Synthesis, characterization and electrochemical properties of metal-doped nanoporous carbon

N Ben Mansour\textsuperscript{1}, M Hjiri\textsuperscript{1,2}, R Dahari\textsuperscript{1,2}, L El Mir\textsuperscript{1,3}, M Bonyani\textsuperscript{2,4}, A Mirzaei\textsuperscript{2,4}, S G Leonardi\textsuperscript{2}, G Neri\textsuperscript{2,*}

\textsuperscript{1}Lab. of Physics of Materials and Nanomaterials Applied at Environment, Faculty of Sciences of Gabes, Tunisia. \\
\textsuperscript{2}Dept. of Electronic Engineering, Chemistry and Materials Engineering, Univ. of Messina, Italy. \\
\textsuperscript{3}Dept. of Physics, Al Imam Mohammad Ibn Saud Islamic University, Riyadh, Saudi Arabia. \\
\textsuperscript{4}Dept. of Engineering, Materials Science and Engineering, Shiraz University, Iran.

E-mail: gneri@unime.it

Abstract. A novel nickel/nanoporous carbon (Ni-NC) composite has been synthesized via sol-gel method after the incorporation of metal oxide nanoparticles in an organic matrix based on pyrogallol-formaldehyde and successive heating under inert atmosphere. The nanocomposites have been characterized by various techniques such as XRD, SEM-EDX and TEM. The Ni-NC composite was successfully used to fabricate a modified screen printed carbon electrode (SPCE) and applied in the determination of glucose. The electrochemical behavior of the Ni-NC nanocomposite has been investigated by cyclic voltammetry performed under different experimental conditions (potential, scan rate and analyte concentration). Based on the modified Ni-NC/SPCE electrode, an amperometric sensor for glucose determination with a sensitivity of 146.4 µA mM\textsuperscript{-1}cm\textsuperscript{2} and lower detection limit of 10µM, has been developed.

1. Introduction
Glucose is one of the vital substances for life activities, as it is widely distributed in blood of being livings it can provide energy to maintain the normal life activities by ingesting directly in the metabolic process [1]. In spite of this benefit, enhanced blood glucose levels could cause diabetes, one of the most serious causes of death and disability in the world [2]. So the glucose detection is one of the most popular research topics in the field of sensors both in blood and in other sources such as foods and pharmaceuticals, for clinical analysis, food industry, biotechnology, and so forth [3, 4]. Till now many techniques including UV fluorescence [5], chemiluminescence [6, 7], titrimetry [8] and electrochemical biosensors have been reported in literatures for the detection of glucose. Among them, electrochemical sensors result to be the most simples, reliable, fast, sensitives and cheaper [9].
Most previous studies on this subject involved the use of enzymatic electrochemical sensors with high sensitivity as well as excellent selectivity, but many factors such as temperature, humidity, pH, toxic chemicals and the insufficient long-term stability originating from the nature of the enzymes could...
affect the activity of enzyme [10-12]. Then, many efforts have been put into producing non-enzymatic 
alternatives with excellent catalytic effect, reproducibility, and stability.

Recent advancements in this field have suggested that a variety of nano-structured transition metals or 
transition metal oxides dispersed onto a conductive matrix (carbon, graphite, carbon nanotubes) 
continued to receive great attention for glucose sensing due to their outstanding properties such as low 
cost, excellent semi-conductivity, and good biocompatibility [15-17]. As a conductive matrix, porous 
carbons have attracted extensively research interest all over the world because of its stable 
physicochemical property, high electrical conductivity, low cost, and availability which makes it one 
of the ideal electrode supports for electrochemical sensors [13, 14]. At present, the development of 
new metal-nanoporous carbon composite materials (M-NC) opened new opportunities for developing 
electrochemical sensors, due to their tunable electrocatalytic activity depending on the metal nature 
and loading.

Here, new electrode materials based on nanoporous carbon with Ni nanoparticles (Ni-NC) were 
proposed. In the specific, Ni-NC nanocomposites were successfully prepared by sol-gel method after 
the incorporation of metal nanoparticles in an organic matrix based on pyrogallol-formaldehyde (PF) 
and successive heating under inert atmosphere. Thus formed Ni-NC showed very good electrocatalytic 
ability for the oxidation of glucose in alkaline medium.

2. Experimental

2.1. Synthesis of Ni-nanoporous carbon

The synthesis of Ni-NC samples has been carried out in three steps. NiO nanoparticles were first 
prepared by sol-gel process using the nickel (II) chloride (NiCl$_2$·6H$_2$O) precursor dissolved in methanol. After 15 min under magnetic stirring at room temperature, the solution was then placed in 
an autoclave and dried in supercritical condition of ethyl alcohol and the obtained aerogel was 
annealed at 500 °C in air for 2 hours. In the second one, organic wet gels were prepared by mixing 
formaldehyde (F) with dissolved pyrogallol (P) in water, using picric acid as a catalyst and nickel 
oxide (NiO) as an incorporated element with 5% of mass ratio. In the third step, the obtained wet gels 
were dried in humid atmosphere at 50 °C for two weeks, and in the aim to obtain a structured xerogel, 
the sample was transferred in an incubator and dried at 150 °C at a heating rate of 10 °C/day. The 
drying temperature was then maintained for two days.

In the present study, the Ni-NC sample synthesized was treated thermally in a tubular furnace under nitrogen atmosphere at 675 °C. The sample was heated up to the desired pyrolysis temperature with a 
heating rate of 5 °C/min. A constant selected pyrolysis temperature was then maintained for 2 h after 
that, the sample was cooled naturally.

2.3. Apparatus and procedures

X-ray diffraction patterns were obtained with Bruker D8 Advance X-ray diffractometer equipped with 
graphite monochromatized CuKα radiation (λ= 0.15418 nm) from 10’ to 80’ (2θ). Transmission 
electron microscopy (TEM) was performed using a JEOL JEM 2100 system operating at 200 kV.

Electrochemical measurements were performed with a Dropsens μStat 400 potentiostat. A 
conventional three-electrode system cell was employed. The working electrodes were made by casting 
carbon-supported nanoparticles (M-NC nanocomposites) as a thick film onto a glass carbon. The 
counter electrode was carbon, and a silver pseudo-reference electrode. Cyclic voltammetry (CV) and 
amperometry was carried out at room temperature in 0.1 M NaOH (pH 13) in presence and absence of 
glucose. All measurements were performed at room temperature (25 °C).
3. Results and discussion

3.1. Characterization of the Ni-NC nanocomposite

The morphology and microstructural characterization of composite obtained after pyrolysis at 675 °C were investigated by electron microscopy. SEM image in Fig. 1a shows that at this temperature pyrogallol-formaldehyde precursors have been transformed in an amorphous carbon matrix. TEM image in Fig. 1b evidence clearly that the metal oxide precursor has been, in the same conditions, transformed in the corresponding metallic phase, as highlighted by XRD analysis reported in the inset. Ni metallic nanoparticles appears to be well dispersed on the surface of amorphous carbon matrix.

![Image](image1.png)

Figure 1. a) SEM and b) TEM analysis of the Ni-NC sample annealed at 675 °C. Inset shows XRD analysis of as prepared (black) and calcined (red) sample.

3.2 Electrocatalysis of glucose at the Ni-NC nanocomposite electrode

To investigate the electrocatalytic behaviour of the Ni-NC nanocomposite towards glucose reduction, cyclic voltammetry (CV) was performed in 0.1 M NaOH. The CV spectra obtained under the following conditions, potential range 0 − 0.7 V and scan rate 50 mV/s, in the absence and presence of glucose, are displayed in Fig. 1a and b. As shown in Fig. 1a, CV pattern of bare SPCE electrode exhibits no redox process in the absence of glucose. Instead, CV of 5%Ni-NC nanocomposite modified electrode, shows two peaks at the potential of 0.38 and 0.55 V, respectively, which can be assigned to the electrochemical redox reaction of Ni^{2+}/Ni^{3+} couple on the electrode surface [18].

![Image](image2.png)

Figure 2. a) CV of SPCE and Ni-NC/SPCE electrodes in 0.1 M NaOH solution; b) CV of Ni-NC/SPCE electrode in the presence of different glucose concentrations.
CV carried in the presence of glucose (not shown) indicated that no process occurs on the bare SPCE electrode also in this condition. Vice versa, with the modified electrode, we noted a change in the CV pattern (see Fig. 1b). In the specific, the above described anodic peak at 0.55 V shows a remarkable increase in the peak current when glucose concentration increases while, correspondingly, the cathodic peak current decrease. The typical current-time curve is shown in the inset of Fig. 2b, displaying a linear trend in the range from 0 to 2mM.

Data above reported indicated that Ni species are responsible of the electrochemical behaviour observed; in particular, the Ni^{2+}/Ni^{3+} redox couple play an important role. Alkaline medium is responsible of the formation of the Ni^{3+}active sites. It can be considered indeed that, initially, Ni is electrochemically oxidized to strong oxidizing Ni (III) species such as NiOOH:

\[ \text{Ni} + 3\text{OH}^- \rightarrow \text{NiOOH} + 3\text{e}^- + \text{H}_2\text{O} \quad (1) \]

Then glucose is oxidized catalytically by generated Ni^{3+} species and produce gluconic acid and/or other intermediates:

\[ \text{NiOOH} + \text{e}^- + \text{H}_2\text{O} + \text{glucose} \rightarrow \text{Ni(OH)}_2 + \text{OH}^- + \text{gluconic acid} \quad (2) \]

As shown in Scheme 1, during glucose oxidation the electrocatalytic specie NiOOH is readily reduced to Ni(OH)\(_2\). The applied oxidative potential on the electrode surface leads to the conversion to the oxidized form and the collected electrons can be directly correlated to the concentration of glucose in the solution.

Scheme 1. Electrocatalytic behavior of modified Ni-NC/SPCE electrode.

The effect of scan rate (25-200 mVs\(^{-1}\)) on cyclic voltammetry response, at a glucose concentration of 1mM in 0.1 M NaOH, was also investigated (Fig. 3a). The result from CV shows that the redox peak current varies with the scan rate; also the oxidation and reduction potential shifts to more negative and positive values respectively with increasing scan rate. The peak current for both the oxidation and reduction processes were proportional to the square root of scan rate (Fig. 3b). Such behavior of peak current vs. square root of scan rates relationship generally appears in CV in case of diffusion of an ionic species in the vicinity of the electrode surface, which defines the rate of the reaction, i.e. under diffusional limitation.
The amperometric response of Ni-NC/SPCE electrode with successive addition of 20µM glucose in the 0.1 M NaOH solution was investigated and the results are shown in Fig. 4a-b. At the applied potential of 0.6 V it is clearly visible the remarkable enhancement in the current response upon each addition of glucose.

From the calibration figure, we can draw the linear regression equations as: \( y = 18.366x + 0.5731 \). The detection limit for Ni-NC/SPCE was calculated to be 10µM (S/N = 3) with a sensitivity of 146.4 µA mM\(^{-1}\)cm\(^{-2}\).

4. Conclusions

In this work, a non-enzymatic glucose sensor based on Ni nanoparticles dispersed in the porous surface of carbon was developed. The electrochemical performance of the sensor in the determination of glucose in alkaline medium has been investigated. It has been demonstrated that both the nanostructured Ni particles and porous surface of carbon carrier offer particular advantages due to their large specific surface areas. Based on the modified Ni-NC/SPCE electrode, an amperometric sensor for glucose determination with a sensitivity of 146.4 µA mM\(^{-1}\)cm\(^{-2}\) and lower detection limit of 10µM, has been developed. These good analytical performances, coupled with low cost and straightforward preparation method make this novel electrode material promising for the development of an effective glucose sensor.
5. Reference

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