



# Uniformly dispersed PtNi alloy nanoparticles in porous N-doped carbon nanofibers with high selectivity and stability for hydrogen peroxide detection

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## ABSTRACT

Highly dispersed Pt-based nanoparticles with superior electrocatalytic selectivity and stability are urgently needed for non-enzymatic electrochemical detection of H<sub>2</sub>O<sub>2</sub>. Herein, we prepared PtNi alloy nanoparticles dispersed in N-doped carbon nanofibers (PtNi/NCNFs) by pyrolyzing electrospun nanofibers composites from polyvinyl pyrrolidone and Pt/Ni-based salts. Characterization results indicated that PtNi alloy nanoparticles (average 9.0 nm) were homogeneously dispersed and embedded in NCNFs porous matrix. The electrochemical tests suggested that PtNi/NCNFs(3:1) displayed the highest electrocatalytic activity for H<sub>2</sub>O<sub>2</sub> reduction compared with Pt/NCNFs, Ni/NCNFs and other PtNi/NCNFs samples. PtNi/NCNFs(3:1)-based sensor showed excellent analytical properties towards H<sub>2</sub>O<sub>2</sub> with wide linear range (0.5 μM–8 mM), high sensitivity (248.5 μA mM<sup>-1</sup> cm<sup>-2</sup>), low detection limit (0.0375 μM), high selectivity and anti-interference, attributing to the highly dispersion of nanoparticles and synergistic effect between PtNi alloy nanoparticles and NCNFs. The PtNi/NCNFs-based sensor had superior reproducibility due to the uniformity of PtNi/NCNFs and good stability because of the embedded structure, which prevented the aggregation and detachment of nanoparticles during repeated uses. More interestingly, the as-fabricated sensor displayed satisfactory recoveries and relative standard deviation (RSD) for detection of H<sub>2</sub>O<sub>2</sub> in milk samples. The above results manifested that PtNi/NCNFs had potential to be selected as a candidate for fabricating non-enzymatic H<sub>2</sub>O<sub>2</sub> sensors.

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## 1. Introduction

H<sub>2</sub>O<sub>2</sub> is widely applied in the fields of textile industry, medicine manufacture, clinical, food production, mining and environment [1–4]. It is also a co-product of many enzyme-catalyzed biological processes and is regarded as a signaling molecule to manage these reactions. As one kind of reactive oxygen species, H<sub>2</sub>O<sub>2</sub> is an important biochemical mediator in the process of pathological study. It participates in various cellular metabolism of human body, or conversely, changes the structure of alive cell, leading to inflammatory diseases. It also has relation with human diseases of cardiovascular disorder, Alzheimer and cancer [5–7]. In addition, H<sub>2</sub>O<sub>2</sub> can be used as a reporter molecule in the electrochemical detection of nonelectroactive molecules [8,9]. Therefore, fast and accurate detection of

H<sub>2</sub>O<sub>2</sub> has aroused general concern of bioanalytical scientists due to its practical significance for industrial or academic purposes.

In the past few decades, many efforts have been made on various techniques for H<sub>2</sub>O<sub>2</sub> detection, such as spectrophotometry, fluorimetry, chromatography, chemiluminescence, titrimetry, surface plasmon resonance and electrochemical sensing. Among these detection techniques, the method of electrochemical sensing (including enzymatic and non-enzymatic sensing) displayed outstanding analytical performances like rapid response, low determination limit and high sensitivity [10–14]. It is well known that the high cost, instability and strict operation condition of enzyme-based sensors restricted their practical applications. In recent years, numerous researches have been done to fabricate non-enzymatic H<sub>2</sub>O<sub>2</sub> sensors based on various electrocatalysts, and the results showed that non-enzymatic H<sub>2</sub>O<sub>2</sub> sensors had the advantages of low cost, stability and convenient operation.

In previous years, nanomaterials have been widely explored to construct non-enzymatic H<sub>2</sub>O<sub>2</sub> sensors with excellent properties due to their unique electronic structure and catalytic properties

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[15,16]. Among them, noble metal nanoparticles, especially Pt nanoparticles have aroused general concern because of its high electrocatalytic activity, fast detection and high sensitivity [17]. However, these Pt-based sensors have a main restriction that they are prone to be interfered by other electroactive species, such as acetaminophen, ascorbic acid, uric acid and dopamine [18,19]. The coexistence of these species may lead to an inaccurate even a faulty measurement. It has been reported that alloying Pt with a second metal and preparing carbon-supported Pt nanoparticle could improve its catalytic activity and selectivity [4,20]. Recently, PtNi alloy nanoparticles have been widely investigated and non-precious metal Ni has showed a synergistic effect in electrocatalytic  $\text{H}_2\text{O}_2$  detection [21]. Usually, Pt nanoparticles and Pt-based alloy nanoparticles are loaded on the surface of carbon supports, which may lead to detachment and aggregation of nanoparticles in the process of application and further affect the stability of the as-prepared nanocomposites. In addition, the aggregation or non-dispersability of nanoparticles restricts their electrocatalytic performance for  $\text{H}_2\text{O}_2$  detection. Consequently, it is desirable to develop a non-enzymatic  $\text{H}_2\text{O}_2$  sensor with excellent analytical performances, high selectivity, anti-interference and good stability to solve the above problems.

Recently, electrospinning a nitrogenous organic precursor (e.g., PVP or PAN) with metal salts precursor combined with post-carbonization process has become an efficient method of producing metal nanoparticles decorated on polyporous N-doped carbon nanofibers [22,23]. During the post-carbonization process, metal ions are reduced to metals or alloys and nitrogenous organic precursor is carbonized to N-doped porous carbon nanofibers. The high surface area and porous structure of the as-prepared carbon nanofibers can provide enough space and routes for mass and electron transport, and thus greatly improves the electrocatalytic performance. In addition, N-doped carbon materials themselves have electrocatalytic activity for the redox reaction of  $\text{H}_2\text{O}_2$  and they display better performances for  $\text{H}_2\text{O}_2$  detection in comparison to those pure carbon materials [16,24,25]. Most important of all, nanoparticles can be uniformly dispersed and embedded in the N-doped carbon nanofibers, which significantly prevents their aggregating and detaching during use.

Herein, in this work, we prepared PtNi alloy dispersed and embedded in polyporous N-doped nanofibers (PtNi/NCNTs) by electrospinning  $\text{H}_2\text{PtCl}_6$ ,  $\text{NiCl}_2$  and PVP precursors followed by a simple thermal treatment process. A series of characterization results of the as-prepared composites showed that PtNi alloy nanoparticles were homogeneously dispersed in NCNFs porous matrix, rather than weakly absorbed on its surface. Such an embedded nanocomposite not merely showed outstanding analytical performances but also had good selectivity, anti-interference, reproducibility and excellent stability towards  $\text{H}_2\text{O}_2$ . More importantly, its application to the detection of  $\text{H}_2\text{O}_2$  in milk samples were demonstrated successfully.

## 2. Experimental section

### 2.1. Reagents and materials

Polyvinyl pyrrolidone (PVP,  $M_w = 1,300,000$ ), 4-acetamidophenol (AP) and dopamine (DA) were purchased from Aladdin Industrial Corporation.  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ,  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ ,  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ ,  $\text{K}_3[\text{Fe}(\text{CN})_6]$  were obtained from Sinopharm Chemical Reagent Co., Ltd. Ethanol absolute (EtOH),  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 30%) and KCl were purchased from Tianjin Fengchuan Chemical Reagent Technologies Co., Ltd. Glucose (Glu), ascorbic acid (AA), glutamic acid (GA) and citric acid (CA) were from Tianjin Kemiou Chemical Reagent Co.,

Ltd. Phosphate buffer solution (PBS, 0.2 M, pH = 7.0) was prepared by mixing  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  and  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$  solution. Milk samples were purchased from a local supermarket in Zhengzhou (China).  $\text{KMnO}_4$  and sodium oxalate were obtained from Luoyang Chemical Reagent Factory and Tianjin Chemical Reagent Research Institute Co., Ltd, respectively. All chemicals were used without further purification. Double-distilled water was employed during the whole experiment process.

### 2.2. Instruments

Scanning electron microscopy (SEM) images were taken with JEOL JSM-6701F FE-SEM. Transmission electron microscopy (TEM) figures, selected area electron diffraction (SAED) pattern, high-angle annular dark field (HAADF)-scanning transmission electron microscopy (STEM), line-scan energy dispersive X-ray (EDX) images and EDX maps were observed by FEI TalosF200S TEM. X-Ray Diffraction (XRD) pattern was measured using Rigaku Ultima III X-ray diffractometer. X-ray photoelectron spectroscopy (XPS) pattern was obtained by VG ESCALAB250 X-ray photoelectron spectrometer.  $\text{N}_2$  adsorption/desorption isotherms and the distribution of pore size were recorded by Quantachrome NOVA4200 specific surface area and pore size distribution analyzer. All electrochemical experiments were conducted using a ParSTAT MC electrochemical workstation with a conventional three-electrode system. In the three-electrode system, saturated calomel electrode, platinum foil and bare or modified glassy carbon electrode (GCE, 3 mm in diameter) were used as reference electrode, auxiliary electrode and working electrode, respectively.

### 2.3. Preparation of PtNi/NCNFs

PtNi/NCNFs nanocomposites were synthesized by electrospinning and subsequent thermal treatment. Taking PtNi/NCNFs(3:1) for example, 39.4 mg  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  and 20.1 mg  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (with initial mass ratio of Pt:Ni = 3:1) were dissolved into 10 mL EtOH and then 0.75 g PVP was added to the above metal salt solution followed by being stirred for 12 h at 25 °C. Then, the electrospinning was performed under a positive high voltage of 15 kV and a negative voltage of 1000 V with a solution feeding rate of  $0.6 \text{ mL h}^{-1}$ , and the distance of the needle tip and the collector was set as 15 cm. Finally, reduction and carbonization of the as-prepared nanofibers were conducted to obtain one-dimensional PtNi/NCNFs(3:1) as follows: (1) annealed at 150 °C for 2 h and then at 250 °C for 2 h in air to stabilize the electrospun nanofibers, (2) further heated up to 1000 °C at a rate of  $5 \text{ °C min}^{-1}$  and kept at the temperature for 8 h in Ar for reduction of  $\text{Pt}^{4+}$  and  $\text{Ni}^{2+}$  and carbonization of PVP. For comparison, a series of PtNi/NCNFs with different mass ratios of Pt and Ni (1:0, 1:1, 1:3 and 0:1) were also prepared using the same method and named as Pt/NCNFs, PtNi/NCNFs (1:1), PtNi/NCNFs (1:3) and Ni/NCNFs, respectively.

### 2.4. Preparation of PtNi/NCNFs-modified GCE

GCE was polished with  $0.3 \mu\text{m}$  alumina slurry and rinsed with double-distilled water and EtOH successively to obtain mirror-like surface. Then, 2.0 mg nanocomposite was dispersed into 1 mL Nafion (0.5%) and sonicated for 20 min. Finally,  $10 \mu\text{L}$  well-dispersed suspension was carefully dropped onto the mirror-like surface of GCE, and then dried at 25 °C in air to obtain PtNi/NCNFs-modified GCE (PtNi/NCNFs-GCE). Pt/NCNFs-GCE and Ni/NCNFs-GCE were also obtained by the same process.

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