

Preparation and characterization of Ni(II)/polyacrylonitrile and carbon nanotube composite modified electrode and application for carbohydrates electrocatalytic oxidation

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Abstract A nickel(II) into porous polyacrylonitrile–carbon nanotubes composite modified glassy carbon electrode (Ni/PAN-CNT/GCE) was fabricated by simple drop-casting and immersing technique. The unique electrochemical activity of Ni/PAN-CNT composite modified glassy carbon electrode was illustrated in 0.10 M NaOH using cyclic voltammetry. The Ni/PAN-CNT/GCE exhibits the characteristic of improved reversibility and enhanced current responses of the Ni(III)/Ni(II) couple compared with Ni/PAN/GCE and Ni/CNT/GCE. The results of electrochemical impedance spectroscopy and scanning electron microscopy indicated the successful immobilization for PAN-CNT composite film. Kinetic parameters such as the electron transfer coefficient, α , and rate constant, k_s , of the electrode reaction were determined. Ni/PAN-CNT/GCE also shows good electrocatalytic activity toward the oxidation of carbohydrates (glucose, sucrose, fructose, and sorbitol). The electrocatalytic response showed a wide linear range (10–1,500, 12–3,200, 7–3,500, and 16–4,200 μM for glucose, sucrose, fructose, and sorbitol, respectively) as well as its experimental limit of detection can be achieved 6, 7, 5, and 11 μM for glucose, sucrose, fructose, and sorbitol, respectively. The

modified electrode for carbohydrates determination is of the property of simple preparation, good stability, and high sensitivity.

Keywords Polyacrylonitrile · Carbon nanotube · Carbohydrates · Nickel · Modified electrode

Introduction

Direct electrochemical oxidation of sugars is of a very high interest from several points of view ranging from biomedical applications involving blood sugar analysis, fuel cell applications to ecological approaches like wastewater treatment in food industries [1–5]. The detection of blood glucose levels is a challenging problem for diagnosis and therapy of diabetics. Electrochemical biosensors have been applied successfully for the determination of glucose. [6–12]. Some of the electrodes like platinum [13, 14], copper [15–17], nickel [18, 19], and gold [20–23] and also on modified surfaces such as ruthenium dioxide [24], nickel oxide [25–27], cobalt oxide [28], alloy [29, 30], and metallic complexes such as cobalt phthalocyanine [31] have been explored to investigate the direct electrochemical oxidation of sugars in alkaline medium. Among the various possible electrocatalysts, nickel hydroxide has attracted much investigation, specifically as a fuel cell catalyst, secondary batteries and electrocatalyst for organic synthesis [32–34]. Its unique electrocatalytic effect arises from the unpaired “d” electrons and vacant “d” orbitals associated with the oxidized form of nickel oxyhydroxide that are readily available to bind any adsorbed species [35]. It is also well known that nickel and nickel hydroxide exhibit excellent electrocatalytic behavior in alkaline medium [36].

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An inert porous material with a large surface area and high permeability could be a promising candidate for efficient catalyst carriers. Porous polymer materials having polar groups can satisfy these requirements. Different porous polymeric materials have found wide application as immobilization matrix [37–41]. In this manner, a necessary condition is that the size of micropore should be a little larger than the size of an immobilized particle. Polyacrylonitrile has been successfully applied as membrane materials in the fields of dialysis [42], ultrafiltration [43], enzyme immobilization [44], and evaporation [45]. It has also been reported as a membrane to support the attachment of hepatocytes in an artificial liver system [46].

Carbon nanotubes can be functionalized covalently or noncovalently with various polymers. Noncovalent interactions such as π - π interaction, π -cation interaction and ionic interaction between carbon nanotubes (CNTs) and polymers enable the absorption of polymers onto the CNT surfaces [47–50].

The purpose of this study was to make nickel(II) into porous polyacrylonitrile-carbon nanotube (Ni/PAN-CNT) conductive composite and the detailed investigation of carbohydrates oxidation on Ni/PAN-CNT composite in alkaline solution. It is well known that high-surface-area CNTs when combined with metal oxide can improve the performance of the final material, sensitivity, and stability of sensors. The electrocatalytic oxidation of carbohydrates on this type of electrode is attractive because of the interest and needs in sensitive and stable sugar sensors for medical and food industry, as well as sugar-oxygen fuel cell application.

Experimental

Chemicals and apparatus

Multiwalled carbon nanotubes (MWCNTs) were purchased from Shenzhen Nano-Technologies Port Co., Ltd. (China) and were purified using a mixture of sulfuric acid and nitric acid in a composition of 3:2 by volume. Glucose, sucrose, fructose, and sorbitol were of analytical grade from Merck. Other reagents were of analytical grade and purchased from Aldrich or Merck and used as received without further purification. The concentration of carbohydrates was adjusted by injection with a syringe of the required volume of 0.01 M carbohydrates in the 0.1 M NaOH solution. For determination of glucose in human blood serum, 50 μ L samples are transferred to the cell with 10 mL 0.1 M NaOH solution, and the response of the modified sensor into mentioned solution is investigated by cyclic voltammetry at a scan rate of 50 mV s^{-1} .

All voltammetric measurements (cyclic voltammetry) were performed with an Autolab Potentiostat/Galvanostat

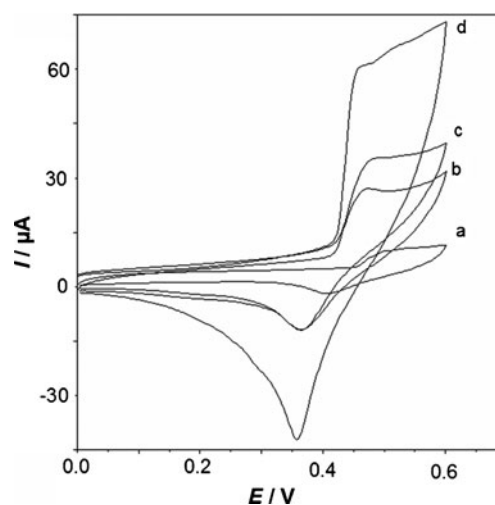


Fig. 1 Cyclic voltammograms of the Ni/GCE (a), Ni/CNT/GCE (b), Ni/PAN/GCE (c), and Ni/PAN-CNT/GCE (d) in 0.1 M NaOH solution at a scan rate of 50 mV s^{-1}

(The Netherlands) coupled to a Pentium IV personal computer. The experiments were performed using a conventional three-electrode cell at room temperature. A working modified glassy carbon (GC) electrode, a saturated Ag|AgCl|KCl_{3M} reference electrode, and a platinum wire

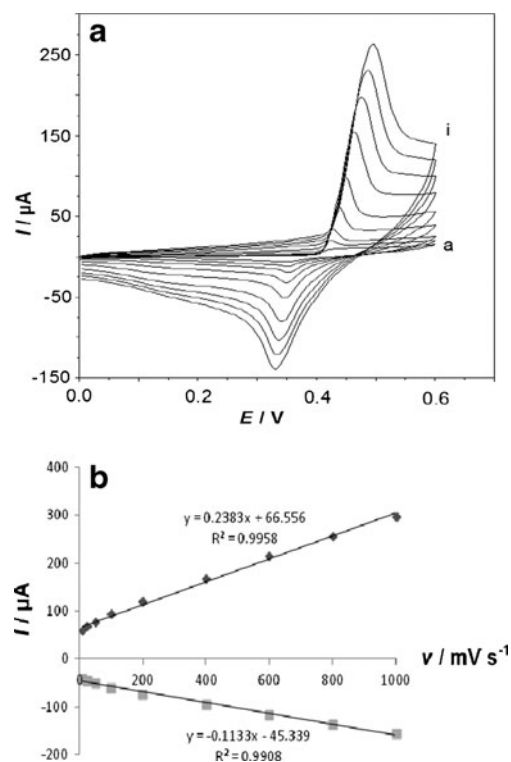


Fig. 2 a Cyclic voltammograms of Ni/PAN-CNT/GCE in 0.1 M NaOH solution at different scan rates. The scan rates are a 10, b 25 mV s^{-1} , c 50 mV s^{-1} , d 100 mV s^{-1} , e 200 mV s^{-1} , f 400 mV s^{-1} , g 600 mV s^{-1} , h 800 mV s^{-1} , and i 1,000 mV s^{-1} , respectively. b The plot of cathodic and anodic peak currents vs. scan rates

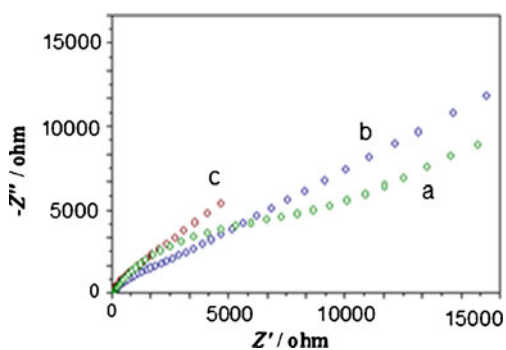


Fig. 3 Impedance plots of bare GCE (a), PAN/GCE (b), and PAN-CNT/GCE (c) in the presence of 1.0 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ containing 0.1 M KCl as supporting electrolyte

auxiliary electrode were used. All potentials were measured and reported versus the $\text{Ag}|\text{AgCl}|\text{KCl}_{3\text{M}}$ reference electrode. The cyclic voltammetric scanning was carried in the potential range from 0.0 to 0.6 V at scan rate 50 mV s^{-1} . Hitachi S-3500N scanning electron microscope (SEM) with electron diffraction and energy dispersive X-ray (EDX) analysis was used for surface image measurements and chemical characterization of a specimen. All experiments were carried out at room temperature.

Preparation of modified electrodes

Prior to modification, the bare glassy carbon electrode (GCE) was polished on chamois leather with $0.05 \mu\text{m}$ alumina powder. Then, it was thoroughly sonicated in deionized water and absolute ethanol, respectively. MWCNT (1.0 mg) was dispersed in 5 mL *N,N*-dimethyl formamide (DMF) with the aid of ultrasonic agitation to give a black dispersion. PAN (1.0 mg) was dissolved in 1.0 mL DMF. PAN and MWCNT solutions with a volume ratio of 1:1 were mixed, and then the mixture was agitated in an ultrasonic bath for 0.5 h to form a uniform mixture. The cleaned GCE was coated by casting $5 \mu\text{L}$ of the black PAN-CNT suspension and dried at 50°C in an oven air to remove the solvent. Then, the PAN-CNT/GCE was immersed in

1.0 mM nickel nitrate solution for 30 min to obtain Ni/PAN-CNT/GCE. For comparison, Ni/GCE, Ni/PAN/GCE, and Ni/CNT/GCE were prepared with the similar procedure as described above.

Results and discussion

Properties of modified electrode

Figure 1 shows the cyclic voltammetric responses obtained at the Ni/GCE, Ni/CNT/GCE, Ni/PAN/GCE, and Ni/PAN-CNT/GCE in 0.10 M NaOH. The anodic and cathodic peaks corresponding to Ni(III)/Ni(II) couple are observed in both cases. Although the cathodic and anodic peak potentials are nearly the same for modified electrodes, the cathodic and anodic peak currents for Ni/PAN-CNT/GCE are increased significantly, relative to those for the Ni/GCE, Ni/CNT/GCE, and Ni/PAN/GCE. The increase in peak current results from a large surface area of the Ni/PAN-CNT/GCE.

The redox potential of the Ni/PAN-CNT/GCE is scan rate dependent. Figure 2a shows the cyclic voltammograms of the Ni/PAN-CNT/GCE in 0.1 M NaOH at various scan rates. It was observed that the values of E_{pa} and E_{pc} shift slightly to the positive and negative directions, respectively, and ΔE_p increases with increasing scan rate. The anodic and cathodic peak currents are linearly proportional to scan rate (Fig. 2b), suggesting that the reaction is not a diffusion-controlled process but a surface-controlled one, as expected for immobilized systems [51].

A plot of E_p versus $\log \nu$ yields straight line with slopes of $-2.3RT/anF$ and $2.3RT/(1-a)nF$ for the cathodic and anodic peak, respectively, so that a can be estimated as 0.62 from the slope of the straight lines. The surface concentration of the electroactive Ni on Ni/PAN-CNT/GCE, Γ (in mol/cm^2), can be estimated using the equation [52]:

$$\Gamma = Q/nFA \quad (1)$$

where Q is the charge consumed in coulombs, obtained from

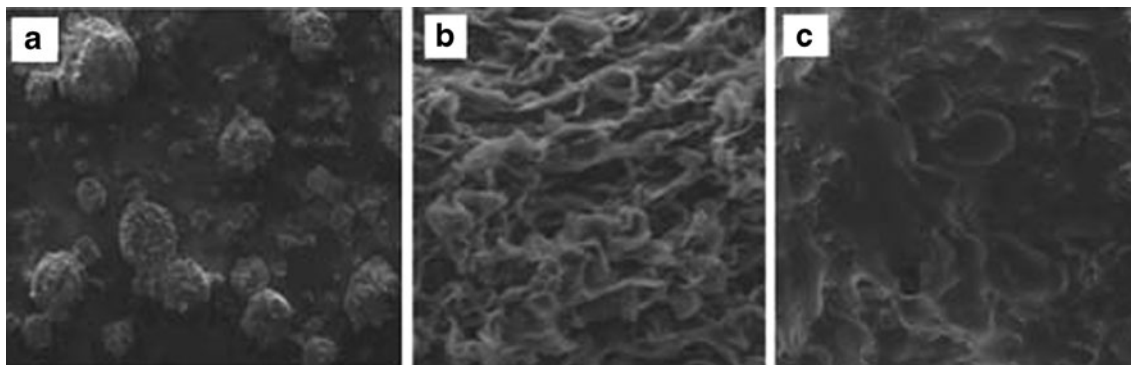


Fig. 4 SEM photographs of PAN/GCE (a), PAN-CNT/GCE (b), and Ni/PAN-CNT/GCE (c)

integrating the anodic (or cathodic) peak area in cyclic voltammograms under the background correction. The average Γ value of $(3.24 \pm 0.67) \times 10^{-10}$ mol/cm² was obtained.

Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) was employed to further investigate the impedance changes of the electrode surface in the modified process. Figure 3 shows the results of the EIS of bare GCE, PAN/GCE, and PAN-CNT/GCE in the presence of 1.0 mM Fe(CN)₆^{3-/4-}. To understand clearly the electrical properties of the as-prepared electrodes/solution interfaces, the semicircle diameter equals the charge transfer resistance (R_{ct}). This resistance exhibits the electron transfer kinetics of the redox probe at the electrode interface. As shown in Fig. 3, there is charge transfer resistance about $1.15 \times 10^4 \Omega$ for Fe(CN)₆^{3-/4-} at bare GCE (curve a). After modifying GCE with PAN film, the R_{ct} decreased to about $5.31 \times 10^3 \Omega$ (curve b), indicating that the PAN film is porous material with a large surface area. While when CNT was attached to the PAN, it can be seen that R_{ct} decreases to about $7.39 \times 10^2 \Omega$ (curve c), implying that the CNT may play an important role similarly to a electron conducting tunnel, which makes it easier for the electron transfer to take place. These data showed that the CNT and PAN film have been successfully attached to the electrode surface and formed a tunable kinetic barrier.

The surface morphology of polyacrylonitrile film

The SEM micrographs of PAN/GCE, PAN-CNT/GCE, and Ni/PAN-CNT/GCE are shown in Fig. 4. PAN film shows porous structure with pore diameter of about 200 nm (Fig. 4a). In general, the size of Ni(II) is in the range of 0.06–0.09 nm. Therefore, Ni(II) ion can be absorbed into PAN micropores, which was testified by the experimental result. From Fig. 4b, it can be seen that the hybrid films are compact, homogeneous, and densely packed on the electrode surface, and CNTs are dispersed on the surface of PAN-CNT/GCE. After adsorbed Ni by immersing method,

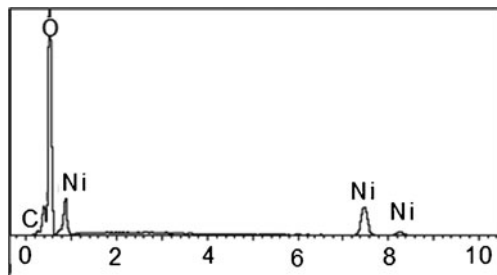


Fig. 5 EDX of Ni/PAN-CNT/GCE

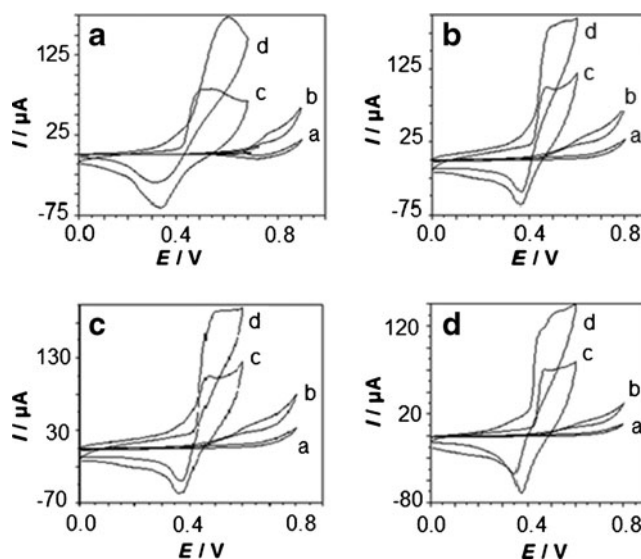


Fig. 6 Cyclic voltammograms obtained for bare GCE in a absence and b presence of 1.0 mM of of glucose (A), sucrose (B), fructose (C) and sorbitol (D). c as a and d as b at Ni/PAN-CNT/GCE in 0.1 M NaOH at scan rate 50 mV s⁻¹

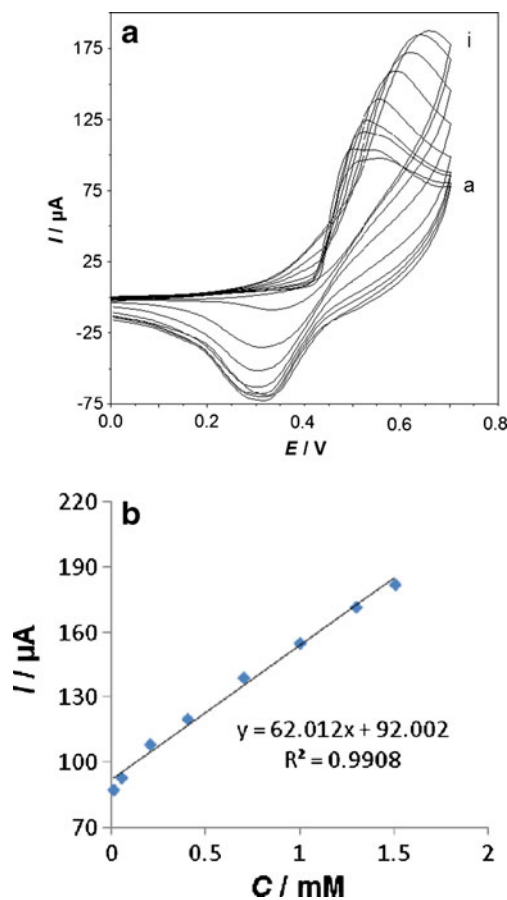


Fig. 7 a Cyclic voltammograms of Ni/PAN-CNT/GCE in the presence of a 0.00 mM, b 0.01 mM, c 0.05 mM, d 0.20 mM, e 0.40 mM, f 0.70 mM, g 1.00 mM, h 1.30 mM, and i 1.50 mM of glucose in 0.1 M NaOH solution at scan rate of 50 mV s⁻¹. b Plot of anodic peak current vs. glucose concentrations

Table 1 Analytical parameters for voltammetric determination of carbohydrates at different modified electrodes

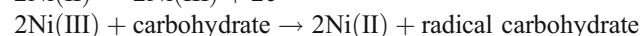
Modifier	Sensitivity ($\mu\text{A mM}^{-1} \text{cm}^{-2}$)	LDR (μM)	LOD (μM)	References
Pt–Pb nanowire	11.25	0–11,000	8 (glucose)	[58]
OMC	10.81	500–2,500	20 (glucose)	[59]
Ni (II) oxide/MWNT	–	200–12,000	160 (glucose)	[44]
CNT–NiCo-oxide	66.15	10–12,120	5 (glucose)	[60]
CNT–NiCo-oxide	35.72	20–675	9.5 (fructose)	[60]
Glucose Oxidase	–	4,000–15,000	– (sucrose)	[61]
SDH-NADC ^a	–	20–800	40 (sorbitol)	[62]
Ni/PAN-CNT	493.73	10–1,500	6 (glucose)	This work
Ni/PAN-CNT	384.53	12–3,200	7 (sucrose)	This work
Ni/PAN-CNT	489.29	7–3,500	5 (fructose)	This work
Ni/PAN-CNT	358.51	16–4,200	11 (sorbitol)	This work

^aSorbitol dehydrogenase and nicotinamide adenine dinucleotide

the micropores of PAN film diminished markedly, and the film surface was covered partly by the Ni (Fig. 4c). Figure 5 gives the EDX distribution of elements for the deposited Ni. The existence of Ni in the prepared film was confirmed by the EDX results.

Electrocatalytic behavior of Ni immobilized on Ni/PAN-CNT/GCE

Previous reports showed that NiO-modified electrodes could display an electrochemical response to glucose [51]. Here, the electrocatalytic activity of the Ni immobilized in Ni/PAN-CNT/GCE to carbohydrates was also observed. As it is seen from Fig. 6, for cyclic voltammograms obtained for bare GCE in 0.1 M NaOH in the absence (curve a) and presence of 1.0 mM carbohydrates (curve b), the oxidation of glucose, sucrose, fructose, and sorbitol requires very high positive potentials, leading to a poorly defined anodic wave involving very slow electrode kinetics. In contrast, oxidation of these carbohydrates at the Ni/PAN-CNT/GCE in 0.1 M NaOH occurred at much less positive potentials with an increase in the oxidation peak current and the decrease in the reduction peak (curve d). The electro-oxidation of carbohydrates due to the existence of Ni(II) ions occurs according to the following reactions:



Ni(III) acts as strong oxidant, reacting with the carbohydrate molecules by subtracting a hydrogen atom to yield a radical. Further reaction of the radical with additional surface sites results in product formation. As reported in the literature, gluconolactone and gluconic acid [53, 54] were detected as the main products of glucose oxidation. In addition, format and oxalate [55] were reported as oxidation products. Sorbitol was transformed into gluconic acid via the formation of

glucose. Glucuronic acid and some degradation side products were also detected [56]. Sucrose was transformed into α -glucose that changed into β -glucose and converted into gluconic acid [57].

Voltammetry response and calibration curve

The cyclic voltammetry response of the carbohydrates sensor is investigated by successively adding various concentrations of carbohydrate into 0.1 M NaOH solutions. Figure 7 illustrates cyclic voltammograms and the calibration plot of response current to different concentrations of glucose. A similar behavior was observed for electro-oxidation of sucrose, fructose, and sorbitol at Ni/PAN-CNT/GCE. The linear dynamic range (LDR), limit of detection (LOD), and sensitivity of mentioned carbohydrates was obtained from calibration plots shown in Table 1.

Interference study

Possible interference for the detection of carbohydrates at the Ni/PAN-CNT/GCE was investigated by the addition of various compounds such as glutathione, cysteine, tryptophan, glycine, alanine, ascorbic acid, dopamine, uric acid,

Table 2 Assay of glucose in human blood serum samples and recovery of carbohydrates in 0.1 M NaOH solution spiked with different concentrations

Sample	Spiked (mM)	Biochemical analyzer in a local hospital (mM)	Found Mean recovery	(n=3) (mM)
Blood serum	–	4.70	4.58	–
Glucose	0.15	–	0.14	93±2
Sucros	0.31	–	0.30	96±4
Fructose	0.15	–	0.16	107±3
Sorbitol	0.22	–	0.21	95±4

penicillamine, methionine, lysine, *N*-acetyl-L-cysteine, and cysteamine into 0.1 M NaOH solution in the presence of 1.0 mM carbohydrates. The results showed that mentioned compounds did not show interference.

Reproducibility and stability of Ni/PAN-CNT/GCE

The reproducibility and storage stability of the modified electrode were also examined. The relative standard deviation (RSD) of the sensor response to 1.0 mM carbohydrates was 2.8–5.8 % for five successive measurements. The RSD for detection of 1.0 mM carbohydrates with four sensors prepared under the same conditions was 3.5–6.2 %. When the sensor was stored dry and measured at intervals of 1 week, it retained about 86 % of its original sensitivity after 5 weeks.

Determination of glucose in human blood serum and analytical recoveries of carbohydrates

The response of the modified sensor to the glucose in human blood serum was investigated. The serum sample obtained from hospitalized patient was analyzed. The results were matched with referenced value obtained by the automated standard colorimetric technique in the hospital. Table 2 shows analytical recoveries of the glucose, sucrose, fructose, and sorbitol solutions added to 0.1 M NaOH solution, suggesting the good accuracy of the method.

Conclusions

A sensor towards the carbohydrates detection is fabricated by immobilization of Ni(II) onto the PAN-CNT composite via immersing method. The sensor shows a quite wide linear range as well as its experimental limit of detection can be achieved as low as micromolars. It also possesses good reproducibility and stability. All these advantageous can make the designed sensor applicable in medical, food, or other areas. Moreover, the investigation also exhibits that the PAN-CNT may be applied as a novel immobilization material for a variety of sensor designs.

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