Rapid, sensitive, and reusable detection of glucose by highly monodisperse nickel nanoparticles decorated functionalized multi-walled carbon nanotubes

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ABSTRACT

Addressed herein, functionalized multi-walled carbon nanotube (MWCNT) supported highly monodisperse nickel nanoparticles modified on glassy carbon electrode (Ni@*f*-MWCNT/GCE) were synthesized through microwave assisted method and examined for non-enzymatic glucose sensing in ionic liquids by cyclic voltammetry and chronoamperometry. The results of Ni@*f*-MWCNT/GCE electrode were compared with Ni NPs/GCE electrode and the results revealed that *f*-MWCNTs increased the electrocatalytic properties of Ni nanoparticles regarding glucose oxidation. They also demonstrated a good linear span of 0.05–12.0 mM and a detection boundary of 0.021 μM. Specifically, in the amperometric signal of the electrodes after 200th cycles, no major change was observed. This non-enzymatic glucose sensor presents one of the record electrocatalytic activity, stability and response towards glucose under the optimized situations. As a result, prepared novel Ni@*f*-MWCNT/GCE was utilized to detect glucose in real serum species.

1. Introduction

Diabetes is a chronic disease caused by increased of blood glucose levels and takes place at the beginning of a major health problem in the worldwide (Fu et al., 2015; Choi et al., 2015). Since 1960, advancement of recognizing small molecules via electrochemical systems has extensively considered very important. Sugar oxidation by electrocatalysis carries importance in various areas, such as therapeutic applications, wastewater treatment, biological fuel cell development, and analytical applications of food enterprises. Glucose oxidation has been accepted as a basic step for the oxidation of substantial organic materials and examined through many scientists (Park et al., 2006; Kang et al., 2007; Li et al., 2009; Wang et al., 2009; Si et al., 2013a, 2013b). In spite of the fact that the glucose oxidation is thermodynamically advantageous, its prolonged reaction kinetics using typical electrodes slows down its usage in analytical analysis (Guo et al., 2013a, 2013b, 2013c). In addition, the extensive over-potential of this reaction needs a high applied potential, bringing about diminished selectiveness and, furthermore, oxidation reaction products usually destroy the surface of the electrodes (Guo et al., 2013a, 2013b, 2013c). Attraction is still existent in the improvement of materials that can be used in the electrocatalytic glucose reduction to lessen the normally large over potentials experienced in its direct reduction at nearly all surfaces of electrodes. For electrochemical glucose detection, enzymatic glucose sensors have made several disadvantages such as high cost, instability, immobilization problems between the electrode and the enzyme. In contrast to enzymatic sensors, non-enzymatic glucose sensors have benefits like being economic, high sensitivity, long-term stability especially for the glucose oxidation (Park et al., 2006; Kang et al., 2007; Li et al., 2009) Electroactivity degree toward carbohydrates, particularly glucose, has been good when various transition metal and metal oxide electrodes (Au, Co, Cu, In, Ni, NiO(OH), Pt, RuO$_2$, Ru,WO$_3$, etc.) (Wang et al., 2009; Si et al., 2013a, 2013b; Guo et al., 2013a, 2013b, 2013c; Wang et al., 2013; Huo et al., 2014a, 2014b; Li et al., 2012; Ye et al., 2004) and different metal combinations or composite electrodes (Au–Cu, Au–Ni, Ni–Cr, Pt–Pd, etc.) (Wang et al., 2009; Si et al., 2013a, 2013b; Gavalas et al., 2004; Merkoci et al., 2005; Wang and Lin, 2008) are utilized. Additionally, a few unique compounds have been reported as electrocatalysts to adjust the surfaces of electrodes to oxidize glucose (Chang et al., 2013; Zhao et al., 2013; Kim

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et al., 2014; Zhao et al., 2007a, 2007b; Li et al., 2011)Since carbon nanotubes (CNTs) (Mu et al., 2011a, 2011b) have unique properties, for example, critical mechanical quality, large surface area, fabulous electrical conductivity, and great chemical stability, they have attracted researchers for various uses. Other than different utilizations of the CNTs, they are additionally of enthusiasm for making biosensors and electrochemical sensors (Nai et al., 2013; Rasee and Fakhari, 2013). Lately, some metal nanoparticles and CNT composites were presented to demonstrate superior sensitivity on small molecules, for example, hydrogen peroxide (Zhao et al., 2007a, 2007b), glucose (Yu et al., 2012) and methanol (Çelik et al., 2016a, 2016b, 2016c). A few examinations managing use of carbon nanotubes (Lu et al., 2009a, 2009b; Gao et al., 2011) as promising catalyst supports have as of now been completed. This study concentrates on utilization of multi-walled carbon nanotubes (MWCNTs) as catalyst support for the adjustment of a glassy carbon–Ni nanoparticles electrode to enhance its electroactivity towards glucose (Lu et al., 2013a, 2013b; Zhang et al., 2013; Liu et al., 2009; Lu et al., 2013a, 2013b; Zhu et al., 2011; Ding et al., 2010; Chen et al., 2013a, 2013b; Si et al., 2013a, 2013b). These metal nanoparticles (NPs), give wide applications, for example, solid adsorption, substance dependability efficient electro catalytic reaction of sensors and biosensors. Moreover, in various studies, carbon-based materials are utilized as support material. Among of these, carbon nanotubes (CNTs) have large surface area, amazing conductivity and repairman toughness. These properties of CNTs give all the more quickly electron-exchange between metal nanoparticles and anode surface. To build the viability and solvency of multi-walled carbon nanotubes, practical gatherings side-dividers are connected by utilizing a great deal of procedures. One of them is the treatment with solid acids. Thusly, metal nanoparticles with altered carbon nanotubes are favoured for particularly sensor applications (Wang et al., 2012a, 2012b; Zhang et al., 2011, 2012a, 2012b; Mathew and Sandhyarani, 2013; Chen et al., 2013a, 2013b). In this study, highly monodisperse Ni nanoparticles supported on functionalized multi-walled carbon nanotubes on glassy carbon (Ni@f-MWCNT/GCE) electrode was used drop-casting method toward the oxidation of glucose for non-enzymatic sensor. Prepared monodisperse Ni@f-MWCNT nanocatalysts were investigated for the stability, selectivity, sensitivity, linear range limit of detection (LOD) for non-enzymatic glucose sensor.

2. Experimental section

2.1. Synthesis of monodisperse Ni@f-MWCNT NPs

To form a stable suspension, 0.25 mmol of Ni(Ac)$_2$ was dispersed in 30 mL ethylene glycol solution under brisk stirring. The pH was adjusted using NaOH–EG solution. Next, the beaker was kept in the centre of microwave oven at 1200 W for 60 s. Under this condition, EG was used as a reducing agent for Ni(Ac)$_2$ reduction. At the end, the final solution was filtered, and then washed several times with deionized water and acetone. To stabilize the metal nanoparticles against agglomeration, the microwave synthesis was carried out in the presence of OA (oleylamine) where OA is used as a capping agent. The prepared NPs were mixed with f-MWCNTs (1:1, v-v) by an ultrasonic tip sonicator. Lastly, the Ni@*f*-MWCNT NPs were dried under vacuum at room temperature (Xiu-tian-feng et al., 2014; Lin et al., 2013).

3. Results and discussion

3.1. Material characterization

The characterization of *f*-MWCNT has been shown in Fig. S1 in detail. Moreover, by the help of SEM, Ni@f-MWCNT NPs' morphologies were determined. The Fig. S1(d) and (e) demonstrates a representative SEM image of monodisperse Ni@f-MWCNT NPs that has the
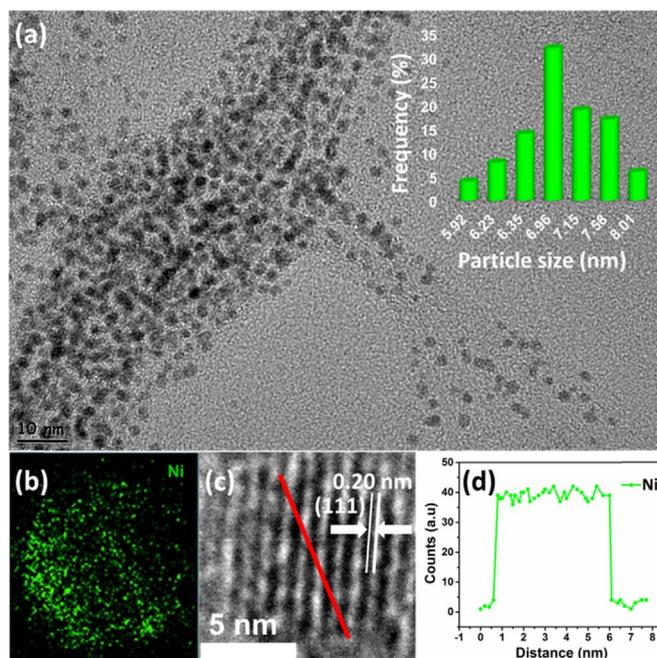

Fig. 1. (a) Representative TEM image and nanoparticle size histogram, (b) EELS elemental color-mapping, (c) Representative HRTEM image, and (d) EELS line profile scanned on the arrow of Ni@f-MWCNT NPs.

mass of the Ni nanoparticles, having an approximate diameter of 9 nm. This image indicates that the pure MWCNT having lengths up to several micrometers and diameters up to few nanometers has no impurity on their surfaces.

It can be seen that the monodisperse Ni nanoparticles decorated MWCNTs are randomly distributed with uneven nanoparticles decorated on the surface of the MWCNT tubes, and it seems like the plant root nodules. The multi-walled-nanotubes were connected with Ni and Ni NPs attached on multi-walled-nanotubes. The existence of nickel and carbon was proved by EDS results (Fig. S1,e) (Xiu-tian-feng et al., 2014; Lin et al., 2013; Huo et al., 2014a, 2014b; Karatepe et al., 2016).

The Fig. 1(a) displays a representative TEM image of monodisperse Ni@f-MWCNT NPs. In this TEM image, it can be seen that all particles exist homogeneously on the CNT surface and no agglomerations or aggregations were observed. The average particle size was measured as 6.96 ± 1.05 nm. The Fig. 1(c) is the HRTEM image of Ni NPs and displays the atomic lattice fringes. Here, Ni (111) spacing of 0.20 nm of Ni NPs is exactly same with nominal Ni (111) spacing which reasserts the nanoparticle formation. The Fig. 1(b) and (d) present the EELS elemental color-mapping and the EELS line profile scanned on the arrow of NPs, respectively. These EELS results also indicate the existence of Ni@f-MWCNT NPs. In this study, XPS was employed to study surface disposition and materials' oxidation state (Yıldız et al., 2016) of the Ni@f-MWCNT NPs. The Fig. 2(a) demonstrates the XPS spectra that exhibits that the core level of Ni 2p^3/2 was at 853.2 eV. This finding suggests that the most of the Ni atoms were in the metallic state (Çelik et al., 2016a, 2016b, 2016c). The particular Ni(II) peak from 861. 5 eV as shown in Fig. 2(a) and (b) may indicate the oxidation occurred in the surface and/or chemisorption of environmental oxygen while the NPs were prepared. Moreover, using the relative peak area of the Ni 2p^3/2 spectrum, Ni(0) to Ni(II) ratio of the catalysts was found to be 3.27. Fig. 2(c) represents the Raman spectrum of f-MWCNTs that shows an augmented D/G ratio compared to the ratio that pristine MWCNTs have (ID/IG=1.25 for f-MWCNTs and ID/IG=1.09 for pristine MWCNTs). Fig. 2(d) and (e) show the atomic force microscopy (AFM) (Çelik et al., 2016a, 2016b, 2016c; Erken et al., 2016; Ertan et al., 2012) results that explain the height and lateral diameter distribution. Although the AFM lateral diameter of the catalyst is much
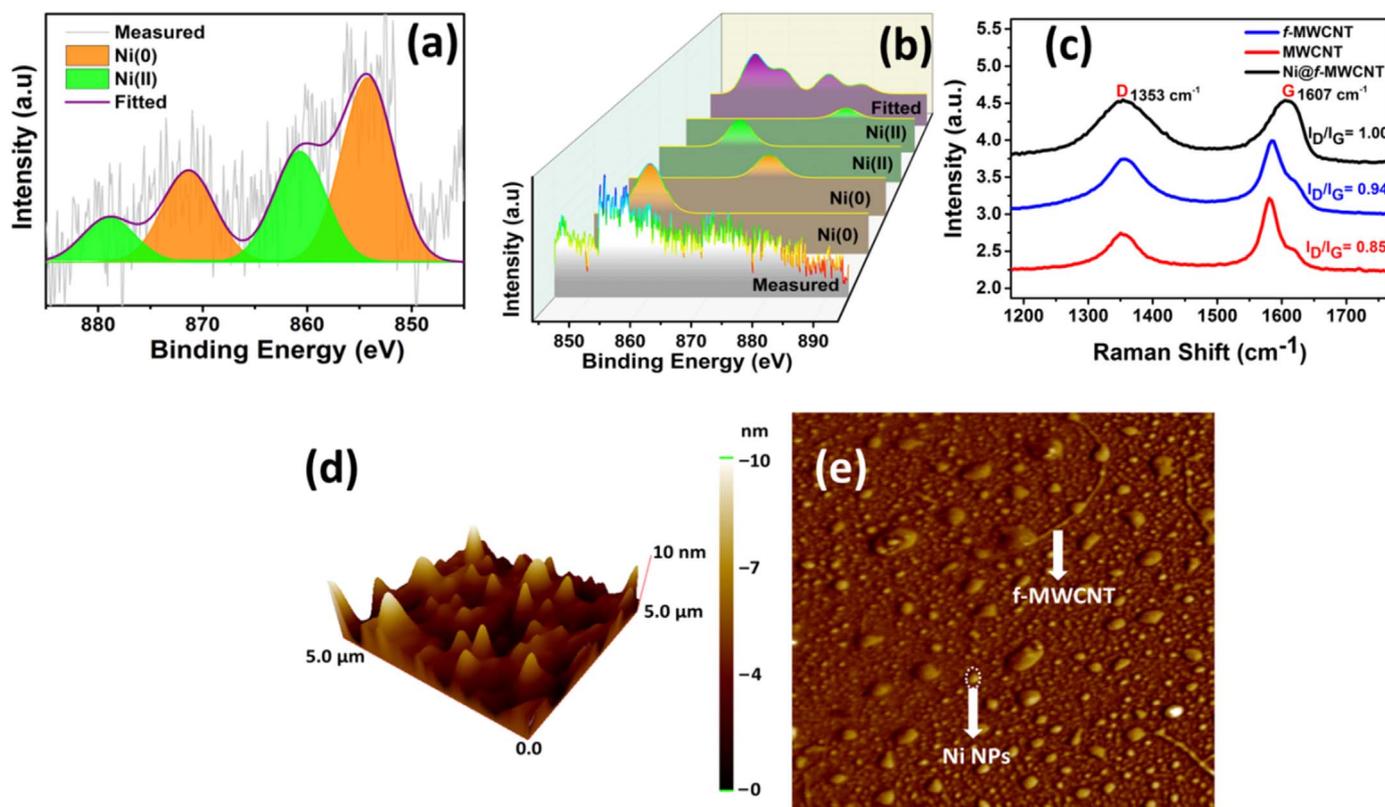
Fig. 2. (a) XPS spectra of Ni 2p for Ni@f-MWCNT, (b) XPS spectra of Ni 2p 3D view, (c) Raman spectrum of f-MWCNT, (d) AFM 3D view, and (e) AFM phase view of Ni@f-MWCNT.

larger than the size of those obtained by the SEM and TEM which is very likely due to the tip contamination and/or the tip convolution. The obtained AFM particle height values of monodisperse Ni@f-MWCNT NPs are in good agreement with the results obtained by the TEM.

3.2. Electrochemical properties

3.2.1. Cyclic voltammetry measurements

By cyclic voltammetry, the glucose oxidation at the bare GC electrodes and modified GC electrodes was studied. Fig. 3(a) shows the cyclic voltammetric responses that were obtained in 0.10 M NaOH at the Ni/GCE and Ni@f-MWCNT/GCE electrodes. In the basic medium, to detect glucose, CV data were obtained by glassy carbon electrode and by glassy carbon electrode exposed to modification.

The data were achieved by Ni@GCE, Ni@f-MWCNT/GCE (a,c-without glucose) and by Ni@GCE, Ni@f-MWCNT/GCE (b,d-with 0.1 mM glucose). The anodic and cathodic peaks stand for Ni(II)/Ni(III) couple were detected at about 0.56 and 0.33 V vs. Ag/AgCl, at a scan rate of 50 mV s^{-1}, respectively. Notwithstanding the cathodic and anodic peak potentials are very close for both Ni/GCE and Ni@f-MWCNT/GCE modified electrodes, the cathodic and anodic peak currents in the Ni@ f-MWCNT/GCE modified electrode are significantly enhanced. This relative enhancement in the peak current is due to a greater surface area of the Ni@f-MWCNT/GCE modified electrode. These results indicated that both Ni/GCE and Ni@f-MWCNT/GCE can catalyse the electro-oxidation of glucose to gluconolactone (Zhu et al., 2011). The glucose detection mechanism involved is proposed as follows: a layer of Ni(OH)$_2$ is generated on the surface of Ni@f-MWCNT/GCE during the
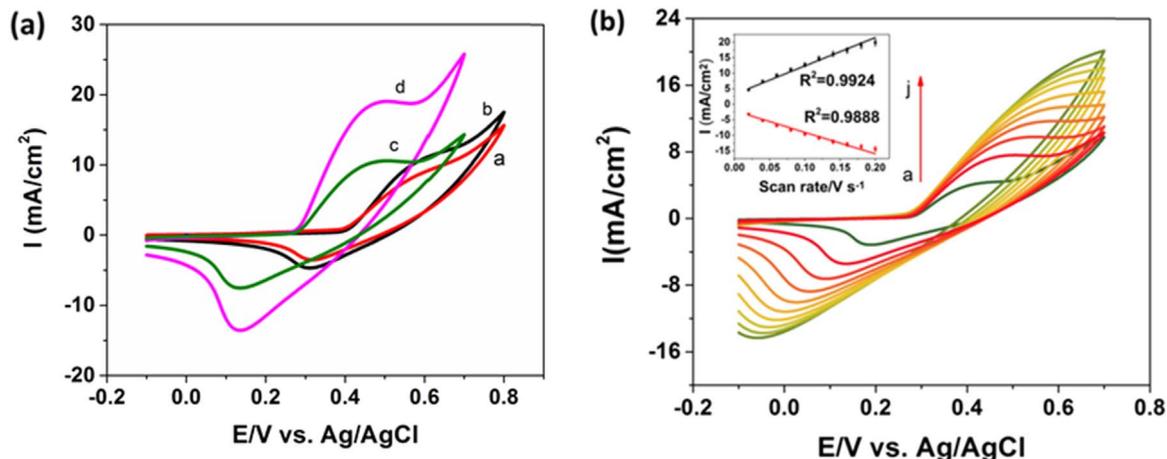

Fig. 3. (a) Cyclic voltammograms obtained for "a)Ni/GCE" and "c)Ni@f-MWCNT/GCE" (without glucose) and "b)Ni/GCE" and "d)Ni@f-MWCNT/GCE" (with 0.1 mM glucose) at 50 mV/s scan rate in 0.1 M NaOH solution. (b) Cyclic voltammograms of the Ni@f-MWCNT/GCE in the presence of 1 mM glucose at varying scan rates: (a) 20, (b) 40, (c) 60, (d) 80, (e) 100, (f) 120, (g) 140, (h) 160, (i) 180, (j) 200 mV s^{-1}, respectively. (Inset: plot of peak current (IP) vs. scan rate (V)).

LSV process in alkaline medium. The produced $Ni(OH)_2$ is further oxidized to NiOOH on the Ni@f-MWCNT/GCE surface. The oxidation of glucose to glucolactone catalyzed by the $Ni(OH)_2$/ NiOOH redox couple according to the following reactions leads to an increase of anodic current:

$$2Ni(II) \rightarrow 2Ni(III) + 2e^-$$

$$2Ni(III) + glucose \rightarrow 2Ni(II) + gluconolactone$$
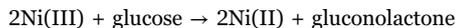
In Fig. 3(b), the anodic peak currents obtained from the Ni@f-MWCNT/GCE electrode in 0.1 M NaOH buffer at different scan rate during the experiments at different scan speeds are demonstrated.

The electrochemical behaviours of Ni@f-MWCNT/GCE were investigated using 0.5 mM glucose at several scan rate values in 0.1 M sodium hydroxide (Fig. 3(b)). As it is seen, reduction-oxidation peak current of glucose was enhanced with increasing scan speed from 20 mV/s to 200 mV/s. This result suggests that the electro-catalytic glucose oxidation is increased charge-transfer kinetic limitations within the reactions among reduction-oxidation of glucose and Ni@f-MWCNT/GCE. At this point, it is worth mentioning that as 0.1 M of NaOH (a strong supporting electrolyte at high concentration) is employed in all electrochemical investigations, expected chance of potential shift to more positive values because of higher ohmic drop is negligible. Furthermore, the anodic peak current measured at the Ni@f-MWCNT/GCE modified electrode was found to be importantly greater than the current value that the Ni/GCE electrode had. The reason for this finding could be high electrode surface area when carbon nanotubes exist (Fig. S2).

3.2.2. Optimization of sensor and amperometric measurements

The effect of glucose amount on anodic peak current was also examined by the cyclic voltammetry using Ni@f-WCNT/GCE. Fig. 4(a) shows CV data obtained by Ni@f-MWCNT/GCE electrode with different glucose amounts (varying from 0.1 mM to 0.6 mM in 0.1 M of sodium hydroxide). In this figure, the relationship between glucose amount and oxidation peak intensity was displayed. It is easy to see that linear results were obtained when the glucose concentration was up to 12 mM. The detection limit was found to be 2.10×10^{-5} mmol/L which was three times of the signal to noise ratio. At higher glucose concentrations, the current varies from the linearity, and the possible reason for this could be passivating the electrode and/or glucose isomers generation as these are known to happen in basic media. In the meantime, saturations of active sites at the electrode surface occurred and therefore the peak current tends to level off at higher glucose concentrations (Fig. 4(a)–(c)).

Fig. 4(b) represents the amperometric responses of the monodisperse Ni@f-MWCNT/GCE electrode in 0.1 M NaOH solution at 0.56 V with increment of glucose in 0.1 mM and 25 μM steps (insets in Fig. 4(b) and Fig. 4(c), respectively). The electrode had an immediate response when glucose was added, and after 3–5 s, the current reached steady-state. In Fig. 4(b), linear equation between the measured current (I) and the glucose was presented. It can be seen that very high correlation coefficients of 0.9983 and 0.9897 were got in the range of 25 μM to 1 mM glucose. One of the lowest detection limits was found to be at the 0.021 μM glucose (S/N=3).

3.2.3. Reproducibility, stability and anti-interference property

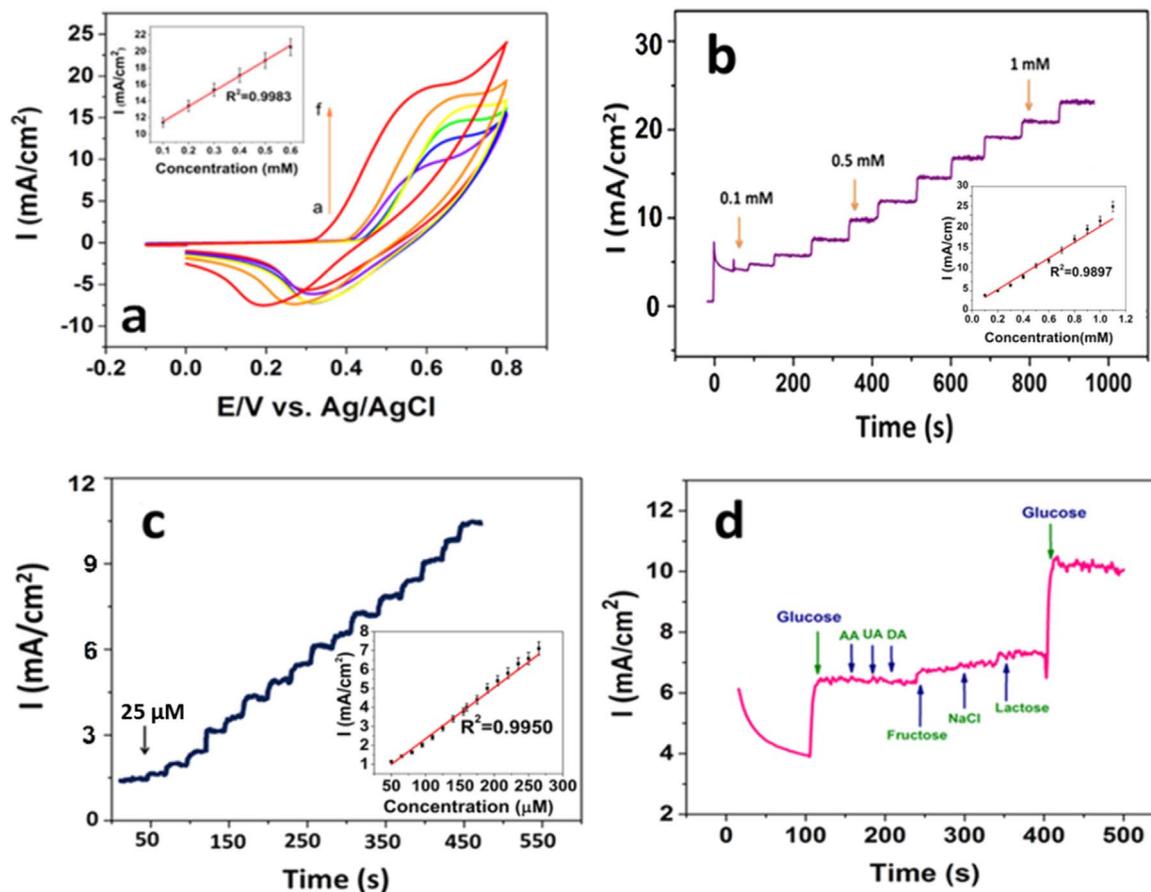The following molecules, namely DA (Dopamine), UA (Uric Acid),

Fig. 4. (a) Cyclic voltammograms of the Ni@f-MWCNT/GCE in 0.1 M NaOH solution at various glucose concentrations: (a) 0.1, (b) 0.2, (c) 0.3, (d) 0.4, (e) 0.5 and (f) 0.6. Inset; plot of peak for linear range. (b) Amperometric responses of monodisperse Ni@f-MWCNT/GCE electrode when there was 0.1 mM of successive glucose additions (c) The amperometric current plotted vs. total glucose concentration, and their corresponding linear calibration curves. (d) Amperometric responses of monodisperse Ni@f-MWCNT/GCE with 1.0 mM successive glucose, 0.1 mM AA, UA, DA, fructose, lactose and NaCl additions. Experiments were run in 0.1 M NaOH solution at +0.50 V.

Table 1
The glucose detection in human blood serum samples (HBS) with the commercial biosensor and our glucose sensor.

Samples	Glucose (mM) (proposed sensor)	RSD (Relative Standart Deviation)$^{\alpha}$ (N=4)	Glucose (mM) (commercial glucose sensor)	Recovery (%)
1	5.8	4.5%	5.6	98.0
2	4.5	4.2%	4.32	96.0
3	7.0	3.7%	6.74	96.4
4	3.8	3.5%	3.75	98.7
5	6.7	4.6%	6.55	97.8

AA (Ascorbic Acid), fructose, lactose and NaCl typically coexist with glucose in real samples such as human blood when the glucose is determined. Therefore, we studied the interference by measuring the amperometric responses and the results were given in Fig. 4(d). In this figure, experimental results run at 1 mM concentrations and at 0.5 V were depicted. In our results, when 0.1 mM of AA, DA, UA, NaCl were added, there was no distinct current response except lactose and fructose. When 0.1 mM of lactose and fructose were added, current response has been observed. Besides, when there was 1 mM glucose addition, an important current response was observed. Thus, using monodisperse Ni@f-MWCNT/GCE, interference of biomolecules to glucose response is negligible.

In the present study, long-term stability of monodisperse Ni@f-MWCNT/GCE was also examined. In this part, 10 mM glucose and 0.1 M NaOH solutions were used, and the results were given in Fig. S3. Here, changes in the anodic peak currents of the electrode under dry conditions at room temperature were measured. For both modified electrodes, declines in peak currents occurred in the first three weeks. It is worth noting that the peak current decline of the Ni/GCE is much more declared than the result of Ni@f-MWCNT/GCE modified electrode. In addition, for both cases, the reproducibility of the responses are found to be 70 days. All these findings present that the Ni@f-MWCNT/GCE modified electrode is stable for long-terms and suitable for storage. Besides, monodisperse Ni@f-MWCNT/GCE are compared with other Ni based sensor as shown in Table S1 in terms of LOD, sensitivity and linear range and this table shows that monodisperse Ni@f-MWCNT/GCE has much higher performances compared to the others. (Lu et al., 2009a, 2009b; Mu et al., 2011a, 2011b; Yang et al., 2013; Wang et al., 2012a, 2012b; Kong et al., 2010; Zhang et al., 2012a, 2012b; Shen et al., 2016).

In our study, the applicability of the monodisperse Ni@f-MWCNT/GCE electrode was tested using five different human blood serum samples to determine glucose concentration. In those experiments, 50 μL of each blood serum was mixed with 10 mL of 0.1 M NaOH and then their anodic peak currents were measured by utilizing the Ni@f-MWCNT/GCE modified electrode. The experimental results obtained from these runs are summarized in Table 1 and these data were compared to a standard hospital blood glucose determination method by using a commercial glucose sensor. In Table 1, it can be seen that the obtained glucose results and commercial sensor results are in good agreement. Furthermore, excellent recovery results were obtained (between 96.4% and 98.7%).

4. Conclusions

Highly monodisperse Ni@f-MWCNT/GCE nanocomposites were successfully synthesized using a simple and solvent-free method. The synthesized nanocomposites were like plant root nodules. These novel nanocomposites were used for glucose detection and a non-enzymatic electrochemical sensor was built. This non-enzymatic glucose sensor displays an outstanding sensitivity (70 mA mM^{-1} cm^{-2}) at +0.5 V. Its

detection limit was achieved as 0.021 μM. As the synthesis of nano-composites is easy and they have excellent electrochemical sensing properties, the Ni@f-MWCNT/GCE is a very good non-enzymatic glucose sensor candidate. Our results showed that the reactivity of Ni@f-MWCNT/GCE was significantly improved when f-MWCNTs was used as a support material for glucose oxidation in alkaline medium. The unique structure, the specific interactions between Ni and f-MWCNTs and large surface area to volume ratio of f-MWCNTs may lead to a one of the record electrocatalytic activity. Another advanta-geous feature of the Ni@f-MWCNT/GCE is its stability, as it showed great stability even it was kept under dry conditions for more than ten weeks. In addition, successful results were gathered when human serum samples were used to determine glucose with the developed modified electrode. As a result, it was observed that the glassy carbon anode altered by Ni nanoparticles and MWCNT (Ni@f-MWCNT/GCE) is profoundly viable electrode for glucose oxidation.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.bios.2017.01.045.

References

Çelik, B., Erken, E., Eriş, S., Yıldız, Y., Şahin, B., Pamuk, H., Sen, F., 2016a. Highly monodisperse Pt(0)@AC NPs as highly efficient and reusable catalysts: the effect of the surfactant on their catalytic activities in room temperature dehydrocoupling of DMAB. Catal. Sci. Technol. 6, 1685–1692.

Çelik, B., Başkaya, G., Sert, H., Karatepe, Ö., Erken, E., Şen, F., 2016b. Nearly monodisperse carbon nanotube furnished nanocatalysts as highly efficient and reusable catalyst for dehydrocoupling of DMAB and C1 to C3 alcohol oxidation. Int. J. Hydrog. Energy 41, 5661–5669.

Çelik, B., Yıldız, Y., Sert, H., Erken, E., Koşkun, Y., Şen, F., 2016c. Monodispersed palladium–cobalt alloy nanoparticles assembled on poly(N-vinyl-pyrrolidone) (PVP) as a highly effective catalyst for dimethylamine borane (DMAB) dehydrocoupling. RSC Adv. 6, 24097–24102.

Chang, H.W., Tsai, Y.C., Cheng, C.W., Lin, C.Y., Wu, P.H., 2013. Preparation of platinum/carbon nanotube in aqueous solution by femtosecond laser for non-enzymatic glucose determination. Sens. Actuators B 183, 34–39.

Chen, C., Xie, Q., Yang, D., Xiao, H., Fu, Y., Tan, Y., Yao, S., 2013. Recent advances in electrochemical glucose biosensors: a review. RSC Adv. 3, 4473.

Chen, Z., Guo, J., Zhou, T., Zhang, Y., Chen, L., 2013b. A novel nonenzymatic electrochemical glucose sensor modified with Ni/Al layered double hydroxide. Electrochim. Acta 109, 532–535.

Choi, T., Kim, S.H., Lee, C.W., Kim, H., Choi, S.-K., Kim, S.H., Kim, E., Park, J., Kim, H., 2015. Synthesis of carbon nanotube–nickel nanocomposites using atomic layer deposition for high-performance non-enzymatic glucose sensing. Biosens. Bioelectron. 63, 325–330.

Ding, Y., Wang, Y., Su, L., Zhang, H., Lei, Y., 2010. Preparation and characterization of NiO–Ag nanofibers, NiO nanofibers, and porous Ag: towards the development of a highly sensitive and selective non-enzymatic glucose sensor. J. Mater. Chem. 20, 9918–9926.

Erken, E., Pamuk, H., Karatepe, Ö., Baskaya, G., Sert, H., Kalfa, O.M., Şen, F., 2016. New Pt(0) Nanoparticles as Highly Active and Reusable Catalysts in the C1–C3 Alcohol Oxidation and the Room Temperature Dehydrocoupling of Dimethylamine-Borane (DMAB). J. Clust. Sci. 27, 9–23.

Ertan, S., Şen, F., Şen, S., Gökağaç, G., 2012. Platinum nanocatalysts prepared with different surfactants for C1–C3 alcohol oxidations and their surface morphologies by AFM. J. Nanopart. Res. 14, 922.

Fu, S., Fan, G., Yang, L., Li, F., 2015. Non-enzymatic glucose sensor based on Au nanoparticles decorated ternary Ni-Al layered double hydroxide/single-walled carbon nanotubes/graphene nanocomposite. Electrochim. Acta 152, 146–154.

Gao, H., Xiao, F., Ching, C.B., Duan, H., 2011. One-step electrochemical synthesis of PtNi nanoparticle-graphene nanocomposites for nonenzymatic amperometric glucose detection. ACS Appl. Mater. Interfaces 3, 3049–3057.

Gavalas, V.G., Law, S.A., Ball, J. Christopher, Andrews, R., Bachas, L.G., 2004. Carbon nanotube aqueous sol-gel composites: enzyme-friendly platforms for the development of stable biosensors. Anal. Biochem. 329, 247–252.

Guo, C., Huo, H., Han, X., Xu, C., Li, H., 2013a. Ni/CdS bifunctional Ti@TiO2 core–shell nanowire electrode for high-performance nonenzymatic glucose sensing. Anal. Chem. 86, 876–883.

Guo, C., Wang, Y., Zhao, Y., Xu, C., 2013b. Non-enzymatic glucose sensor based on three dimensional nickel oxide for enhanced sensitivity. Anal. Methods 5, 1644–1647.

Guo, C., Zhang, X., Huo, H., Xu, C., Han, X., 2013c. Co3O4 microspheres with free-standing nanofibers for high performance non-enzymatic glucose sensor. Analyst 138, 6727–6731.

Huo, H., Guo, C., Li, G., Han, X., Xu, C., 2014a. Reticular-vein-like Cu@Cu2O/reduced graphene oxide nanocomposites for a non-enzymatic glucose sensor. RSC Adv. 4, 20459–20465.

Huo, H., Zhao, Y., Xu, C., 2014b. 3D Ni3S2 nanosheet arrays supported on Ni foam for high-performance supercapacitor and non-enzymatic glucose detection. J. Mater. Chem. A 2, 15111.

Kang, X., Mai, Z., Zou, X., Cai, P., Mo, J., 2007. A sensitive nonenzymatic glucose sensor in alkaline media with a copper nanocluster/multiwall carbon nanotube-modified glassy carbon electrode. Anal. Biochem. 363, 143–150.

Karatepe, Ö., Yıldız, Y., Pamuk, H., Eris, S., Dasdelen, Z., Sen, F., 2016. Enhanced electrocatalytic activity and durability of highly monodisperse Pt@PPy−PANI nanocomposites as a novel catalyst for the electro-oxidation of methanol. RSC Adv. 6, 50851–50857.

Kim, W.S., Lee, G.J., Ryu, J.H., Park, K., Park, H.K., 2014. A flexible, nonenzymatic glucose biosensor based on Ni-coordinated, vertically aligned carbon nanotube arrays. RSC Adv. 4, 48310–48316.

Kong, Y., Chen, X., Ni, J., Yao, S., Wang, W., Luo, Z., Chen, Z., 2010. Palygorskite–expanded graphite electrodes for catalytic electro-oxidation of phenol. Appl. Clay Sci. 49, 64–68.

Li, J., Meng, F., Suri, S., Ding, W., Huang, F., Wu, N., 2012. Photoelectrochemical performance enhanced by a nickel oxide–hematite p–n junction photoanode. Chem. Commun. 48, 8213–8215.

Li, X., Zhu, Q., Tong, S., Wang, W., Song, W., 2009. Self-assembled microstructure of carbon nanotubes for enzymeless glucose sensor. Sens. Actuators B 136, 444–450.

Li, X., Hu, A., Jiang, J., Ding, R., Liu, J., Huang, X., 2011. Preparation of nickel oxide and carbon nanosheet array and its application in glucose sensing. J. Solid State Chem. 184, 2738–2743.

Lin, Kuo-C., Lin, Yu-C., Chen, Shen-M., 2013. A highly sensitive nonenzymatic glucose sensor based on multi-walled carbon nanotubes decorated with nickel and copper nanoparticles. Electrochim. Acta 96, 164–172.

Liu, Y., Teng, H., Hou, H., You, T., 2009. Nonenzymatic glucose sensor based on renewable electrospun Ni nanoparticle-loaded carbon nanofiber paste electrode. Biosens. Bioelectron. 24, 3329–3334.

Lu, L.M., Zhang, L., Qu, F.L., Lu, H.X., Zhang, X.B., Wu, Z.S., Huan, S.Y., Wang, Q.A., Shen, G.L., Yu, R.Q., 2009b. A nano-Ni based ultra sensitive nonenzymatic electrochemical sensor for glucose: enhancing sensitivity through a nano wire array strategy. Biosens. Bioelectron. 25, 218–223.

Lu, Li-M., Zhang, L., Qu, Feng-L., Lu, Hai-X., Zhang, Xiao-B., Zai-Sheng, W., Huan, Shuang-Y., Qiu-A, Shen, Guo-L, Yu, Ru-Q, 2009a. A nano-Ni based ultrasensitive nonenzymatic electrochemical sensor for glucose: enhancing sensitivity through a nanowire array strategy. Biosens. Bioelectron. 25, 218–223.

Lu, W., Qin, X., Asiri, Abdullah, M., Al-Youbib, A.O., Sun, X., 2013a. Ni foam: a novel three-dimensional porous sensing platform for sensitive and selective nonenzymatic glucose detection. Analyst 138, 417.

Lu, W., Qin, X., Asiri, A.M., Al-Y, A.O., Sun, X., 2013b. Facile synthesis of novel Ni(II)-based metal–organic coordination polymer nanoparticle/reduced graphene oxide nanocomposites and their application for highly sensitive and selective nonenzymatic glucose sensing. Analyst 138, 429.

Mathew, M., Sandhyarani, N., 2013. A highly sensitive electrochemical glucose sensor structuring with nickel hydroxide and enzyme glucose oxidase. Electrochim. Acta 108, 274–280.

Merkoci, A., Pumera, M., Llopis, X., P´erez, B., Valle, M. Del, Alegret, S., 2005. New materials for electrochemical sensing VI: carbon nanotubes. TrAC Trends Anal. Chem. 24, 826–838.

Mu, Y., Jia, D., He, Y., Miao, Y., Wu, H.L., 2011a. Nano nickel oxide modified non-enzymatic glucose sensors with enhanced sensitivity through an electrochemical process strategy at high potential. Biosens. Bioelectron. 26, 2948–2952.

Mu, Y., Jia, D., He, Y., Miao, Y., Wu, H.L., 2011b. Nano nickel oxide modified non-enzymatic glucose sensors with enhanced sensitivity through an electrochemical process strategy at high potential. Biosens. Bioelectron. 26, 2948–2952.

Nai, J., Wang, S., Bai, Y., Guo, L., 2013. Amorphous Ni(OH)2 nanoboxes: fast fabrication and enhanced sensing for glucose. Small 9, 3147–3152.

Park, S., Boo, H., Chung, T.D., 2006. Electrochemical non-enzymatic glucose sensors. Anal. Chim. Acta 556, 46–57.

Rasee, B., Fakhari, A.R., 2013. Electrocatalytic oxidation and determination of insulin at nickel oxide nanoparticles-multiwalled carbon nanotube modified screen printed electrode. Biosens. Bioelectron. 46, 130–135.

Shen, Z., Gao, W., Li, P., Wang, X., Zheng, O., Wu, H., Ma, Y., Guan, W., Wu, S., Yu, Y., Ding, K., 2016. Highly sensitive non enzymatic glucose sensor based on nickel nanoparticle–attapulgite-reduced graphene oxide-modified glassy carbon electrode. Talanta 159, 194–199.

Si, P., Huang, Y., Wang, T., Ma, J., 2013a. Nanomaterials for electrochemical non-enzymatic glucose biosensors. RSC Adv. 3, 3487–3502.

Si, P., Huang, Y., Wang, T., Ma, J., 2013b. Nanomaterials for electrochemical non-enzymatic glucose biosensors. RSC Adv. 3, 3487.

Wang, G., He, X., Wang, L., Gu, A., Huang, Y., Fang, B., Geng, B., Zhang, X., 2013. Non-enzymatic electrochemical sensing of glucose. Microchim. Acta 180, 161–186.

Wang, J., Lin, Y., 2008. Functionalized carbon nanotubes and nanofibers for biosensing applications. TrAC Trends Anal. Chem. 27, 619–626.

Wang, J., Bao, W., Zhang, L., 2012a. A nonenzymatic glucose sensing platform based on Ni nanowire modified electrode. Anal. Methods 4, 4009.

Wang, W., Zhang, L., Tong, S., Li, X., Song, W., 2009. Three-dimensional network films of electrospun copper oxide nanofibers for glucose determination. Biosens. Bioelectron. 25, 708–714.

Wang, Z., Hu, Y., Yang, W., Zhou, M., Hu, X., 2012. Facile one-step microwave-assisted Route towards Ni nanospheres/reduced graphene oxide hybrids for non-enzymatic glucose sensing. Sensors 12, 4860–4869.

Xiu-tian-feng, E., Zhang, Zou, Y., Ji-J., Wang, L., Zhang, X., 2014. Oleylamine-protected metal (Pt, Pd) nanoparticles for pseudohomogeneous catalytic cracking of JP-10 jet fuel. Ind. Eng. Chem. Res. 53, 12312–12318.

Yang, J., Yu, J.H., RudiStrickler, J., Chang, W.J., Gunasekaran, S., 2013. Nickel nano-particle-chitosan-reduced graphene oxide-modified screen-printed electrodes for enzyme-free glucose sensing inportable microfluidic devices. Biosens. Bioelectron. 47, 530–538.

Ye, J.S., Wen, Y., Zhang, W. De, Gan, L. Ming, Xu, G.Q., Sheu, F.S., 2004. Nonenzymatic glucose detection using multi-walled carbon nanotube electrodes. Electrochem. Commun. 6, 66–70.

Yıldız, Y., Pamuk, H., Karatepe, Ö., Dasdelen, Z., Sen, F., 2016. Carbon black hybrid material furnished monodisperse platinum nanoparticles as highly efficient and reusable electrocatalysts for formic acid electro-oxidation. RSC Adv. 6, 32858–32862.

Yu, S., Peng, X., Cao, G., Zhou, M., Qiao, L., Yao, J., He, H., 2012. Ni nanoparticles decorated titania nanotube arrays as efficient nonenzymatic glucose sensor. Electrochim. Acta 76, 512–517.

Zhang, Y., Xu, F., Sun, Y., Shi, Y., Wen, Z., Li, Z., 2011. Assembly of Ni(OH)2 nanoplates on reduced graphene oxide: a two dimensional nanocomposite for enzyme-free glucose sensing. J. Mater. Chem. 21, 16949.

Zhang, Y., Wang, Y., Jia, J., Wang, J., 2012a. Nonenzymatic glucose sensor based on graphene oxide and electrospun NiO nanofibers. Sens. Actuators B 171–172, 580–587.

Zhang, Y., Wang, Y., Jia, J., Wang, J., 2012b. Non enzymatic glucose sensor based on graphene oxide and electrospun NiO nanofibers. Sens. Actuators B: Chem. 171–172, 580–587.

Zhang, Y., Xiao, X., Sun, Y., Shi, Y., Dai, H., Ni, P., Hu, J., Li, Z., Song, Y., Wang, L., 2013. Electrochemical deposition of nickel nanoparticles on reduced graphene oxide film for nonenzymatic glucose sensing electroanalysis. 25, pp. 959–966.

Zhao, C., Shao, C., Li, M., Jiao, K., 2007a. Flow-injection analysis of glucose without enzyme based on electrocatalytic oxidation of glucose at a nickel electrode. Talanta 71, 1769–1773.

Zhao, C., Shao, C., Li, M., Jiao, K., 2007b. Flow-injection analysis of glucose without enzyme based on electrocatalytic oxidation of glucose at a nickel electrode. Talanta 71, 1769–1773.

Zhao, J., Wei, L., Peng, C., Su, Y., Yang, Z., Zhang, L., Wei, H., Zhang, Y., 2013. A non-enzymatic glucose sensor based on the composite of cubic Cu nanoparticles and arc-synthesized multi-walled carbon nanotubes. Biosens. Bioelectron. 47, 86–91.

Zhu, J., Jiang, Jian, Liu, J., Ding, R., Li, Y., Ding, H., Feng, Y., Wei, G., Huang, X., 2011. CNT-network modified Ni nanostructured arrays for high performance non-enzymatic glucose sensors. RSC Adv. 1, 1020–1025.