A non-enzymatic Hydrogen Peroxide Sensor with Enhanced Sensitivity based on Pt Nanoparticles

Azka Awais*, Muhammad Arsalan*, Qinglin Sheng*, **,†, Tianli Yue**,†

*College of Chemistry & Materials Science/Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of Ministry of Education/Shaanxi Provincial Key Laboratory of Electroanalytical Chemistry, Northwest University, Xi’an, Shaanxi 710069, China
**College of Food Science and Technology, Northwest University, Xi’an, Shaanxi 710069, China; Laboratory of Nutritional and Healthy Food-Individuation Manufacturing Engineering/Research Center of Food Safety Risk Assessment and Control, Shaanxi, Xi’an, 710069, China

(†Corresponding authors Emails: Qinglin Sheng: qlsheng@nwu.edu.cn; Tianli Yue: yuetl@nwu.edu.cn Tel/Fax: +86-29-88303448)

ABSTRACT
The non-enzymatic electrochemical sensing platform for hydrogen peroxide by using Pt-based nanoparticle was investigated. Characterization of PtNiCo-NPs was done by XRD, TEM, HRTEM, EDS, and XPS. A simple drop-casting technique was used to fabricated the nanomaterial on FTO electrode. The amperometric and cyclic voltammetric results illustrated that PtNiCo-NPs on FTO had excellent electrochemical performance over other mono or bimetallic materials. The catalytic performance for H₂O₂ sensing based on PtNiCo-NPs possessed a wide linear range from 5 μM to 16.5 mM with low detection limit of 0.37 μM and good sensitivity of 1374.4 μAM⁻¹cm² at scan rate of 20 mVs⁻¹ (vs. Ag/AgCl). This work presents a new way of ternary nanomaterial for H₂O₂ sensing with excellent electrochemical performance. In addition, the fabricated nanomaterial showed no interferences for common interfering agents, which indicates the high specificity of the sensor. The PtNiCo-NPs have excellent stability and good reproducibility in real samples.

Key words: PtNiCo-NPs; H₂O₂ sensor; Nanoparticle; Electrochemical detection.
Introduction

The H$_2$O$_2$ modest quantity is essential for many biological processes in the living organism\cite{1}, environmental processes\cite{2}, pharmaceutical and food industry\cite{3}, whereas higher concentration than the required quantity which causes some serious disorders for human like heart diseases, Parkinson and even cancer. Therefore, its accurate and fast detection is much important\cite{4}. Various techniques or methods are in contest for this, among them, electrochemical sensor is more important due to its higher sensitivity, quick response, simple operation and accurate detection\cite{5-7}. Electrochemical sensors are conventionally constructed by using enzymes for quick detection\cite{8}. Nevertheless, H$_2$O$_2$ sensors based on enzymes have several limitations, like high cost, complicated structure, low sensitivity, and difficult immobilization, these limits their use in many practical applications\cite{9,10}. Therefore, enthusiastic efforts are required for developing more efficient, quick, and non-enzymatic H$_2$O$_2$ sensor with stable structure\cite{11}, which is very important for selective, stable, and sensitive detection of enzyme-free H$_2$O$_2$\cite{12}. Thus, it is more important to developed modified electrode material with excellent conductivity and higher electrocatalytic activities\cite{13-15}. So far, some metallic oxides\cite{16}, transition metals\cite{17,18} and simple metals have been applied as effective candidate for successful electrochemical application\cite{19,20}, among all those, noble metals like Pd, Pt, Ag and Au are more widely used catalyst in many electrochemical reactions with good catalytic ability, enhanced conductivity, and stability\cite{21}. In all these noble metals, Pt attained more attraction due to its unique structure, versatile chemical nature, and excellent catalytic ability, which makes it a promising candidate by reducing the oxidation-reduction overvoltage in H$_2$O$_2$ detection\cite{22}. Moreover, when compared with other materials, Pt or Pt-based materials are more efficient, sensitive, and effective in neutral conditions (pH 7.2), all these abilities make Pt-based nanomaterial more suitable for H$_2$O$_2$ detection\cite{23,24}. Recent research paper expressed that good efficiency towards H$_2$O$_2$ detection can be achieved by using simple Pt-based nanomaterial\cite{25}. In spite of the significant progresses have been achieved, there are still some difficulties for H$_2$O$_2$ detection due to the agglomeration of metals nanomaterial\cite{26,27}. Therefore, Pt-based nanomaterial is more important for higher catalytic efficiency, excellent conductivity, more surface area and quick response\cite{28}.

Pt metal has some efficiency towards catalysis and electrocatalysis, by adding other metals makes it more efficient with change in surface morphology, chemical nature, material size, shape, selectivity, and sensitivity as compared to single element\cite{29}. Advances of surface analyzed techniques, facilitates the bimetallic nanoparticles with more important significance in materials detections\cite{30}. The bimetallic Pt-based nanoparticles had been proved that it has good activity, more sensitivity, and improved sensing capacity for H$_2$O$_2$ detection\cite{4}. But there are still many limitations like detection at low concentration, instability, low sensitivity, and less selectivity; therefore, it is important to develop a sensor with enhanced sensitive nature.
Although bimetallic Pt-based nanoparticles like PtNi\(^1\), PtAu\(^{10}\), PtPd\(^6\), PtAg\(^{22}\) prepared by electrochemical methods are important for the detection but for enhanced sensing activity, other nanomaterials are required.

In this work, we constructed a more efficient \(\text{H}_2\text{O}_2\) sensor with enhanced sensing activity. The nanometric PtNiCo-NPs were prepared and modified on fluorine-doped tin oxide by simple deposition technique. The PtNiCo-NPs were well dispersed on the FTO electrode surface with uniform particle size. The PtNiCo-NPs has higher reduction potential with a wide linear range and quick response for \(\text{H}_2\text{O}_2\) detection. The prepared nanomaterial is more selective towards \(\text{H}_2\text{O}_2\) detection with excellent stability and reproducibility. The Pt-based catalyst shows excellent analytical performance to \(\text{H}_2\text{O}_2\) detection at -0.05 V (vs. Ag/AgCl). Therefore, it is useful in many biological and chemical processes. Additionally, further analysis showed that PtNiCo-NPs has excellent electrocatalytic activity, which provides a new way for further study in non-enzymatic \(\text{H}_2\text{O}_2\) determination, based on Pt-based nanomaterial in real samples applications.

**Experimental Section**

*Reagents and Chemicals*

Cobalt acetylacetonate (Co(acac\(_2\)) (CoC\(_{10}\)H\(_{18}\)O\(_4\),97%), Platinum (II) acetylacetonate (Pt(acac\(_2\)) (PtC\(_{10}\)H\(_{14}\)O\(_4\), 97%), Nickel (II) acetylacetonate (Ni(acac\(_2\)) (NiC\(_{10}\)H\(_{14}\)O\(_4\), 97%), benzoic acid (99.5%), \(\text{H}_2\text{O}_2\), ascorbic acid, uric acid, citric acid, alanine, phenylalanine, and dopamine were all purchased from Sigma-Aldrich. All analytical grade chemicals were used without any further purification. A phosphate buffer (PBS, 0.1M, pH 7.0) containing Na\(_2\)HPO\(_4\) and NaHPO\(_4\) were used as supporting electrolyte. Ultra-purify distilled water purified by the Millipore system (18 M\(\Omega\)cm) was used in all the experiments.

*Apparatus*

The TEM (transmission electron microscopy) and EDX analyses were measured by using Tecnai G2 F20 S-TWIN FEI, USA. The XRD analysis was conducted by using D/Max-3C (Japan). The XPS analysis was conducted by using instrument PHI-5000, Ulvac-Phi, Japan. Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and current time graph were all conducted by using CHI660D model, electrochemical work station. In the electrochemical cell, Pt wire was used as a counter electrode, Ag/AgCl used as a reference electrode, and modified FTO (FTO, geometric area= 0.60 cm\(^2\)) was used as a working electrode.
Preparation of modified electrode

Synthesis of PtNiCo-NPs Catalyst

The Pt-based catalyst was synthesized by adding 20 milligram of Pt(acac)$_2$ in 10 milligram of Ni(acac)$_2$ and 2 milligram of Co(acac)$_2$ with 120 milligram of benzoic acid and 10 milliliter of DMF(N,N-dimethylformamide) in round bottom flask. The material was sonicated for a few minutes at 50 °C and after sonication immediately transferred in an oil bath at controlled temperature of 150 °C for 16 hours of continuous heating. After completion of reaction the chemical product was collected and impregnated with Argon for a few minutes, and after that, the product was washed several times with ethanol-acetone mixture to remove all impurities.

Preparation of PtNiCo-NPs modified electrode

Three milligrams of PtNiCo-NPs catalyst were ultrasonically dispersed in 1 mL of Nafion solution for 30 minutes. After dispersion, 20 μL of the material solution was deposited on FTO by simple drop-casting technique and dried at room temperature. The Pt-based catalyst was deposited uniformly on electrode surface. Prior to surface modification, the FTO electrode was rinsed with ethanol and distilled water for several times in ultrasonication bath to clean the electrode surface. After cleaning the electrode surface, it was covered with an insulator layer and just 0.40 cm$^2$ was not insulated for electrochemical reactions. Through this insulation working area is controlled as described in literature$^{31}$. Now Pt-based catalyst was ready for analysis and characterization.

Scheme 1 shows the preparation of PtNiCo-NPs from salts (acetylacetonate) of Pt, Ni, and Co. After preparation, the material solution was deposited on FTO electrode by using a simple drop-casting technique. The physicochemical and electrochemical methods were used to analyze the prepared nanomaterial for H$_2$O$_2$ detection.

Results and discussion

Physicochemical characterization of PtNiCo-NPs catalyst

The physical characterization of synthetic material was conducted by using TEM, XRD and XPS methods. The TEM images of PtNiCo-NPs showed the size obtained from nanomaterial was 4-5 nm (±0.5), as mentioned in Fig. 1(a, and b). It was observed that Pt-based thin layer of nanoparticles was well dispersed on the electrode surface. The edges of the nanomaterial were slightly truncated due to weak structure-directing reagent (benzoic acid) and relatively high temperature (150 °C) used in the preparation of the
nanomaterial. The distance between two crystal lattices was 0.21 nm, as mentioned in Fig. 1(b). The preparation of ternary PtNiCo-NPs with good catalytic activity was performed under controlled environment (after sonication the mixture should be immediately transferred into oil bath for continues heating before cooling down and the temperature should be controlled to obtain good catalytic activity as described in literature)32. In the preparation of nanoparticle, the use of benzoic acid is imperative for the synthesis of PtNiCo nanoparticle. If the material was prepared in the absence of benzoic acid, the product lacks the octahedra or nanoparticle shape. The irregular particles formation of PtNiCo was controlled by using benzoic acid as described in literature33 and made smaller size nanoparticles comparatively34. Therefore, the synthesis procedure is important for the preparation of nanoparticle. The XRD spectra was obtained and shown in Fig. 1(c) for PtNiCo-NPs. The XRD pattern of PtNiCo-NPs showed distinct peaks at (111), (200), (220), and (311) planes indicating that the prepared catalyst formed a single-phase with face center cubic structure35. The results showed the successful synthesis of nanomaterial36. Insert of Fig. 1(c) shows the magnified XRD spectra of the synthesized nanomaterial. The EDS analysis was employed to investigate the chemical composition of the PtNiCo-NPs catalyst as mentioned in Fig. 1(d). The EDS spectra further explained the composition of the prepared material. Pt/Ni/Co molar ratio was observed as 62:32:6, which is in accordance with the molar ratio used in the preparation procedure.

The chemical composition of PtNiCo-NPs was further examined by X-ray photoelectron spectroscopy (XPS) measurements. Fig. 2(a) shows the complete spectrum of PtNiCo-NPs with clear peaks of C, O, Pt, Ni, and Co. As shown in Fig. 2(b), the Pt 4f region of PtNiCo-NPs can be divided into two prominent peaks. The two prominent peaks are present at 71.5 and 74.8 eV, confirming to Pt 4f5/2 and Pt 4f7/2 of metallic Pt, respectively36,37. In addition, two weaker doublets at 72.5 and 76.9 eV was assigned for Pt oxides on the surface of the PtNiCo-NPs32. The Pt 4f peaks of PtNiCo-NPs are shifted to higher energy due to alloy formation with Ni and Co. The shifting of energy at higher level is due to charge transfer from Ni to Pt and Co to Pt atoms. Furthermore, Ni 2p spectra are also blue shifted to lower binding energy, showing the charge transfer from Ni to Pt as mentioned in Fig. 2(c) and the prominent two peaks of Ni are present at 854.6 and 872.3 eV respectively, with two satellite peaks confirming the alloy formation38. The Co 2p spectra was mentioned in Fig. 2(d) with two pair of main and satellite peaks represented the alloy formation39. It was confirmed from XPS analysis that PtNiCo-NPs has successfully formed ternary nanoparticles by the modification of the surface structure of Pt with Co and Ni.

Electrochemical characterization

The EIS measurements were used to obtained the charge transfer resistance of bare FTO, PtNiCo-NPs, PtNi and PtCo in 0.1 mol L⁻¹ KCl and 0.1 mol L⁻¹ K₃[Fe(CN)₆]/K₄[Fe(CN)₆] solution. The Nyquist
plots of the EIS are related to a semicircle at high frequencies, which is corresponding to the charge transfer resistance process, and at low frequencies, a linear part is corresponding to the diffusion process\(^{40}\). The diameter of the semicircular portion is related to the charge transfer resistance (Rct), which shows the kinetics of electron transfer at the electrode surface. As compared to bare FTO, PtNi and PtCo with Rct of 379.2 \(\Omega\), 272 \(\Omega\), and 148 \(\Omega\) respectively, the PtNiCo-NPs has much lower Rct value of 33.4 \(\Omega\), which is the reason of excellent conductivity of Pt-based nanomaterial as mentioned in Fig. 3(a). The CV of all the electrodes were carried out in 0.1 mol L\(^{-1}\) KCl and 0.1 mol L\(^{-1}\) K\(_3\)[Fe(CN)\(_6\)]/K\(_4\)[Fe(CN)\(_6\)] solution. The oxidation peaks of all electrodes were mentioned in Fig. 3(b). The highest redox peak current was monitored for PtNiCo-NPs, while other PtCo and PtNi electrodes showed a low peak current. The bare FTO showed the least redox potential as compared to all other modified electrodes in CV measurements.

The cyclic voltammetry analysis was also performed to find the effect of the scan rate in synthesized catalysts at different ranges from 20 to 120 mVs\(^{-1}\) in PBS (pH 7.0) as mentioned in Fig. 4a. The insert of Fig. 4(a) shows the linearity graph of synthesized nanomaterial with the square root of the scan rate. The sensing performance of the nanomaterial was initially checked by CV at a fixed scan rate (20 mVs\(^{-1}\)) with different concentrations of H\(_2\)O\(_2\) in PBS (pH 7.0) as mentioned in Fig. 4b. Insert in Fig. 4(b) (linear graph of current vs. concentration) revealed that the reduction of H\(_2\)O\(_2\) on PtNiCo-NPs in a surface controlled electrochemical reaction. In order to attain the maximum response of the PtNiCo-NPs sensor, the working potential of the sensor was optimized. The superlative working potential of the modified sensor was selected by successive addition of 0.5 mM of H\(_2\)O\(_2\) at different working potential. Various working potential (0.10 to -0.10 V) was applied, and among them, the optimum working potential for H\(_2\)O\(_2\) sensing was obtained at -0.05 V, as mentioned in Fig. 5(a). As the applied potential was changed into positive, the observed current magnitude did not increase monotonically as shown in Fig. 5(a) due to the nature of sensing material as observed previously in literature\(^{25,41,42}\). After selecting an optimized working potential, long current time graph was acquired with the successive addition of H\(_2\)O\(_2\) to find the detection range. The performance of the sensor was evaluated by considering the reduction peaks (current) due to the successive addition of H\(_2\)O\(_2\) because the reduction current is much higher than the oxidation. The analytical performance of the prepared catalyst was studied by the amperometric method at the applied potential of -0.05 V by the successive addition of H\(_2\)O\(_2\) into the PBS (pH 7.0) solution. The results showed that PtNiCo-NPs possessed excellent sensing capacity towards H\(_2\)O\(_2\). It was also observed in Fig. 5(b) that with the increase of H\(_2\)O\(_2\) concentration, the current is also increased. The linear curve calibration shows that the sensor response increased linearly with the increase of H\(_2\)O\(_2\) concentration up to 16.53 mM as mentioned in Fig. 5(c). The linear regression values were mentioned as Ipa (mA) = 0.1598 + 0.345 c and the correlation coefficient R\(_2\) was found as 0.9972. Insert is the magnified linear graph of the prepared sensor with linear regression value
as $I_{pa} \text{ (mA)} = 0.0048 + 1.1729 \, c$ and correlation coefficient $R^2$ was found as 0.9994. The low detection limit for $H_2O_2$ sensor by PtNiCo-NPs was calculated as 0.37$\mu$M by using (3 $\sigma$/S) as expressed in “Eq. (1) and (2)”.

$$\text{LOD} = 3 \, \sigma / S$$  \hspace{1cm} (1)

Where “$\sigma$” is standard deviation and S is slope of the calibration curve. The standard deviation is calculated by using the following formula.

$$\sigma = \sqrt{\frac{1}{n} \sum_{i=1}^{n} (x_i - \bar{x})^2}$$  \hspace{1cm} (2)

The sensitivity of the PtNiCo-NPs sensor was calculated to be 1374 $\mu$A mM$^{-1}$ cm$^{-2}$ (RSD % = 3.5), which is much higher as compared to previously reported electrochemical sensors mentioned in Table 1.

**Repeatability, Reproducibility, stability and selectivity of PtNiCo-NPs**

The repeatability of the PtNiCo-NPs was investigated by taking 5 measurements using the same electrode in 0.1 M PBS (pH 7.0) solution in the presence of 2 mM $H_2O_2$. After every measurement, the electrode was washed three times with distilled water, and then the electrode was dried for a few minutes and used again for successive repeatability. It was observed from results that the catalyst has over 97% of electrochemical performance, which suggested that the catalyst has excellent reliability. The repeatability and reproducibility of the PtNiCo-NPs were determined by using voltammetry and amperometry techniques. In a series of 5 electrodes prepared under the same condition, a relative standard deviation of 3.2% (RSD) was obtained towards 2 mM $H_2O_2$ in 0.1 M PBS at fixed potential of -0.05 V, indicating a relatively high inter-electrode reproducibility. The results implied the stability of the proposed electrode with reproducible current as it is not poisoned with the reduction products. For reproducibility same size of electrode were used with same experimental conditions. The PtNiCo-NPs catalyst's stability was checked by continues 100 CVs at a fixed scan rate of 20 mVs$^{-1}$, as mentioned in Fig. 6(a). The long-term stability of PtNiCo-NPs was calculated after one month with RSD value of 2.3%, which show its long-term stability. The selectivity of the PtNiCo-NPs catalyst was checked by adding different potential interfering substances commonly present in physiological samples (ascorbic acid, uric acid, citric acid, alanine, phenylalanine and dopamine). The current response of 2 mM of all interfering substances in the presence of 0.1M PBS (pH 7.0) was compared with that of 2 mM of $H_2O_2$, as mentioned in Fig. 6(b) (histogram graph for peaks). The current responses of interfering species exhibited no interference, indicating the excellent selectivity of
PtNiCo-NPs catalyst. It was observed from the selectivity test that, PtNiCo-NPs catalyst can be beneficial for H$_2$O$_2$ detection.

Real Sample Analysis

To check the applicability of the PtNiCo-NPs modified electrode, a sequence of real samples containing a known concentration of H$_2$O$_2$ were analyzed. The H$_2$O$_2$ is used for the sterilization of the equipment for treating milk, but its presence in milk can contaminate the milk. Therefore, it is important to develop convenient sensors to detect the presence of H$_2$O$_2$ in this important consumer product$^{51-53}$. The detection of H$_2$O$_2$ in a sample of milk bought from the local market was made without any pretreatment. Prior to analysis, catalase was employed to confirm whether the milk sample contain H$_2$O$_2$. As shown in insert of Fig. 7a, no changes in current response were observed. In the analysis, the standard addition method was applied, by which a known amount of H$_2$O$_2$ was added into the test solution. The importance of H$_2$O$_2$ sensor for milk was also described in literature$^{54}$. Fig. 7a shows the typical amperometric response with successive addition of 0.2 mL of H$_2$O$_2$ into milk using PtNiCo-NPs electrode, it was observed that base line of the current response in milk sample (Fig. 7a) is lower than PBS (pH 7.0), suggesting fouling of electrode surface in the milk. On the addition of H$_2$O$_2$, the current response quickly reaches the maximum value. The feasibility of the PtNiCo-NPs sensor was further examined by the recovery tests and mentioned in Table 2. In addition, PtNiCo-NPs sensor was used to test H$_2$O$_2$ in toothpaste, for that 2 g of toothpaste was dissolved in 50 mL deionized distal water. The supernatant was obtained after centrifugation; the supernatant was further diluted in 100 mL flask. The amperometric analysis was carried out at an applied potential of -0.05 V in 10 mL of 0.1 M PBS solution under continues stirring condition with 0.1 mL toothpaste sample. The amperometric analysis with successive addition of 0.1 mL of H$_2$O$_2$ was mentioned in Fig. 7b. The recovery tests results obtained from the analyses were mentioned in Table 2, with less than 3 % RSD. The results indicated that the PtNiCo-NPs sensor prepared in this work could be used for the detection of H$_2$O$_2$ in real samples.

Conclusion

It was concluded that Pt-based nanomaterial was synthesized by a facial method and fabricated on FTO electrode by using a simple drop-casting technique. The PtNiCo-NPs exhibited excellent electrochemical performance for H$_2$O$_2$ sensing. The morphology of nanomaterial was characterized by XRD, TEM, XPS, etc. PtNiCo-NPs possessed a size of less than 6 nm with a wide linear range of 5 μM - 16.50 mM, low detection limit (LOD) of 0.37 μM, and high sensitivity 1374.4 μAmM$^{-1}$cm$^{-2}$. The PtNiCo-NPs sensor has excellent stability and no interferences by commonly used interfering substances. The prepared nanomaterial also has excellent reproducibility and high sensitivity in real samples with a good
recovery rate. We believe that the synthesized PtNiCo-NPs sensor may provide a new strategy for simple and easy to use sensor with high electrochemical performance.

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Conflicts of interest

There are no conflicts to declare.

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Table 1. Electrochemical performance of various electrodes towards H₂O₂ Sensing

| Electrode material                  | Sensitivity (μA mM⁻¹ cm⁻²) | Potential applied (V) | Linear range (μM) | Specificity | Stability | Reproducibility | LOD (μM) | Ref |
|-------------------------------------|-----------------------------|-----------------------|-------------------|-------------|-----------|-----------------|----------|-----|
| Pt/Graphene                         | -                           | -0.20 (vs. SCE)       | 2.5-6650          | AA, AP, CA, urea | 1 week   | 4.6%            | 0.8      | 41  |
| PtNPs@SPCEs a                       | 687.3                       | 0.7 (vs. Ag/AgCl)     | 0-215             | AA, AP, CA, urea | 1 week   | 7.8%            | 1.9      | 43  |
| FePt-Au HNPs b                      | -                           | -                     | 20-700            | AA, AP, CA, urea | 1 week   | 4.6%            | 0.8      | 41  |
| PtNi/C Nanoporous                   | 208.5                       | 0.3 (vs. Ag/AgCl)     | 0-2000            | AA, UA       | 1 week   | 4.6%            | 0.8      | 41  |
| PDDA/t-MWCNT s-Pt                   | 353.86                      | -0.1 (vs. Ag/AgCl)    | 1-5000            | AA, glucose, UA | 1 week   | 4.6%            | 0.8      | 41  |
| Pt/CNF d                            | -                           | 0 (vs. Ag/AgCl)       | 1-800             | AA, AP, CA, urea | 2 weeks  | 4.6%            | 0.8      | 41  |
| Pt NP–Ni foam                       | 829                         | 0 (vs. SCE)           | 5-850             | AA, AP, CA, urea | 2 weeks  | 4.6%            | 0.8      | 41  |
| Pt-N-graphene/ITO                   | 61.23                       | 60-4290               | K₃[Fe(CN)]₆, DO₃⁻ | AA, AP, DA, glucose | 2 weeks  | 4.6%            | 0.8      | 41  |
| Pt/PG                               | 341.14                      | -0.1 (vs. Ag/AgCl)    | 1-1477            | AA, AP, CA, glucose | 2 weeks  | 4.6%            | 0.8      | 41  |
| PdCu/SPCE                           | 87.0                        | -0.3 (vs. Ag/AgCl)    | 1-500             | AA, AP, DA, glucose | 2 weeks  | 4.6%            | 0.8      | 41  |
| NP-PtAu                             | -                           | 0.7 (vs. Ag/AgCl)     | 200-5400          | AA, DA, AA    | 2 weeks  | 4.6%            | 0.8      | 41  |
| PtNiCo-NPs                          | 1374.4                      | -0.05 (vs. Ag/AgCl)   | 5-16500           | AA, UA, CA, Ala, Phe, DA | 1 month  | 4.6%            | 0.8      | 41  |

Ref: a. screen-printed carbon electrodes  
   b. hybrid nanoparticles  
   c. Multiwall carbon nanotube  
   d. loaded carbon nanofiber  
   e. acetamido phenol  
   f. alanine  
   g. phenylalanine  
   h. dopamine  
   i. dissolved oxygen
Table 2. Detection of H₂O₂ in real samples

| Samples     | H₂O₂ added | H₂O₂ found | Recovery (%) | RSD (%) |
|-------------|------------|------------|--------------|---------|
| Milk        | 1          | 0.2        | 0.195        | 97.5    | 2.92    |
|             | 2          | 0.4        | 0.387        | 96.7    | 2.96    |
|             | 3          | 0.6        | 0.589        | 98.1    | 2.67    |
|             | 1          | 0.1        | 0.096        | 96      | 2.98    |
| Toothpaste  | 2          | 0.2        | 0.197        | 98.5    | 2.53    |
|             | 3          | 0.3        | 0.294        | 97.6    | 2.91    |

Schemes and Figures

Scheme 1. Schematic diagram of the experimental system showing; preparation; fabrication; and electrochemical analysis (sensing) of the prepared nanomaterial.

Fig. 1 a, TEM of PtNiCo-NPs catalyst was mentioned; b, HRTEM image of the PtNiCo-NPs catalyst; c, The XRD of well-defined PtNiCo-NPs was mentioned and insert is the magnified spectra of the nanomaterial; d, The EDS spectra of PtNiCo nanoparticle was mentioned.

Fig. 2 XPS spectra of the PtNiCo nanoparticles was mentioned, a, XPS spectra of C 1s; b, Pt 4f; c, Ni 2p; d, Co 2p.

Fig. 3 a, The Nyquist plots of bare FTO, PtNiCo-NPs, PtNi and PtCo in 0.1 M KCl containing 0.1 M K₃[Fe(CN)₆]/K₄[Fe(CN)₆] solution; b, the CV of all electrode was mentioned in0.1 M KCl containing 0.1 M K₃[Fe(CN)₆]/K₄[Fe(CN)₆] solution.

Fig. 4 a, Cyclic voltammetry of PtNiCo-NPs catalyst at different scan rates (20 to 120 mVs⁻¹); insert is a linear graph of nanoparticle; b, The CV of PtNiCo-NPs at a fixed scan rate of 20 mVs⁻¹ with different molar concentration; Insert is linearity graph of nanomaterial (current vs. concentration).

Fig. 5 a, the response of PtNiCo-NPs for the successive addition of 0.5 mM H₂O₂ at various potential; b, Amperometric response for PtNiCo-NPs modified FTO in 0.1M PBS (pH 7.0) with successive addition of H₂O₂ at a constant working potential of -0.05 V. Insert is the magnified image of lower concentration; c, is the linear graph of current vs. concentration, and the insert is the magnified graph at a lower concentration.

Fig. 6 a, The Stability of PtNiCo-NPs catalyst was checked by 100 continuous CVs at a fixed scan rate of 20 mVs⁻¹; b, the selectivity/interference test is performed by adding different potential interfering substances in the presence of 0.1M PBS (pH 7.0); c, Structure of some interfering substance was mentioned.
Fig. 7  a, Amperometric responses of PtNiCo-NPs towards successive addition of H$_2$O$_2$ in a PBS (pH 7.0) and b milk sample at -0.05 V; Insert show the amperometric response of PtNiCo-NPs with no addition of H$_2$O$_2$ (using Catalase: 40.0 U/l); b, show the amperometric responses of the PtNiCo-NPs towards successive addition of 0.1 M H$_2$O$_2$ in mixture of PBS and toothpaste.

Scheme 1
Fig. 1
Fig. 2

Fig. 3
Fig. 4

Fig. 5
Fig. 6

- Ascorbic acid
- Uric acid
- Citric acid
- Alanine
- Dopamine
- Phenylalanine

Fig. 7