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Highly sensitive, non-enzymatic and precious metal-free electrochemical glucose sensor based on a Ni–Cu/TiO₂ modified glassy carbon electrode

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Abstract: Herein, a facile one step synthesis of Ni–Cu supported on TiO₂ alloy nanoparticles through the polyol method, which reflect high catalytic performance in enzymeless electrochemical glucose sensing and applied onto glassy carbon, is reported. The morphology imaging and physical properties of the Ni–Cu/TiO₂ nanocomposite were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) analysis, and energy dispersive X-ray spectroscopy (EDS). The electrochemical studies/characterizations of glucose oxidation were realised in a basic medium and the new sensor was found to be a better electrochemical glucose sensor than Ni/TiO₂/Ti and CuO/TiO₂/Ti modified electrodes. The fabricated sensor was highly sensitive (719.9 $\mu\text{A mM}^{-1} \text{cm}^{-2}$), had a wide linear range (from 0.1 to 6 mM), selective and tolerant towards endogenous species, such as ascorbic acid, uric acid, acetaminophen and sodium chloride.

Keywords: SEM; cyclic voltammetry; chronoamperometry; polyol method.

INTRODUCTION

Glucose is an abundant naturally occurring molecule and is an important component of the energy production and consumption systems in both plants and animals. Blood glucose level of a normal healthy human is around 3–8 mM.¹ Any excess or low blood glucose levels can cause a number of serious health issues, eventually leading to disability and death.² Therefore, glucose detection in humans is an important test, especially for patients with diabetes.² Its detection or sensing by chemical or any other method is, therefore, quite challenging. Among the available tests for glucose, the ones based on electrochemistry bear a number of advantages and superiorities.³ However, the existing and commercialized glucose electrochemical sensors rely on the use of the enzyme glucose oxi-

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dase to activate the glucose to be detected electrochemically. Enzymes are biological substances and they are sensitive to several factors, including temperature and solution pH. Therefore, these can generate results that may be non-reproducible as well as misleading.⁴ Current research is therefore focused on the development of electrochemical sensors that are free of enzymes, through which glucose can be detected directly by the electrode. One approach that has been investigated is the utilization of noble metal nanoparticles catalysts, such as Pt, Ag, Au, Pd⁵⁻⁷ and their alloys, Pt-Pd and Pt₂Pd,^{8,9} but these are costly materials and are prone to fouling by the irrelevant species present in the real human blood samples. Another reported approach is the use of conducting polymers in the form of composites with metals or as conducting supports for metal nanocatalysts.¹⁰ Highly conducting carbon-based materials, such as single walled carbon nanotubes (SWCNTs),¹¹ multiwalled carbon nanotubes (MWCNTs),¹² graphene,¹³ *etc.*, have also turned out to be excellent supports for precious metal catalyst, which assist nanoparticle stability and their electrocatalytic behaviour.¹²

In addition, transition metal oxides have also been used for this purpose,^{14,15} *e.g.*, NiO₂, CuO₂, ZnO₂,^{16,17} *etc.* Metal and metal alloy nanomaterials have high catalytic and electrocatalytic activities due to which they have large number of applications in different fields, *e.g.*, corrosion protection, catalysis, fuel cell, solar energy system, sensors,¹⁸⁻²¹ *etc.* To the best of our knowledge, only a few reports are available on the electrochemical oxidation of glucose on Ni nanoparticles. Actually, pure nickel nanoparticles are not stable under highly oxidizing condition. Thus, alloying copper with nickel stabilizes the nickel surface that arises from the synergetic effect presented in a bimetallic nanostructure system.¹⁸ Similarly, the electrochemical activity of Cu-Ni alloy is high as compared to pure copper or nickel²¹ and also sometime in the case of pure metallic catalyst (alloy or non-alloyed), the redox behaviour of the metals is exploited. It could be stated that such a type of metal catalyst act as an immobilized mediator.^{16,22}

In the present study, a low cost, electrochemical glucose sensor based on Ni-Cu/TiO₂ nanoparticles is reported that is more sensitive and selective than the previously reported Ni or CuO nanoparticles supported on TiO₂ (shown in Table I).

EXPERIMENTAL

Chemicals

NiCl₂·2H₂O, 98 %, CuCl₂·6H₂O > 98 %, and glucose (purity > 98 %) were provided by Daejung, ethylene glycol, hydrazine, sodium hydroxide (purity >97 %) and sodium chloride (purity > 99 %) were obtained from Sigma-Aldrich, acetone (purity >99 %) and alumina (purity > 99 %) were purchased from Analar and were used as received without further purification. Double distilled water (18 MΩ) was used in the preparation of all solutions.

Instruments

A PGSTAT302 (Metrohm Autolab, Netherlands) was used to perform the cyclic voltammetric and chronoamperometric experiments. A standard/conventional three electrode cell

system was used. A modified glassy carbon electrode (GCE, 3 mm diameter), Ag/AgCl, saturated KCl, and a custom-made gold electrode (2 cm² surface area), were used as working, reference and counter electrodes, respectively. All potentials in the paper are referred to Ag/AgCl scale.

Synthesis of Ni-Cu/TiO₂ nanocomposite

Ni-Cu alloy nanoparticles supported on TiO₂ were synthesized using the well-known polyol method described in the literature.²³ Briefly, TiO₂ (112 mg) was dispersed in 26.5 mL of ethylene glycol in a round bottom flask by sonication for 30 min. A mixture of the metal salt precursors was made by mixing 16 mL 0.02 M CuCl₂·2H₂O and 24 mL 0.02 M NiCl₂·2H₂O in a definite ratio of copper and nickel. This mixture was then added to the TiO₂ dispersion under continuous stirring. The resulting mixture was then heated up to 180 °C. Then, hydrazine hydrate (3.33 mL) was added drop wise into the reaction mixture. The heating was stopped after 20 min and the reaction mixture was allowed to cool to room temperature. The product was collected by centrifugation and washed with ethanol and water several times. The product was then dried at 50 °C in a vacuum oven for 4 h.

Fabrication/modification of electrode

The glassy carbon electrode surface was modified using the typical drop cast method. The as-prepared Ni-Cu/TiO₂ nanoparticles were dispersed in ethanol and chitosan solution to obtain a uniform dispersion (3 mg ml⁻¹). 10 µL of the dispersed sample was drop casted on a carefully polished glassy carbon electrode (3 mm diameter). Prior to each modification, the working electrode was polished with alumina powder (0.3 to 0.05 mm) and rinsed with water and acetone, followed by sonication (in distilled water) and again rinsing with distilled water and acetone. The electrode was then allowed to dry at room temperature. Both the cyclic voltammetric and amperometric measurements were performed in a basic medium (0.10 M NaOH) supporting electrolyte. All the experiments were performed at room temperature.

RESULTS AND DISCUSSION

Surface characterization

Scanning electron microscopy (SEM). Generally, the morphology and size of nanoparticles depend on the preparation conditions and they may affect the electrocatalytic activity of catalyst. Thus, the morphology of the nanoparticles was analyzed using scanning electron microscopy. SEM images of the as-prepared Ni/TiO₂, Cu/TiO₂, and Ni-Cu/TiO₂ nanoparticles are shown in Fig. 1. In these SEM images, morphology of the as prepared nanoparticles seems to be spherical. Moreover, a slight agglomeration was observed in the case of Cu/TiO₂ and Ni/TiO₂ (Fig. 1a and b, respectively), while, negligible aggregation was observed for Ni-Cu/TiO₂, which may be due to the introduction of Cu metal into Ni nanoparticles or may be due to the synergetic effect of the bimetallic nanomaterial. These SEM images suggested that the as-synthesized nanoparticles were approximately uniform in size and well-ordered.

Energy diffraction X-ray spectroscopy (EDS). The percent mass composition of the various components in the Ni-Cu/TiO₂ sample were examined by EDS and the results are shown in Fig. 2. The content of O₂, Ti, Ni and Cu was found

to be 36.42, 46.40, 13.03 and 4.15 mass %, respectively. These observations reveal that the as-prepared sample was highly pure because no extra peaks were observed in the EDS spectrum.

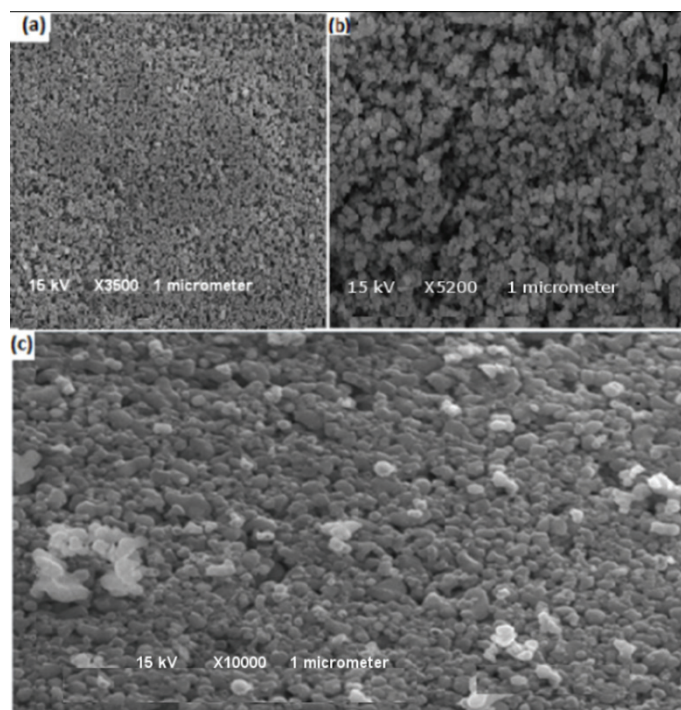


Fig. 1. SEM images of: a) Ni/TiO₂, b) Cu/TiO₂ and c) Ni-Cu/TiO₂.

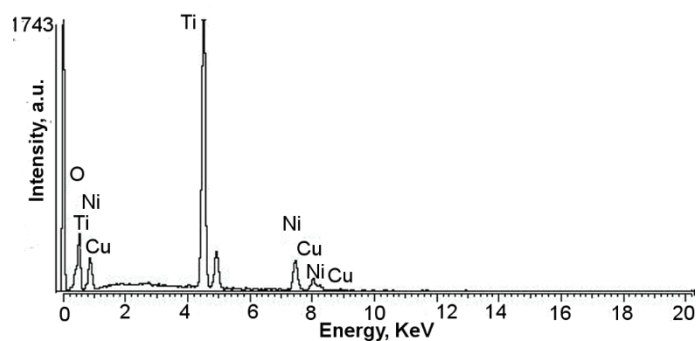


Fig. 2. EDS spectrum of Ni-Cu/TiO₂.

XRD Analysis. XRD analysis results of Ni-Cu supported on TiO₂ electro-catalyst are shown in Fig. 3. The strong diffraction peaks observed at 27, 36 and 55° in the XRD spectra were attributed to the rutile phase of TiO₂ (JCPDS No.: 88-1175).²⁴ No diffraction peaks were observed for Ni, Cu or Ni-Cu, which

indicates that Ni and Cu nanoparticles were either well dispersed or they interacted with TiO₂. Similar results for Ni-Cu/TiO₂ were also reported by Zhu *et al.* They found a metal phase in the XRD spectra of Ni-Cu/TiO₂ at high metal concentration (above 5 mass %).²⁵

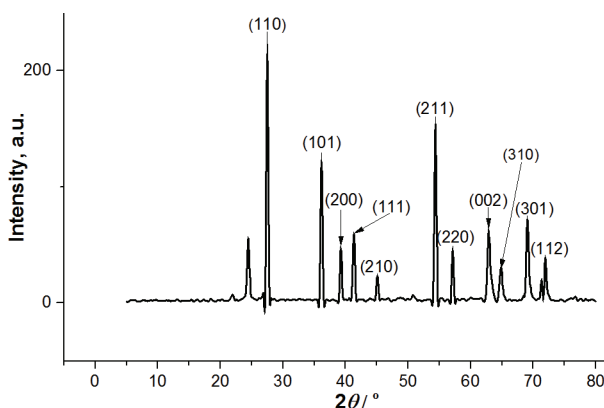


Fig. 3. XRD spectrum of Ni-Cu/TiO₂.

However, in the present work, diffraction peaks for Ni, Cu or Ni-Cu at high metal concentration were still absent, which suggest that the Ni-Cu nanoparticles were highly dispersed on TiO₂. These observations strengthen the idea that the use of ethylene glycol in the synthesis of nanocomposite prevents the aggregation of metal nanoparticles. These results are also in agreement with previous studies reported by Riaz *et al.*²⁶

Electrochemical characterization of Ni-Cu/TiO₂-modified glassy carbon electrode

Voltammetric sensing of glucose on a Ni-Cu/TiO₂ modified GCE. Electrochemical oxidation of glucose in basic media at a scan rate of 50 mV s⁻¹ on a Ni-Cu/TiO₂-modified GCE was investigated using CV (Fig. 4). No CV peak was observed in the absence of glucose on the Ni-Cu/TiO₂-modified GCE. However, an irreversible anodic peak was observed in the presence of 0.0021 M glucose in the potential range 0.6–0.7 V. This indicates that the Ni-Cu/TiO₂-modified GCE was active towards glucose sensing/electro-oxidation in basic media. This redox behaviour may be due to the synergetic and electronic effect of the bimetallic nanomaterial.^{27,28} To further ensure the electrocatalytic activity of Ni-Cu alloy nanoparticle toward glucose oxidation, a GCE modified with just TiO₂ was also used for glucose oxidation. However, no redox peak was observed on addition of glucose, indicating that TiO₂ is featureless towards glucose. The mechanism for high electrocatalytic activity of Ni-Cu alloyed nanoparticles toward glucose oxidation may be due to the formation of a Ni(OH)₂ layer on the surface of Ni-Cu

alloyed nanoparticles at low potential, which further assists the formation of copper oxide layer. The CuO_2 layer is then transferred into Cu(OH)_2 that promotes the formation of Cu(III) oxide.^{29,30} Moreover, the formation of a γ -NiOOH phase is associated with volume expansion of nickel electrodes. Thus, the β -NiOOH phase was supposed to be formed because β -NiOOH is usually considered to be a better electroactive material for high electrochemical performance in alkaline solutions.³¹ Similarly, a β -NiOOH phase has lower inter electrode spacing, which leads to lower internal resistance. Furthermore, alloying phenomenon of Ni with Cu may also suppress the formation of disadvantageous species, such as γ -NiOOH and stabilize β -NiOOH in alkaline media through the following proposed mechanism given by Eqs. (1) and (2):^{18,19}

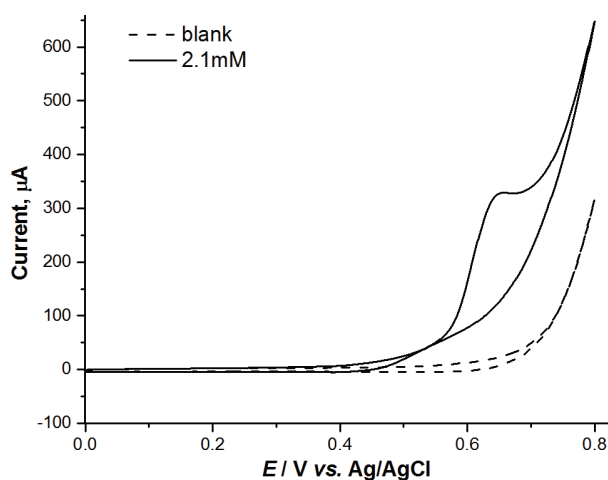
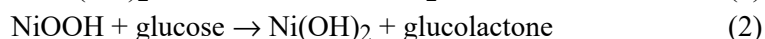
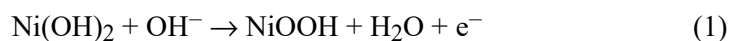


Fig. 4. Cyclic voltammogram of glucose on Ni-Cu/TiO₂ modified GCE in 0.10 M NaOH at scan rate of 50 mV s⁻¹.

Effect of concentration on the CVs of glucose. To check whether the CV peak current (i_p) linearly increase with concentration, the effect of concentration on the cyclic voltammograms of glucose at the nanostructure (Ni-Cu/TiO₂) modified GC electrode in basic media (0.1 M NaOH) was investigated (Fig. 5). It was found that the anodic peak current linearly increased with increasing glucose concentration (Fig. S-1 of the Supplementary material to this paper). In addition, a shift in the anodic peak towards more positive potentials was observed, indicating that the electro-oxidation of glucose on this electrode material was diffusion controlled.

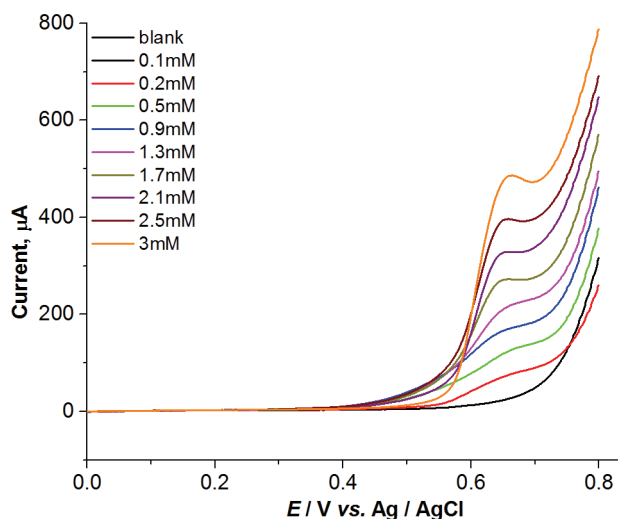


Fig. 5. Cyclic voltammograms at various glucose concentrations on Ni-Cu/TiO₂ nanoparticles in 0.10 M NaOH at a scan rate of 50 mV s⁻¹.

Effect of scan rate on the CVs of glucose. The effect of scan rate on the CVs of 3.0 mM glucose on the Ni-Cu/TiO₂ modified GCE was recorded in the range of 10 to 200 mV s⁻¹ (Fig. 6).

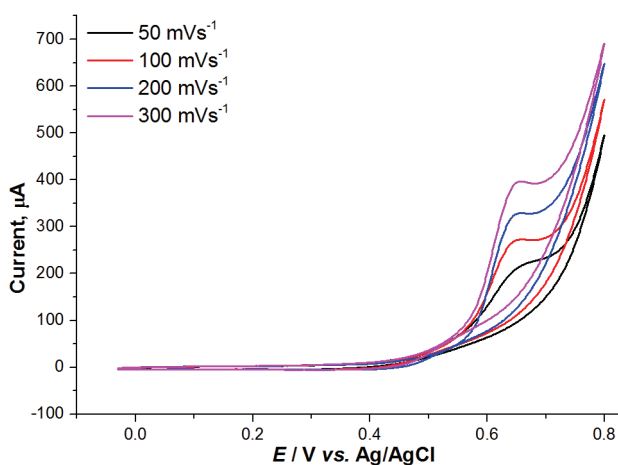


Fig. 6. Effect of scan rate on the cyclic voltammogram on the Ni-Cu/TiO₂ modified GCE.

It was found that the anodic peak current had linear relation with the square root of scan rate. This confirms that the electro-oxidation process of glucose was diffusion controlled, which is ideal for the electrochemical sensing of glucose (Fig S-2 of the Supplementary material).

Chronoamperometry

Chronoamperometric technique was used for evaluation of electrocatalytic activity of Ni–Cu/TiO₂-modified GCE. The current at fixed potential was monitored by adding analyte (glucose) and interfering biomolecules.^{32–34}

The optimized set potential was found to be 0.6 V with good signal to noise ratio as shown in Fig. 7. All the other parameters like sensitivity, limit of detection, and limit of quantification were determined from chronoamperogram. The chronoamperogram was recorded at different concentration of glucose at a fixed set potential (0.6 V) in basic medium (0.10 M NaOH) on Ni–Cu/TiO₂ modified electrode under stirring condition (Fig. 8). It was found that the current response of glucose on modified electrode increases linearly with glucose concentration up to 6 mM (Fig S-3 of the Supplementary material). The sensitivity and detection limit of the sensor was found to be 30 μM and 719.9 μA mM⁻¹ cm⁻², respectively, Eq. (3):

$$LOD = 3 \left(\frac{\text{Standard deviation "s"}}{\text{Slope of } i_p \text{ vs. [glucose] plot}} \right) \quad (3)$$

where the standard deviation “s” of replicate of amperometric measurement was calculated for glucose oxidation in 0.10 M NaOH.

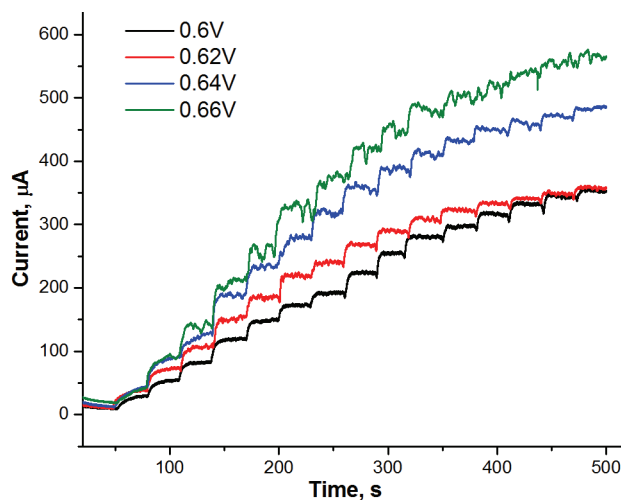


Fig. 7. Chronoamperograms recorded for glucose oxidation in 0.10 M NaOH solution on a Ni–Cu/TiO₂ modified GCE for optimization of the point potential for further amperometric measurements.

The sensitivity, detection limit, and linear concentration range were compared with those reported for other TiO₂-supported glucose sensors summarized in Table I. It could be seen that Ni–Cu/TiO₂ is a better material in term of sensi-

tivity, detection limit and linear concentration range than the other reported TiO₂-based sensors. This may be attributed to the coupling of Cu with Ni improving the mediator properties of Ni or the synergetic effect of the bimetallic nano-material.

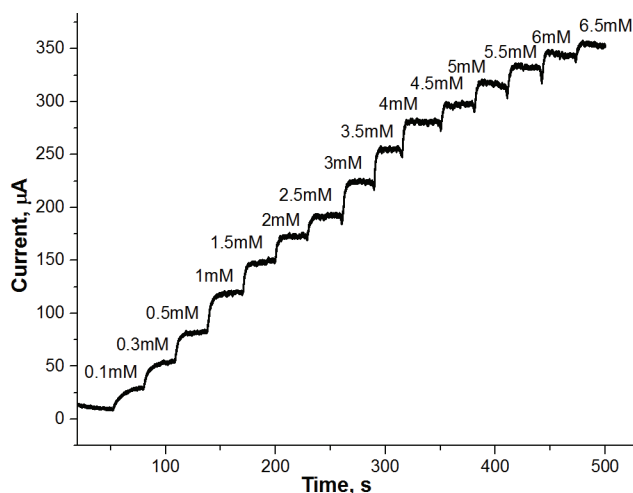


Fig. 8. Chronoamperometric response of various glucose concentrations at the Cu-Ni/TiO₂-modified GCE in 0.1 M NaOH solution. Current increases upon increasing glucose concentrations.

TABLE I. Comparison of various parameters in this work with those in the reported studies

Electrode	Sensitivity $\mu\text{A mM}^{-1} \text{cm}^{-2}$	LOD μM	Linear range mM	Ref.
Ni/TiO ₂ /Ti	200	4	0.1–1.7	35
CuO/TiO ₂ /Ti	79.79	1	Up to 2.0	36
Ni-Cu/TiO ₂	719.9	30	6	This work

Effects of interfering species

To check the selectivity of biosensor, glucose was monitored electrochemically in the presence of uric acid (UA), ascorbic acid (AA), acetaminophen (AP), and sodium chloride (NaCl) present in physiological fluid using chronoamperometry. As mentioned earlier, the concentration of glucose in blood of a normal healthy human is around 3–8 mM, which is higher than the concentration of 0.10 mM of interfering species, such as UA, AA and AP. However, the reaction rates of these interfering species are higher as compared to the reaction rate of glucose. Thus, they could disturb the sensitivity and selectivity of the biosensors. Hence, the interfering effects of AA, UA and AP were studied in the presence of 1.0 mM glucose at a fixed potential of 0.6 V (Fig. 9). Negligible current response was

monitored upon addition of the interfering species. This suggests that sensor is highly selective towards glucose.

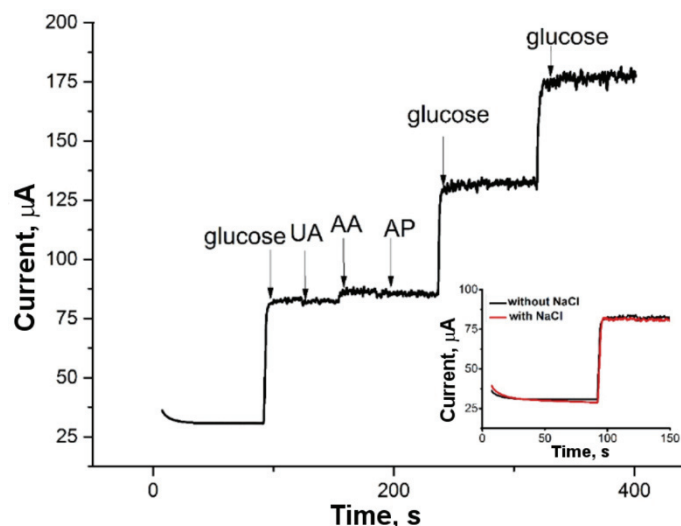


Fig. 9. Effect of interfering species (0.10 mM of UA, AA and AP) on the catalytic activity of Ni-Cu/TiO₂. The inset shows the effect of NaCl on the electrocatalytic activity of the modified electrode.

Application in real blood samples

The Ni-Cu/TiO₂-modified electrode was tested for glucose determination in real serum. The as prepared sensor was applied in real blood serum of three people for glucose determination. Physiological fluid (40 mL) was diluted with 10 mL of 0.10 M NaOH solution and the current response of the modified electrode was measured at 0.6 V as shown in Table II. Although, the *LOD* of glucose on the Ni-Cu/TiO₂-modified electrode was a little higher, the sensitivity and linear range on the Ni-Cu/TiO₂-modified electrode were much better as compared to those of the other electrodes.^{35,36} These results demonstrate that the Ni-Cu/TiO₂-modified electrode may become a potential candidate in the realm of electrochemical glucose sensors.

TABLE II. Determination of glucose in real blood serum sample

Sample	Concentration mM	Amount of glucose added, mM	Amount of glucose found, mM	RSD %	Recovery %
1	4.7	0.10	4.06	3.8	96
2	4.8	0.10	4.66	1.9	95
3	5.3	0.10	5.29	1.3	98

CONCLUSIONS

It could be concluded that highly dispersed Ni-Cu/TiO₂ nanoparticles were synthesized through the polyol method for the first time. The electrochemical characterizations revealed that the fabricated electrode showed high sensitivity (719.9 $\mu\text{A mM}^{-1} \text{cm}^{-2}$) and a wide linear range (0.10 to 6.0 mM). The detailed electrochemical investigations of the modified electrode showed high tolerance towards major interfering species (AA, UA and AP) present in real blood serum and high electrocatalytic activity in the presence of a high concentration of chlorides (0.10 M), bearing in mind the poisoning of precious metal nanomaterials (*e.g.*, Pt, Au, *etc.*), that also decreases their activity in high concentrations of chlorides. The above-mentioned features confirm that the Ni-Cu/TiO₂-modified electrode is an excellent candidate in the realm of non-enzymatic glucose sensors. □

SUPPLEMENTARY MATERIAL

Additional experimental data are available electronically at the pages of the journal website: <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

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ИЗВОД

ВИСОКО ОСЕТЉИВИ, НЕЕНЗИМСКИ ЕЛЕКТРОХЕМИЈСКИ СЕНЗОР ЗА ГЛУКОЗУ БЕЗ ПЛЕМЕНИТИХ МЕТАЛА НА БАЗИ СТАКЛАСТОГ УГЉЕНИКА МОДИФИКОВАНОГ ЧЕСТИЦАМА Ni-Cu/TiO₂

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У раду су приказани резултати једноставне једноступене синтезе честица Ni-Cu на носачу од нанолегуре TiO₂ применом полиолне методе, које су показале добру каталитичку активност у сензору за глукозу који не садржи ензиме а које су нанете на стакласти угљеник. Морфологија и физичке карактеристике нанокомпозита Ni-Cu/TiO₂ су одређене скенирајућом електронском микроскопијом, дифракцијом X-зрака и енергетском дисперзионом спектроскопијом X-зрака. Електрохемијска испитивања оксидације глукозе су урађена у базној средини. Показано је да је нови сензор за глукозу бољи од електрода Ni/TiO₂/Ti и CuO/TiO₂/Ti. Он је испољио високу осетљивост (719,9 $\mu\text{A mM}^{-1} \text{cm}^{-2}$), широк опсег линеарности (од 0,10 до 6,0 mM), селективност и толеранцију на ендogene врсте као што су аскорбинска киселина, урична киселина, ацетаминофен и натријум-хлорид.

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