrode toward H_2O_2 was verified by using cyclic voltammetry (CV) and amperometry. The as-prepared CPANFs and CPNFs (about 2 mg) were incubated with 5 mg/mL HRP solution (1 mL) at 6°C overnight. Then, the CPANFs and CP-NFs modified by HRP were attached to the pretreated GCE using an aqueous nafion solution and left to dry under N₂ atmosphere at room temperature.^{32–35} After that, the CV measurements were performed in 0.1 M PBS (pH = 6.8) in a three-electrode electrochemical cell, using platinum foil as the auxiliary electrode and a saturated Ag/AgCl electrode as the reference electrode. The electrochemical performances of the fabricated electrodes were tested using a three-electrode system by cyclic voltammetry (CV).

Instrumentation.—X-ray photoelectron spectra (XPS) of the CPNFs and CPANFs were recorded using an X-ray photoelectron spectrometer (Kratos Axis Ultra DLD) with an aluminum (mono) Ka source (1486.6 eV). The aluminum Ka source was operated at 15 kV and 10 mA. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 5700 FTIR spectrometer in transmittance mode at a resolution of 4 cm⁻¹ and 32 scans. Field emission scanning electron microscopy (FE-SEM) images of the synthesized CPNFs and CPANFs were obtained using a JSM-6700F FE-SEM (JEOL, Japan). Transmission electron microscope (TEM) characterization was performed on a JEOL JEM-2100 electron microscope operating at 200 kV. Cyclic voltammograms were recorded using a computer controlled CHI660E electrochemical workstation (CHI, Shanghai Chenhua, Shanghai). Xray diffraction (XRD) patterns of the CPNFs and CPANFs were characterized with a SIEMENS Diffraktometer D5000 X-ray diffractometer using Cu K α radiation source at 35 kV, with a scan rate of 0.02° 2 θ s^{-1} in the 2 θ range of 5–80°. The HAADF-STEM mages and STEM mapping mages were recorded by a STEM (Tecnai G2 F30 S-Twin, Philips-FEI) at an acceleration voltage of 300 kV.

Results and Discussion

The formation mechanism of the CPANFs is depicted in Fig. 1. The PAN solution was initially electrospun into nanofibers and then carbonized to CNFs. The CNFs were then immersed into a solution



Figure 1. Schematic illustration of the formation of CPANFs.

Pre-oxidatio



Figure 2. FE-SEM of the PAN nanofibers (a), CNFs (b), CPNFs (c, d) and CPANFs (e, f); the EDS of CPANFs (inset in f).

containing aniline and $HClO_4$ for polymerization, and the aniline cations were absorbed onto the surface of CNFs. The polymerization was initialized with the addition of APS into the reaction solution with mild stirring under N₂ atmosphere. The solution turned green as the PANI nanorods were generated. In addition, PANI tended to form a certain angular chain-conformation rather than other morphologies under this condition. HAuCl₄ was then employed as an oxidant for this polymerization to form CPANFs, which were acquired by the reduction of PANI nanorods by HAuCl₄ and the interaction between -SH groups and AuNPs. The distribution of AuNPs on the surface of PANI nanorods could be controlled by using TA.

The electrospun PAN nanofibers were smooth and uniform in diameter, as seen in Fig. 2a. Fig. 2b shows that CNFs with uniform morphology were successfully prepared through a pre-oxidation and carbonization process in a muffle furnace. Fig. 2c–2f show the SEM images of successfully synthesized CPNFs and CPANFs. The magnified SEM images in Fig. 2c, 2d clearly show that the surfaces of CNFs became rough after the PANI nanorods were loaded. According to Fig. 2e, 2f, it is apparent that the hybrid nanostructures of CPANFs with well-dispersed AuNPs were obtained. Other than the morphology change, there is no obvious difference in diameter between CPANFs and CPNFs. Moreover, the EDS spectrum revealed the presence of S and Au on the resulting CPANFs, as shown in the inset of Fig. 2f, which further supports the distribution of AuNPs on the surface of CPANFs.

Fig. 3a, 3b show the TEM images which reveal the triangle-like PANI vertically coated on the surface of CNFs, with the length of the PANI nanorods reaching nearly 80 nm. TEM measurements show that CPANFs with well-defined multilayered structures were successfully manufactured, with the PANI matrix coated by the AuNPs. HRTEM images of the CPANFs reveal distinct lattice fringes with a d spacing of 0.23 nm, which is attributed to the (111) lattice planes of face-centered cubic (fcc) gold (inset in Fig. 3d).^{36–38} Fig. 3c shows that the SAED pattern of the CPANFs reveals the polycrystal rings indexed to the (200), (220), (111) and (311) planes of fcc gold, respectively, indicating the polycrystallinity of AuNPs.³⁶

It was also found that the diameter of the AuNPs could be controlled by the concentration of HAuCl₄. Fig. 4 shows that the diameter of the AuNPs was 1.1 ± 0.36 nm when the concentration of HAuCl₄



Figure 3. TEM images of the CPNFs (a, b), CPANFs (c, d); selected area electron diffraction (SAED) pattern (inset in (c)) and HRTEM image of the AuNPs (inset in (d)), respectively.

was about 0.1 mM. While when the concentration of HAuCl₄ increased to 0.25 mM the diameter of the AuNPs loaded on the surface of PANI nanorods increased to 2.2 ± 0.29 nm (Fig. 4h). Furthermore, when the concentration of HAuCl₄ significantly increased to about 0.5 mM), as expected, the diameter of the AuNPs increased to 24.3 \pm 4.1 nm (Fig. 4i), and the PANI was not visible through the vast coverage by large AuNPs (Fig. 4c, 4f). These results suggest that the concentration of HAuCl₄ had a profound effect on the diameter of AuNPs and the morphology of CPANFs.

To further explore the morphology of the perpared CPANFs, the HAAD-STEM images and STEM-EDS mapping are shown in Fig. 5. Fig. 5a shows the HAADF-STEM image of the CPANFs. The triangle-like PANI can be clearly observed and the STEM-EDX mapping of Au and S elements also indicate that the AuNPs successfully loaded onto the surface of PANI nanorods. In the mapping of C element (Fig. 5b), the signal-dense area belongs to the CNFs, while other C signals are attributed to the PANI.

FT-IR analysis was utilized to observe the formation and chemical structures of the present CPANFs, CNFS and CPNFs. In Fig. 6a, the peaks at 1634 cm⁻¹ and 1401 cm⁻¹ wavenumbers are attributed



Figure 5. STEM analysis of the CPANFs. HAADF-STEM images, high-resolution element mappings taken on the CPANFs.

to the C=C stretching and C-H stretching. The characteristic bands located at 1588 cm⁻¹ and 1498 cm⁻¹ are ascribed to the C=C stretching vibration of bezenoid and quinoid rings, respectively, indicating the oxidation state of PANI. The peak at 1139 cm⁻¹ belongs to the characteristic of $A = NH^+-B$ (where A and B denote quinoid ring and benzene ring, respectively). The peak at 1296 cm⁻¹ corresponds to a C-N stretching vibration with aromatic conjugation.^{32,37} Additionally, we found the intact peak intensity values and the intensity ratio of 1588/1498 cm⁻¹ of CPANFs were higher than those of pure CPNFs, which indicates the presence of more quinoid rings in the CPANFs. The obvious increase in quinoid rings of the resulting CPANFs reveals that the CNFs had stronger interactions with the quinoid ring than those with the benzene ring.³⁹ In order to better characterize the phase components and crystallinity of the material, XDR measurements of pure CNFs and CPANFs were carried out. Fig. 6b shows that the as-prepared pure CNFs do not exhibit any obvious crystal diffraction peaks, but there is a weak and broad diffraction peak at 25° , which can be ascribed to the (002) layers of the pure CNFs. The (100) and (004) layers are not noticeable, suggesting that the as-prepared CNFs are amorphous.^{40,41} Compared to the pure CNFs, the CPANFs display four additional peaks at 38.10°, 44.41°, 64.70° and 77.62°. These values are consistent with JCPDS: 65-2870, which indexed as the (111), (200), (220) and (311) crystal planes of AuNPs, respectively, indicating that crystalline Au had been formed on the CPANFs.42



Figure 4. TEM images of CPANFs under varying concentrations of HAuCl₄: about 0.1 mM (a, d), 0.25 mM (b, e) and 0.5 mM (c, f); (g, h, i) the corresponding particle size distribution of AuNPs.



Figure 6. FTIR spectra of pure CNFs, CPNFs and CPANFs (a) and XRD patterns of the CNFs and CPANFs (b).

For the sake of investigating the chemical bond formation in CPANFs, XPS characterization was performed and the resulting spectra of CPNFs and CPANFs are shown in Fig. 7. The Au 4f XPS spectrum of CPANFs displays peaks at 87.1 eV and 84.1 eV, in Fig. 7a, corresponding to the binding energies (BE) of Au 4f7/2 and Au 4f5/2, respectively. The standard BE of Au^0 is at 87.7 eV and 84.0 eV based on previous work, and the changes in the BE suggest strong interactions between AuNPs and the PANI nanofibers.

The core level S 2p spectrum of the CPANFs is shown in Fig. 7b. Two S 2p spin-orbit coupled doublets located at 162.1 eV and 163.2 eV corresponding to the BE of S 2p3/2 and 2p1/2, respectively, demonstrating the presence of thiolate species in PANI nanorods.⁴³ The wide scan and N 1s peaks for the CPNFs are shown in Fig. 7c. The N 1s core-level spectrum of CPNFs at binding energies of 398.4 eV, 399.4 eV and 401.1 eV are detected, which belong to the positively charged nitrogen (N+), quinonoid imine (=N-) and benzenoid amine (-NH-), respectively.⁴⁴ The above binding energies shift to 399.2 eV, 400.0 eV and 402.3 eV in CPANFs (Fig. 7d), and the relative intensity of the quinonoid imine (=N-) is stronger than the benzenoid amine (-NH-) in CPANFs, which is attributed to the redox reaction between PANI and HAuCl₄. These results are consistent with the FTIR spectra results. The intrinsic characteristics of PANI and AuNPs will influence their electrochemical properties. To investigate the basic electrochemical properies of the CPNFs and CPANFs, the cyclic voltammetry (CV) analysis was conducted in a 1 M H₂SO₄ electrolyte solution at different scan rates ranging from 20 mV/s to 500 mV/s.⁴⁵ Fig. 8a shows pairs of broad redox peaks with similar shapes, which correspond to the two redox processes, namely, the leucoemeraldine-emeraldine and emeraldine-pernigraniline transformations.⁴⁶ In addition, Fig. 8b shows the capacitance of the CPANFs-GCE electrode. The clear redox current increase in intensity when compared to the CPNFs-GCE electrode resulted from the facilitation of AuNPs of the electronic responsiveness.

A series of CPANFs with different concentration of HAuCl₄ compared to the current intensity under cyclic voltammograms (200 mV/s) were prepared. As demonstrated in Fig. 9a, an obvious change at current intensity with increasing the density of AuNPs loading on the surface of CPNFs. When the concentration of HAuCl₄ was about 0.1 mM, a few separated AuNPs can be observed from Fig. 4a, 4d and the current intensity was only about 36 uA/mg. Accompanied with the concentration of HAuCl₄ from 0.1mM to 0.25mM, the current intensity drastically increased to 68 uA/mg, indicating that a higher concentration of AuNPs provides more efficient electron transfer in



Figure 7. Au 4f (a) and S 2p XPS spectra (b) of the CPANFs; N 1s XPS spectra of CPNFs (c) and the CPANFs (d).



Figure 8. CV curves of CPNFs (a) and CPANFs (b) at a series of scan rates in 1 M H_2SO_4 .

Figure 9. CV curves of the CPANFs with different concentration of HAuCl₄ (200 mV/s) (a) and (b) different pH from 5.5 to 8.3.

the CPANFs. However, when the concentration gradually increased to 0.5 mM, the current intensity decreased to about 52 uA/mg. This phenomenon is attributed to the decrease in the number of active sites on the surface of CPANFs caused by the agglomeration of AuNPs, which was consistent with Fig. 4c, 4f.

In orded to study the effect of pH toward the electrochemical property of CPANFs, a series of electrolyte with different pH from 5.5 to 8.3 compared to the current intensity under cyclic voltammograms were prepared. As the Fig. 9b demonstrated, the CPANFs/GCE electrodes show stable oxidation-reduction peaks under a wide broad pH range from 5.5 to 8.3. With the pH of electrolyte increased, the Epc and Epa gradually moved to the negative potential which demonstrated the process of transformation of proton to eletron. Moreover, the current intensity increased from 50 uA/mg to 100 uA/mg under acid electrolyte. However, when the pH increased to 8.3, the current intensity decreased to 50 uA/mg which demonstrated the electrochemical activity was weaker under alkaline electrolyte.

As shown above, we believe that the CPANFs can be employed as efficient substrate materials integrated in electrochemical detector of H₂O₂. To demonstrate the function of the electrochemical characteristics of as-prepared CPANFs, we fabricated electrochemical detector for H₂O₂ detection using HRP. HRP was tightly attached to the negatively charged AuNPs through electrostatic attraction due to the positive charge of HRP retains in an acidic environment. From the results of Fig. 9a, the CPANFs (0.25 mM) were chosen as the substrate materials to fabricate the electrochemical detector of H_2O_2 . In the electrolyte (pH = 6.8) contain HQ (1 mM) and H₂O₂ (10 mM), the reduction current caused by HQ was observed, accompanied by the disappearance of the oxidation current peak. The electrochemical behavior of the CPANFs/GCE electrode was then exhibited by using cyclic voltammetry at a gradually increased scanning voltage from 20 mV/s to 200 mV/s, and the drastically step-up redox peak potentials at -0.25V were obtained, as shown in Fig. 10a, indicating the high electroactivity of CPANFs. The CV



Figure 10. CVs of CPANFs functionalized GCE with 5.0 mM HQ in 0.1 M PBS (pH 6.8) in 10 mM H₂O₂ with different scan rates (a), and CVs of CPANFs-GCE in 0.1 M PBS with different concentrations of H₂O₂ (b), and amperometric response of the fabricated CPANFs electrochemical detector of H₂O₂ to successive addition of H₂O₂ into the stirred PBS solution containing 1.0 mM HQ (c); the applied potential was -0.25 V vs Ag/AgCl, and calibration curve and linear fitting curve between the current and the H₂O₂ concentration (d).



Figure 11. The CVs cycles of HRP/CPANFs/GCE in the presence of 10 mM H_2O_2 in the same conditions at the scan rate of 100 mVs⁻

responses of CPANF-modified GCE in PBS with 1 mM HQ and different concentrations of H₂O₂ were shown in Fig. 10b. The reduction current attributed to HQ increased noticeably with increasing H2O2 concentration.

As shown in Fig. 10c, we employed CPANFs as substrate materials to evaluate their analytical performance in accurately recording the amperometric response toward the redox of H2O2 upon successive addition of H₂O₂ (1 uM-605 uM) every 50 s at a working potential of -0.25 V (according the Fig. 10a) with constant stirring. A rapid increase of the current was detected after each addition of H2O2 into the solution, and a stepwise increased response is attained. Moreover, the CPANFs-GCE electrode exhibited excellent sensitivity for 3 µM H_2O_2 (inset picture in Fig. 10c). A linear relationship between H_2O_2 oxidation currents and concentrations was observed with a linear relative coefficient of 0.966 and a detection limit of 0.18 μ M (S/N = 3) (Fig. 10d). The excellent electrocatalytic oxidation of H_2O_2 on the CPANFs modified CPE is attributed to the enhancement of charge transport through the CPANPs matrix, which facilitates the electron transfer between the redox center of H₂O₂ and GCE, leading to an electrocatalytic effect on the oxidation of H_2O_2 .

Moreover, to determine the reproducibility of CPANFs-GCE toward H₂O₂, a series CVs under same scanning voltage compared to the current intensity were carried out. As illustrated in Fig. 11, the CVs were almost the same and did not show distinct change. From this fact, we could draw the conclusion that the HRP/CPANFs/GCE electrodes exhibit good reproducibility and stability of the excellent characteristics toward the H₂O₂ detection. The performance of the HRP/CPANFs electrochemical detectors of H₂O₂ developed in this work was compared with others reported in the literatures (Listed in Table I), and from the table it can be found that the electrode in the present study show lower detection limit and comparative detection range, demonstrating that the CPANFs can be acted as a efficient electrode material for detection toward low concentration H₂O₂.

Table I. Summary of the detection range and detection limit of as-prepared biosensors in comparison with other sensors.

Biosensors	detection Range (uM)	detection Limit (uM)	Reference
HRP-CNFS/PANI/Au	1-605	0.18	this work
hybrid nanostructures			
HRP-Au	4-8000	1	47
NPs/CaCO ₃ /silica			
HRP-Au NPs/PVA	1-500	0.5	48
HRP-Au NPs/carbon	12.2-1100	6.1	49
Ti/TiO2/Au/HRP/GCE	4-400	2	50
HRP-AgNPs/(PVA/PEI)	5-550	No data	51
HRP-Noble metal/PVA	10-560	0.56	52

Conclusions

In summary, CPNFs with high electrochemical activity were successively fabricated. The size and distribution of AuNPs on surfaces of PANI nanorods can be tailored by simply changing the concentration of HAuCl₄. The CPANFs were applied to the chemically modified electrode and the HRP-CPANFs/GCE modified electrode showed enhanced electrochemical activity toward the reduction of H₂O₂ when compared to that of the pure CPNF-modified electrode. The favourable enhancement is mainly attributed to the synergistic effects of AuNPs with CPNFs.

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