

Comparative study of NiO-ZnO/PANI-CNTs and NiO-ZnO/PANI-graphene nanocomposites for fabrication of aqueous methanol sensors

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Abstract. In this study, we fabricated and compared two composite interfaces, ZnO-NiO/PANI-CNTs (TNZ) and ZnO-NiO/PANI-Gr (GNZ), for electrochemical detection of methanol in aqueous media. The composite were examined by XPS, SEM, TEM, SAED, and electrochemical techniques, including cyclic voltammetry (CV) and chronoamperometry (CA). Both composites contained NiO/NiOOH-ZnO active species distributed on conductive PANI-carbon networks and were able to catalyze methanol oxidation in alkaline solution. In the presence of 100 mM methanol, TNZ produced a higher voltammetric response than GNZ, indicating more effective charge transfer through the CNT-containing PANI framework. The Ni(II)/Ni(III) redox process appeared at approximately 0.45 and 0.30 V (vs. Ag/AgCl). Chronoamperometric measurements showed a response time of about 5 s and two linear concentration ranges of 0 - 300 and 300 - 600 ppm. For the higher range, the calibration gave $R^2 = 0.932$. The response was also clearly observed in RON 92 gasoline samples containing methanol. The results demonstrate that both electrodes are applicable to methanol detection, with TNZ showing the better overall electrochemical response.

Keywords: polyaniline; n-p heterojunction, nickel oxide, zinc oxide, electrochemical methanol sensor.

Classification numbers: 2.2.2, 2.4.4, 3.2.1.

1. INTRODUCTION

Volatile organic chemicals, including methanol, provide a substantial hazard to both living beings and the environment [1]. Methanol is widely used in pharmaceutical and agricultural

industries, in laboratories as a chemical feedstock or organic solvent, and as a potential alternative fuel [2, 3]. However, exposure through inhalation, ingestion, or skin contact may cause severe effects such as headache, visual impairment, blindness, organ failure, and even death [4]. Its low cost has also led to the illegal adulteration of alcoholic beverages [5]. Therefore, simple and reliable methods for methanol detection are required.

Methanol can be determined using high-performance liquid chromatography, UV–Vis spectrophotometry [6], and gas chromatography with flame-ionization detection [7]. Although these methods are effective, electrochemical sensing is attractive because of its rapid response, simplicity, portability, low cost, and high sensitivity toward alcohols in biological and non-biological samples [8]. Sensor performance strongly depends on the electrode interface. Hybrid materials combining conducting polymers, carbon nanomaterials, and metal oxides are promising because they provide high surface area, good conductivity, and synergistic electrochemical properties [9].

Polyaniline (PANI) is a suitable matrix for sensor fabrication owing to its electrochemical activity, stability, low cost, structural flexibility, and ease of processing [10, 11]. Incorporating carbon nanotubes (CNTs) or graphene (Gr) can further improve charge transport, mechanical properties, and accessible surface area [12, 13]. Meanwhile, NiO is a p-type semiconductor widely used for alcohol sensing because nickel oxide/hydroxide species participate in methanol oxidation in alkaline media [14, 16]. ZnO, an n-type semiconductor, offers good chemical stability, low cost, high electron mobility, and defect-related donor behavior [15, 17, 18]. The formation of a NiO–ZnO heterojunction may also facilitate interfacial charge transfer and enhance the sensing response [19].

In this work, mixed ZnO–NiO active centers were combined with either PANi–CNTs or PANi–Gr films on Fluorine-doped tin oxide (FTO) electrodes. The main aim was to compare these two carbon-supported PANi interfaces under similar fabrication conditions and to identify which architecture is more suitable for aqueous methanol sensing.

2. MATERIALS AND METHODS

2.1. Materials and electrochemical measurement setup

All chemicals used were of analytical grade. Aniline (ANI, 99 %, ACROS OrganicsTM) was distilled before use; NaOH (98 %), ZnCl₂·6H₂O (99 %), NiCl₂ (98 %), H₂SO₄ (99 %), methanol (99.9 %), ethanol (99 %), isopropanol, and acetone were used as received. Multiwalled CNTs (15–20 nm diameter, 5–20 μ m length; Sigma-Aldrich), graphene (< 5 nm thickness, 10–20 μ m lateral size; ANTECH JSC), and FTO substrates (8 m Ω ·cm, 2.2 mm; Dyesol) were employed. Double-distilled water was used for all solutions.

Electrochemical experiments were conducted with a Gamry Interface 1010T in a three-electrode cell. Bare or composite-modified FTO (1.0 cm²) served as the working electrode, with Pt mesh and Ag/AgCl (3.5 M KCl) as counter and reference electrodes, respectively.

2.2. Fabrication of NiO–ZnO/PANi–CNTs and NiO–ZnO/PANi–Gr composites

The NiO–ZnO/PANi–CNTs (TNZ) and NiO–ZnO/PANi–Gr (GNZ) were fabricated using the same sequential electrodeposition protocol [13, 20], with CNTs or graphene as the only changed

carbon scaffold. FTO substrates were ultrasonically cleaned in ethanol and water for 15 min, dried at 120 °C for 10 min, and used with a 1.0 cm² active area.

PANI-CNT/FTO and PANI-Gr/FTO films were first electropolymerized from 0.1 M aniline and 0.5 M H₂SO₄ containing 0.01 mg·mL⁻¹ CNTs or graphene in H₂O/IPA (1:1, v/v). Ni and Zn were then co-deposited from 0.025 M ZnCl₂, 0.025 M NiCl₂, and 0.1 M KCl by cycling from -0.3 to -0.9 V for 20 cycles at 100 mV·s⁻¹. The deposits were oxidized in 0.1 M NaOH by five cycles from 0.0 to 0.8 V at 50 mV·s⁻¹, yielding TNZ/FTO and GNZ/FTO. A NiO/PANI-CNT/FTO electrode without ZnO (TN/FTO) was prepared for selected comparisons.

2.3. Methods for structural and morphological characterizations of materials

Phase composition was examined by XRD (D8 Advance Eco, Bruker), and surface morphology by FE-SEM (JEOL JSM-6480LV). High-resolution TEM and selected-area electron diffraction (SAED) were recorded with a JEM-2100 microscope operated at 200 kV (JEOL JEM 2100). XPS measurements were performed with a Thermo Fisher K-Alpha spectrometer. Binding energies were calibrated to C 1s at 284.5 eV, and components were fitted using a Shirley background and mixed Gaussian-Lorentzian profiles [21].

2.4. Detection of methanol using TNZ/FTO and GNZ/FTO electrodes

Methanol sensing was evaluated by CV and chronoamperometry (CA) in 30 mL of 0.1 M NaOH. CV scans were recorded from 0.0 to 0.8 V at 100 mV·s⁻¹. CA measurements were conducted at 0.6 V by successive additions of a 10 mM methanol stock solution at 150 s intervals; the current response was taken after 5 s. Both aqueous standards and RON 92 gasoline samples were tested.

3. RESULTS AND DISCUSSION

3.1. Electrochemical synthesis and behavior of NiO-ZnO/PANI-CNTs and NiO-ZnO/PANI-Gr composites on FTO electrodes

Figure 1 displays the cyclic voltammograms of PANI-CNTs, PANI-Gr, and PANI during electrodeposition onto FTO from a solution containing 0.1 M aniline, 0.5 M H₂SO₄, and 0.01 mg·mL⁻¹ CNTs or Gr in an H₂O/IPA mixture. The first, fifth, and tenth cycles are presented. The increase in current density with cycle number confirms the progressive electrodeposition of PANI and PANI-based composites.

During the first cycle (Figure 1A), almost no current was observed from -0.5 to approximately 1.1 V (vs. Ag/AgCl), which may be related to initial activation of the FTO surface. Above 1.1 V, the current increased sharply because of aniline oxidation and the formation of reactive cation-radical species initiating polymer growth [22]. On the reverse scan, cathodic peaks appeared at 0.059, 0.393, and 0.612 V, associated with the reduction of intermediate or degradation products. The similar first-cycle profiles indicate that CNTs and Gr had limited effects at the initial stage.

By comparing the current densities of the 5th and 10th cycles (Figure 1C), we can observe an increased polymerization rate in the presence of CNTs or Gr compared to pure PANI. This indicates that CNTs or Gr interacted with the PANI film, resulting in an increase in the conductivity of the film.

At the fifth cycle, three characteristic redox couples of PANI were observed, corresponding mainly to the leucoemeraldine/emeraldine and emeraldine/permanganiline transitions [23]. Higher current densities at the fifth and tenth cycles for PANI-CNTs and PANI-Gr indicate enhanced polymerization and conductivity compared with pure PANI.

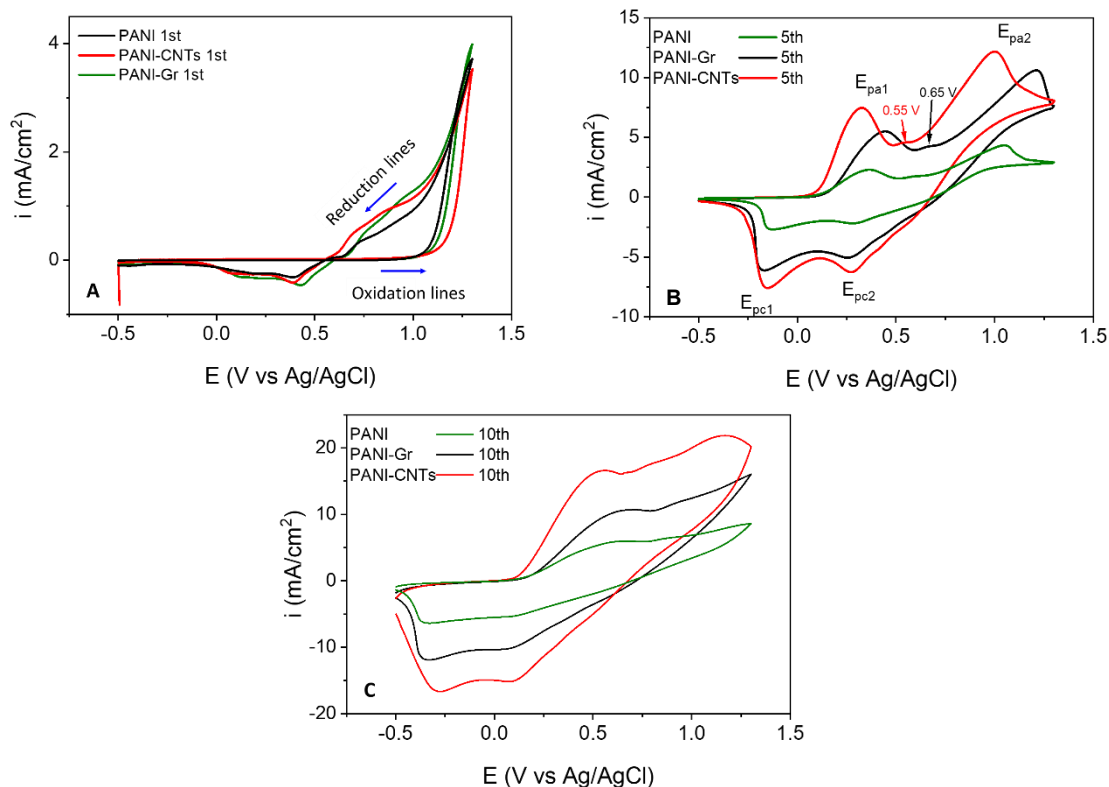


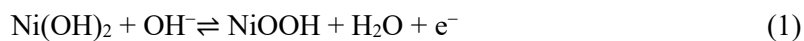
Figure 1. CVs of the electrodeposition of PANI (green), PANI-Gr (black), and PANI-CNTs (red) onto FTO at (A) the 1st, (B) the 5th and (C) the 10th cycles; potential range of -0.5 to 1.3 V; scan rate of 50 mV·s⁻¹.

After the PANI-CNTs and PANI-Gr composites were successfully synthesized on the FTO electrode, the electrodeposition of a metal mixture of nickel and zinc was carried out onto the electrode, followed by the oxidation of this metal mixture to an oxide mixture using the CV technique (Figure 2).

During co-deposition (Figure 2A), the first scan showed a broad reduction feature near -0.55 V. At 10 mV·s⁻¹, the inset resolved Ni²⁺/Ni at approximately -0.45 V and Zn²⁺/Zn at approximately -0.60 V. The sharp decrease in current after the first scan indicates rapid formation of the Ni-Zn deposit.

Oxidation in 0.1 M NaOH produced the NiO-ZnO-containing films (Figure 2B), with most oxidation occurring during the first cycle. The lower current of GNZ relative to TNZ indicates less effective charge transfer through the graphene-based architecture. The TN control also showed a weaker response than TNZ, supporting a contribution from Zn-containing species.

Under alkaline conditions, surface NiO can convert to Ni(OH)₂ and then reversibly form NiOOH. The anodic and cathodic peaks near 0.50 and 0.40 V, respectively, are assigned to the Ni(II)/Ni(III) couple [24]:



The presence of Ni(III) could be confirmed by XPS analysis in the following section.

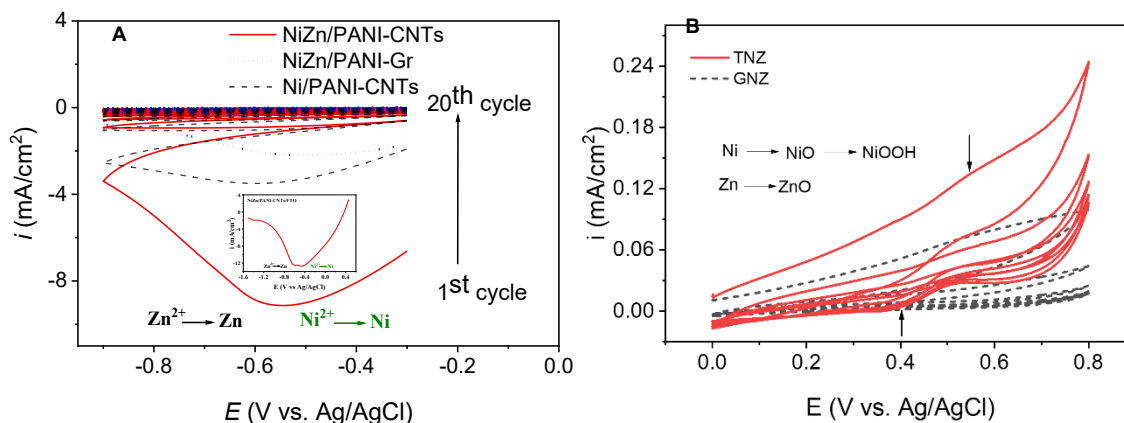


Figure 2. (A) Electrodeposition of NiZn and (B) NiZn oxidation to form NiO-ZnO on PANI-CNTs (TNZ) and PANI-Gr (GNZ) composites in a 0.1 M NaOH solution; scan rate of 50 mV·s⁻¹.

3.2. Characteristics of composite materials

Figure 3 compares the XRD patterns of TNZ/FTO and GNZ/FTO. Weak reflections at 31.3° and 34.1° correspond to the (100) and (002) planes of wurtzite ZnO (JCPDS 36-1451), while strong peaks marked with asterisks originate from FTO. NiO/NiOOH reflections overlap the substrate signals [25]. GNZ additionally shows a feature near 26.2° assigned to graphene [26].

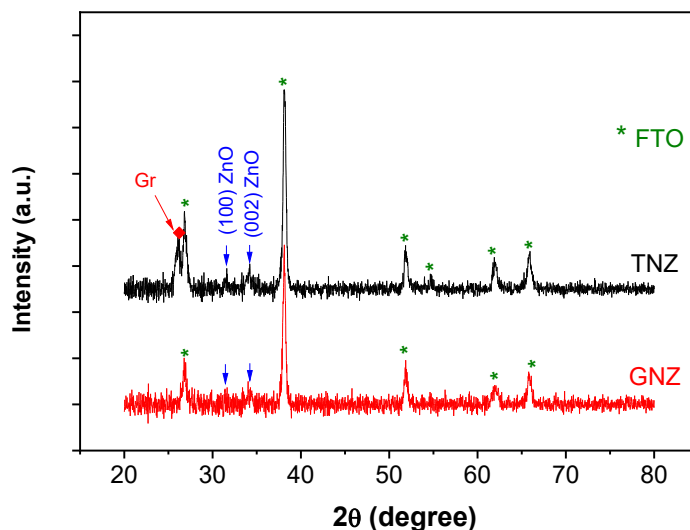


Figure 3. XRD patterns of NiO-ZnO/PANI-CNTs (TNZ) (red line) and NiO-ZnO/PANI-Gr (GNZ) (black line) composites on FTO.

Figure 4 presents the XPS analysis of TNZ and GNZ composites. The survey spectra (Figure 4A) show similar elemental compositions, including C 1s (~284 eV), N 1s (~400 eV), O 1s (~530 eV), Ni 2p (850 - 890 eV), and Zn 2p (1020 - 1050 eV). The relatively weak Ni and Zn signals indicate their low contents on the composite surfaces.

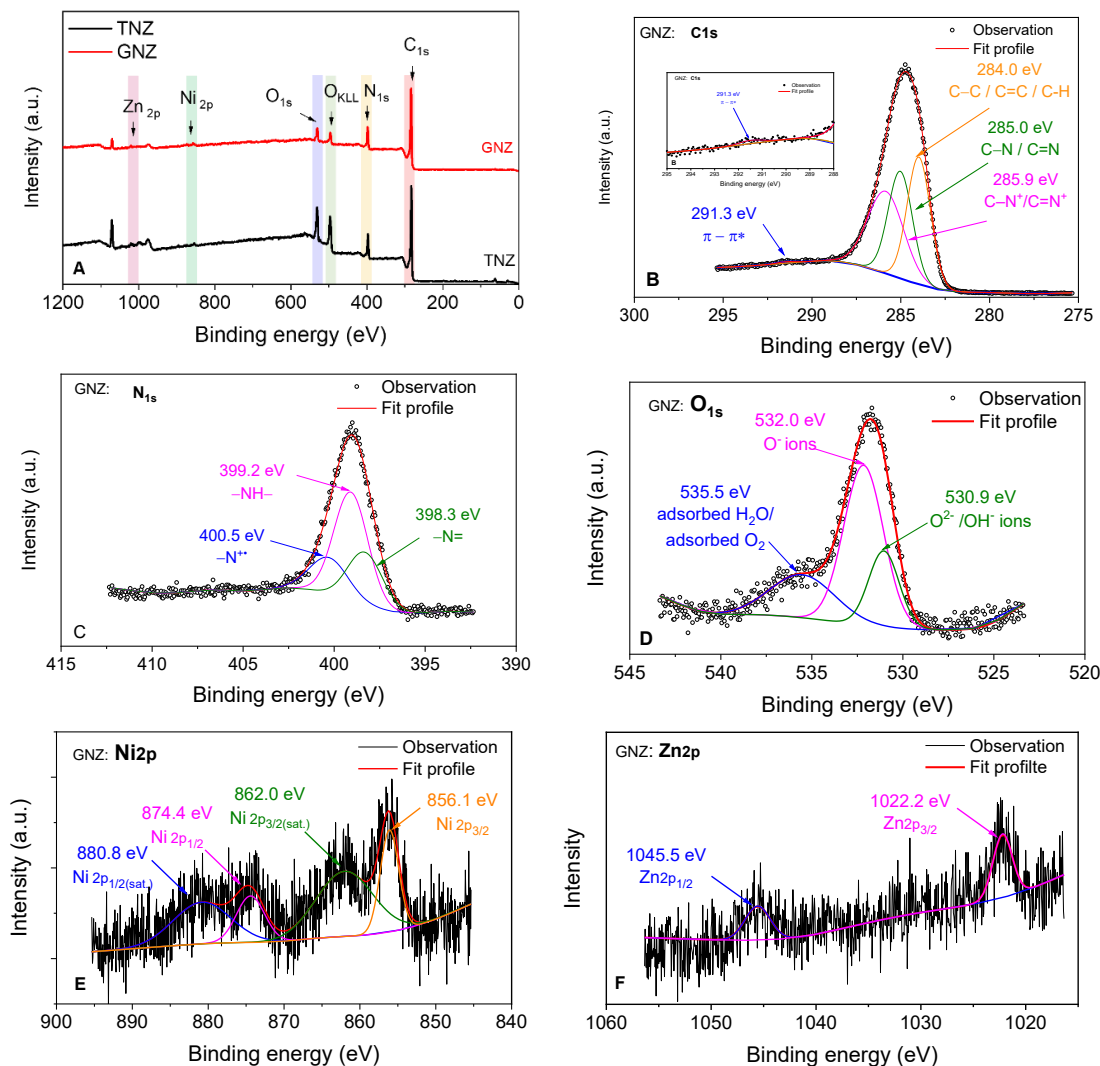


Figure 4. (A) XPS survey spectrum structure of TNZ and GNZ composites and (B-F) XPS high resolution peaks corresponding to the states of C 1s, N 1s, O 1s, Ni 2p, and Zn 2p of GNZ.

The deconvoluted C 1s spectrum of GNZ (Figure 4B) contains peaks at 284.0, 285.0, and 285.9 eV, assigned to non-oxygenated carbon (C–C, C=C, and C–H), carbon bonded to neutral nitrogen (C–N and C=N), and carbon bonded to polaronic or bipolaronic nitrogen species, respectively [27]. The component at 291.3 eV corresponds to the π – π^* (HOMO–LUMO) transition of graphitic carbon, and its low intensity may result from graphene-layer stacking [28]. The N 1s spectrum (Figure 4C) exhibits quinoid imine, benzenoid amine, and cationic radical nitrogen at 398.3, 399.2, and 400.5 eV, respectively, confirming the emeraldine salt state of PANI

[29]. The O 1s components at 530.9, 532.0, and 535.5 eV are attributed to lattice O^{2-}/OH^- species in NiO, ZnO, or NiOOH, defect-related oxygen, and adsorbed water or oxygen, respectively [30].

In the Ni 2p spectrum (Figure 4E), the Ni 2p_{3/2} and Ni 2p_{1/2} peaks occur at 856.1 and 874.4 eV, accompanied by satellite peaks at 861.3 and 880.7 eV [29]. These features confirm the coexistence of NiO and NiOOH [31, 32]. The Zn 2p_{3/2} and Zn 2p_{1/2} peaks at 1022.8 and 1045.4 eV, with a spin-orbit separation of 22.6 eV, confirm the formation of ZnO [33, 34]. Overall, the XPS characteristics of GNZ are similar to those previously reported for TNZ [20].

The morphology of the TNZ and GNZ surfaces on the FTO electrodes were determined using SEM analysis (Figure 5). The measurement of the pure PANI film was also performed for comparison. The obtained SEM images show that the PANI film and PANI composites were successfully synthesized on the electrode surface.

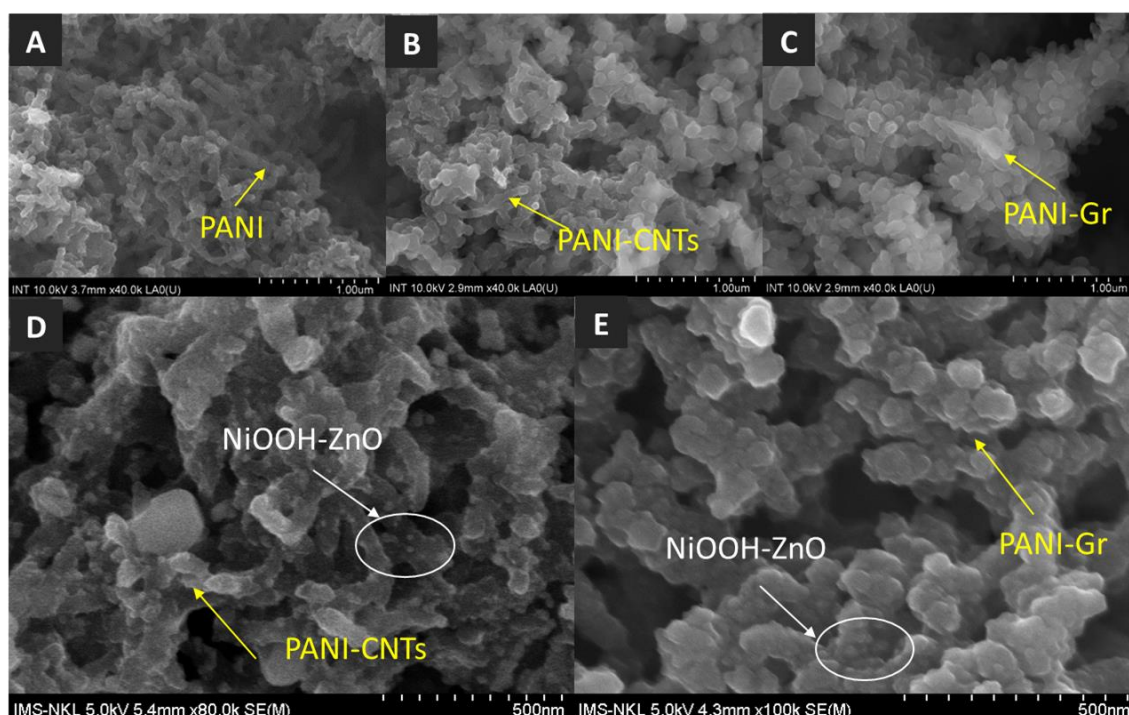


Figure 5. SEM images of (A) pure PANI; (B) PANI-CNTs; (C) PANI-Gr; and (D) NiO-ZnO/PANI-CNTs (TNZ) and (E) NiO-ZnO/PANI-Gr (GNZ).

Figure 5A demonstrates that a PANI film was successfully electro-synthesized after 10 cycles onto the FTO electrode. This film possesses a network-like layer that was formed by thin interconnected fragments, with the size of each fragment was about 50 - 60 nm wide and 0.2 - 0.5 μm long, similar to another study [35]. These PANI thin fragments were linked together and arranged randomly, creating a porous film with a large surface area.

In the presence of CNTs and graphene (Gr), good conducting materials, the PANI-CNTs and PANI-Gr composites became more porous, and the composite covered the electrode surface better than pure PANI (Figures 5B and 5C). It seems that the presence of CNTs generated a fibrous structured composite with the width of fibers being about 60 - 80 nm (Figure 5B). It could be explained by the development of polyaniline chain around the structured fibers of CNTs. On the other hand, in the presence of graphene, the structure of PANI-Gr composite became hierarchical

(Figure 5C) because of the distribution of short PANI fragments among the Gr flakes. In Figure 5B, the morphology of the PANI-CNTs composite clearly shows two different structures, including long fibers with a small diameter and short fibers with a larger diameter. The PANI-Gr composite (Figure 5C) showed small flakes, resulting from the growth of PANI chains onto graphene sheets. Both PANI-CNTs and PANI-Gr films have a large surface area that increases the contact area between the electrode and the analytical medium. In addition, highly porous surface properties of the materials can favor the adsorption of substances onto the surface.

The presence of a NiOOH-ZnO mixture on the PANI-CNTs or PANI-Gr composite surface is displayed in Figures 5D and 5E. Both composites showed the presence of numerous small particles. The TNZ composite had particle sizes estimated to be 20-30 nm, while the GNZ composite had smaller particles that were hardly visible on its surface.

The insight into the morphological properties of the GNZ composites is analyzed with HR-TEM images and SAED patterns (Figure 6).

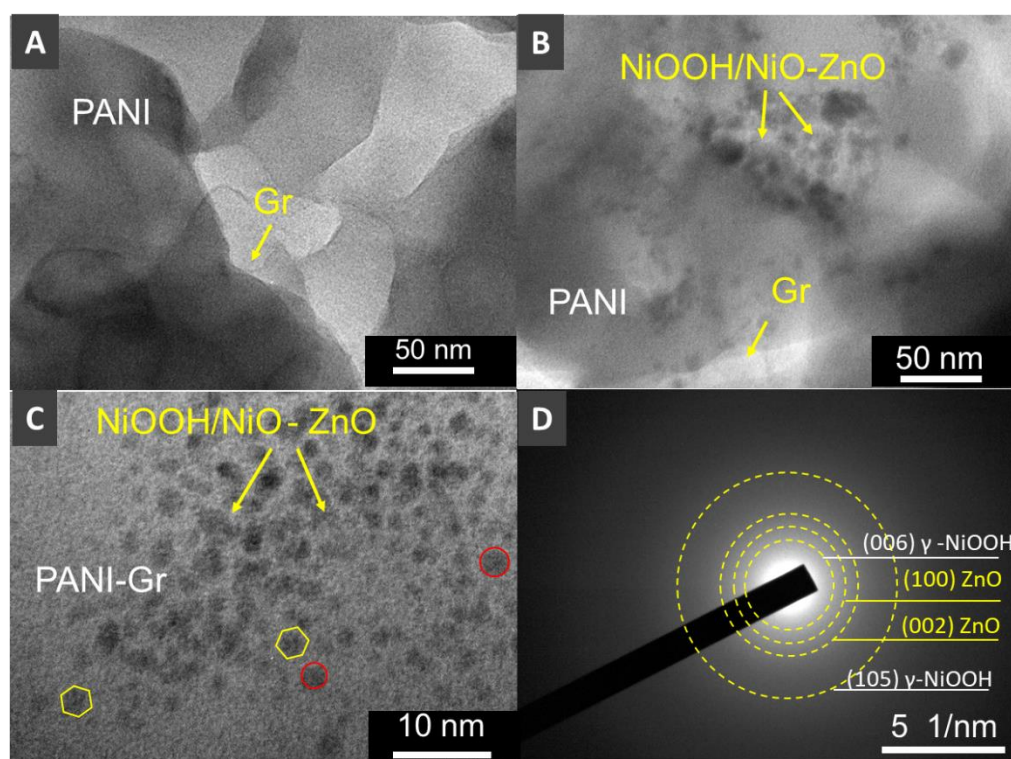


Figure 6. TEM images (A, B, C) and the SAED pattern (D) for GNZ.

The results showed that the NiOOH/NiO-ZnO clusters were well-dispersed within the polymer network, with the size of these particles ranging from 3 to 5 nm in GNZ (Figures 6B, C). The shape of these particles was close to the hexagonal form of ZnO with some change due to the combination with the shape of the nickel oxyhydroxide particle. Besides, the SAED patterns (Figure 6D) of GNZ composites showed weak diffraction rings of the (100) and (002) crystal planes of the hexagonal wurtzite phase of ZnO (JCPDS 036-1451) and a weak ring of the (105) plane corresponding to the γ -NiOOH structure (JCPDS 6-75). This HRTEM-SAED pattern result proves the presence of nanoparticles that contain γ -NiOOH and ZnO in the composite, a component that plays an important role in the sensing activity of the material [36].

Hence, the nanocomposite is made up of three components: PANI, which is a conducting polymer that acts as a matrix and binds various substances together; nanocarbon materials that have a high surface area and good electrical conductivity; and the γ -NiOOH-ZnO nanoparticles with catalytic properties that can enhance the methanol detection. Therefore, the porous composites provide a significant advantage for the electrochemical reaction that takes place on the electrode surface in electrochemical sensor fabrication.

3.3. Electrochemical behavior of TNZ and GNZ composite toward methanol detection

Figure 7 displays the electrochemical behavior of the TNZ/FTO and GNZ/FTO electrodes with and without MeOH (100 mM) in a supporting electrolyte solution of 0.1 M NaOH in the potential range of 0.0 to 0.8 V at a scan rate of 100 mV·s⁻¹.

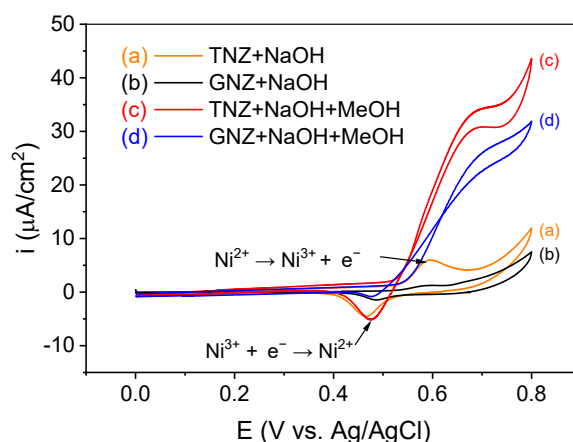


Figure 7. Electrochemical activity of Ni³⁺/Ni²⁺ during oxidation-reduction of nickel species in the potential range of 0 ÷ 0.8 V vs Ag/AgCl (a,b) in 1 M NaOH solution, scan rate of 100 mV·s⁻¹; and (c,d) in the presence of methanol, [MeOH] = 100 mM.

The cyclic voltammograms indicate a redox pair of the Ni(II)/Ni(III) couple, with an anodic peak and a cathodic peak at +0.45 V and +0.3 V, respectively. The peaks correspond to the oxidation to higher oxidizing Ni(III) and vice versa, as presented in equation (1). There was no observation of the zinc (II) involvement in the redox reaction of nickel species. This may be attributed to the fact that ZnO only serves as a support owing to its high chemical stability, large surface-to-volume ratios, biocompatibility, and electromobility [37].

In comparison to the PANI-Gr composite, the electrochemical activity was noticeably greater for the PANI-CNTs hybrid in a neutral environment. This difference can be attributed to the bulky structure of the GNZ composite, which has a higher number of large pores that potentially disrupt the charge transfer between the substrate and conductive materials [38].

The standard curves of MeOH detection using CA techniques and the signals of MeOH appeared when MeOH was continuously added into real gasoline samples using GNZ/FTO electrode or TNZ/FTO electrode are presented in Figure 8. The corresponding linear equations of the standard curves are $\Delta i = 0.00138 \times C_{\text{MeOH}} - 0.0486$ in the MeOH concentration range of 0 – 300 ppm and $\Delta i = 3.47 \times 10^{-4} C_{\text{MeOH}} + 0.28259$ with $R^2 = 0.93173$ (in the range of 300 - 600 ppm of the MeOH concentration) (Figure 8A).

The CA response curve when MeOH was consistently added to gasoline RON 92 sample in alkaline environment is presented in Figure 8B in both cases TNZ/FTO and GNZ/FTO electrodes. The results show the current signals appeared once MeOH was spiked, indicating the possibility of using these electrodes for methanol detecting purpose.

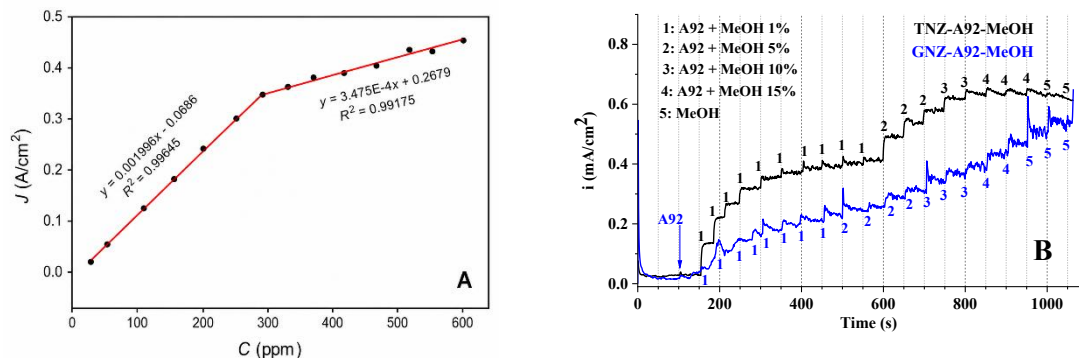


Figure 8. (A) Calibration curve of the GNZ/FTO electrode via and chronoamperometric (CA) response with a continuously adding methanol into a 0.1 M NaOH solution, (B) CA responses of TNZ/FTO and GNZ/FTO electrodes in gasoline RON A92 in 0.1 M NaOH environment.

The supposed mechanism for the detection of methanol was proposed in our previous work [36], in which there was the formation of γ -Ni^{III}OOH species on the composite surface at an oxidation potential higher than 0.5 V (vs. Ag/AgCl, see Figure 7). These species are the active sites where the irreversible oxidation of MeOH occurs:



in which MOR means methanol oxidation reaction.

However, the ZnO also played an important role when it was introduced into the composites. It provides several advantages, such as a good support matrix for the dispersion of Ni species that, in turn, increased the active sites (i.e., Ni^{III}OOH), enhancing the adsorption of methanol and consequently promoting methanol oxidation activity. Besides, the presence of ZnO increases the internal stress in the main lattice due to the difference in ionic radii of zinc and nickel, disrupting the local equilibrium of the crystal structure. It leads to increasing oxygen vacancies so that this stress can be released [39]. The existence of oxygen vacancies facilitates the adsorption of methanol molecules and MOR species, which contributes to its high catalytic sensitivity and selectivity [40].

4. CONCLUSIONS

Two composites of oxyhydroxide-oxide (NiOOH/NiO-ZnO) with PANI-CNTs and PANI-Gr were synthesized via electrodeposition. Various techniques, such as SEM, TEM-SAED, XPS, XRD, and CV, were used to identify these materials. The results revealed the crystalline structure of these zinc and nickel species as well as the morphological structures of the two composites. The oxidation state of the Ni element in both materials was the mixture of NiOOH/NiO, which plays a role of active sites. The electrochemical behavior showed that TNZ had better performance in detecting methanol. However, both composites have ability to electrocatalysis for the oxidation of methanol and significantly increase the response current with a good recognizable signal when testing real gasoline samples.

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CRedit authorship contribution statement. Pham Thi Nam: Writing – original draft, Methodology, Investigation, Writing – review & editing. Nguyen Thi Thom: Investigation, Data curation. Vo Thi Kieu Anh: Methodology, Investigation. Nguyen Thi Thu Trang: Data curation. Nguyen Thi Kim Ngan: Methodology, Investigation. Huynh Le Thanh Nguyen: Methodology. Nguyen Thai Hoang: Methodology, Investigation. Pham Van Viet: Methodology. Nguyen Van-Anh: Writing – original draft, Writing – review & editing. Le Viet Hai: Conceptualization, Writing – review & editing. Tran Dai Lam: Conceptualization, Writing – review & editing, Project administration, Funding acquisition.

Declaration of competing interest. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

REFERENCES

1. Tephly T. R. – The toxicity of methanol. *Life Sci.*, **48** (1991) 1031–1041. [https://doi.org/10.1016/0024-3205\(91\)90504-5](https://doi.org/10.1016/0024-3205(91)90504-5).
2. Dalena F., Senatore A., Marino A., Gordano A., Basile M., Basile A. – Chapter 1 - Methanol Production and Applications: An Overview, In: A. Basile, F. Dalena (Eds.) *Methanol*, Elsevier (2018) 3–28. <https://doi.org/10.1016/B978-0-444-63903-5.00001-7>.
3. Encinar J. M., Pardal A., Sánchez N. – An improvement to the transesterification process by the use of co-solvents to produce biodiesel. *Fuel*, **166** (2016) 51–58. <https://doi.org/10.1016/j.fuel.2015.10.110>.
4. Hashemi S. A., Bahrani S., Mousavi S. M., Omidifar N., Arjmand M., Lankarani K. B., Shokripour M., Ramakrishna S. – Differentiable detection of ethanol/methanol in biological fluids using prompt graphene-based electrochemical nanosensor coupled with catalytic complex of nickel oxide/8-hydroxyquinoline. *Anal. Chim. Acta*, **1194** (2022) 339407. <https://doi.org/10.1016/j.aca.2021.339407>.
5. Arslan M. M., Zeren C., Aydin Z., Akcan R., Dokuyucu R., Ketten A., Cekin N. – Analysis of methanol and its derivatives in illegally produced alcoholic beverages. *J. Forensic Leg. Med.*, **33** (2015) 56–60. <https://doi.org/10.1016/j.jflm.2015.04.005>.
6. Wrobel K., Rodríguez D. M., Aguilar F. J. A., Wrobel K. – Determination of methanol in *o,o*-dimethyldithiophosphoric acid (DMDTPA) of technical grade by UV/vis spectrophotometry and by HPLC. *Talanta*, **66** (2005) 125–129. <https://doi.org/10.1016/j.talanta.2004.10.008>.
7. Joseph J. A., Akkermans S., Van Impe J. F. M. – Processing method for the quantification of methanol and ethanol from bioreactor samples using gas chromatography-flame ionization detection. *ACS Omega*, **7** (2022) 24121–24133. <https://doi.org/10.1021/acsomega.2c00055>.
8. Park D.-S., Won M.-S., Goyal R. N., Shim Y.-B. – The electrochemical sensor for methanol detection using silicon epoxy coated platinum nanoparticles. *Sens. Actuators B Chem.*, **174** (2012) 45–50. <https://doi.org/10.1016/j.snb.2012.08.017>.
9. Maity D., Minitha C. R., Rajendra Kumar R. T. – Glucose oxidase immobilized amine terminated multiwall carbon nanotubes/reduced graphene oxide/polyaniline/gold nanoparticles modified screen-printed carbon electrode for highly sensitive amperometric glucose detection. *Mater. Sci. Eng. C*, **105** (2019) 110075. <https://doi.org/10.1016/j.msec.2019.110075>.
10. Konwer S., Guha A. K., Dolui S. K. – Graphene oxide-filled conducting polyaniline composites as methanol-sensing materials. *J. Mater. Sci.*, **48** (2013) 1729–1739. <https://doi.org/10.1007/s10853-012-6931-z>.
11. Nguyen V. H., Shim J.-J. – Green synthesis and characterization of carbon nanotubes/polyaniline nanocomposites. *J. Spectrosc.*, **2015** (2015) 1–9. <https://doi.org/10.1155/2015/297804>.
12. Dumitrescu I., Unwin P. R., Macpherson J. V. – Electrochemistry at carbon nanotubes: perspective and issues. *Chem. Commun.* (2009) 6886–6901. <https://doi.org/10.1039/b909734a>.

13. Nguyen N. X. A., Viet Hai L., Nguyen T. K. N., Pham T. N., Nguyen T. T., Huynh L. T. N., Pham V. V., Nguyen T. T. T., Thai Hoang N., Dai Lam T. – Efficient nickel or copper oxides decorated graphene-polyaniline interface for application in selective methanol sensing. *RSC Adv.*, **11** (2021) 28573–28580. <https://doi.org/10.1039/d1ra04164a>.
14. Spinner N., Mustain W. E. – Effect of nickel oxide synthesis conditions on its physical properties and electrocatalytic oxidation of methanol. *Electrochim. Acta*, **56** (2011) 5656–5666. <https://doi.org/10.1016/j.electacta.2011.04.023>.
15. Kang Y., Yu F., Zhang L., Wang W., Chen L., Li Y. – Review of ZnO-based nanomaterials in gas sensors. *Solid State Ionics*, **360** (2021) 115544. <https://doi.org/10.1016/j.ssi.2020.115544>.
16. Li S.-J., Xia N., Lv X.-L., Zhao M.-M., Yuan B.-Q., Pang H. – A facile one-step electrochemical synthesis of graphene/NiO nanocomposites as efficient electrocatalyst for glucose and methanol. *Sens. Actuators B Chem.*, **190** (2014) 809–817. <https://doi.org/10.1016/j.snb.2013.09.047>.
17. Das J., Pradhan S. K., Sahu D. R., Mishra D. K., Sarangi S. N., Nayak B. B., Verma S., Roul B. K. – Micro-Raman and XPS studies of pure ZnO ceramics. *Phys. B Condens. Matter*, **405** (2010) 2492–2497. <https://doi.org/10.1016/j.physb.2010.03.020>.
18. Bumika M., Kumar Mallick M., Mohanty S., Nayak S. K., Palai A. K. – One-pot electrodeposition of polyaniline/SWCNT/ZnO film and its positive influence on photovoltaic performance as counter electrode material. *Mater. Lett.*, **279** (2020) 128473. <https://doi.org/10.1016/j.matlet.2020.128473>.
19. Bai S., Han J., Meng J. C., Sun L., Sun J., Zhao Y., Tang P., Luo R., Li D., Chen A. – NiO/ZnO composite decorated on rGO for detection of NO₂. *Sens. Actuators B Chem.*, **339** (2021) 129720. <https://doi.org/10.1016/j.snb.2021.129720>.
20. Nam P.T., Thom N.T., Kieu Anh V.T., Le Thanh Nguyen H., Thu Trang N.T., Hoang N.T., Văn-Anh N., Anh N.T., Hai L.V., Lam T.D. – Fabrication and characterization of a NiO–ZnO/PANI-CNTs composite for sensing of methanol in an aqueous environment, *RSC Adv.*, **13** (2023) 36060–36070. <http://doi.org/10.1039/D3RA06850A.21>.
21. Castle J. E., Salvi A. M. – Interpretation of the Shirley background in x-ray photoelectron spectroscopy analysis. *J. Vac. Sci. Technol. A*, **19** (2001) 1170–1175. <https://doi.org/10.1116/1.1378074>.
22. Sayah A., Habelhames F., Bahloul A., Boudjadi A. – The effect of electrodeposition applied potential on the electrochemical performance of polyaniline films. *J. Mater. Sci. Mater. Electron.*, **32** (2021) 10692–10701. <https://doi.org/10.1007/s10854-021-05725-9>.
23. Li G.-R., Feng Z.-P., Zhong J.-H., Wang Z.-L., Tong Y.-X. – Electrochemical synthesis of polyaniline nanobelts with predominant electrochemical performances. *Macromolecules*, **43** (2010) 2178–2183. <https://doi.org/10.1021/ma902317k>.
24. Strano V., Mirabella S. – Hierarchical ZnO nanorods/Ni(OH)₂ nanoflakes for room-temperature, cheap fabrication of non-enzymatic glucose sensors. *RSC Adv.*, **6** (2016) 111374–111379. <https://doi.org/10.1039/c6ra22062b>.
25. Putra R. P., Rachman I. B., Horino H., Rzeznicka Izabela. I. – γ -NiOOH electrocatalyst derived from a nickel dithiooxamide chelate polymer for oxygen evolution reaction in alkaline solutions. *Catal. Today*, **397–399** (2022) 308–315. <https://doi.org/10.1016/j.cattod.2021.08.017>.
26. Yasin G., Arif M., Shakeel M., Dun Y., Zuo Y., Khan W. Q., Tang Y., Khan A., Nadeem M. – Exploring the nickel-graphene nanocomposite coatings for superior corrosion resistance: manipulating the effect of deposition current density on its morphology, mechanical properties, and erosion-corrosion performance. *Adv. Eng. Mater.*, **20** (2018) 1701166. <https://doi.org/10.1002/adem.201701166>.
27. Golczak S., Kanciurzevska A., Fahlman M., Langer K., Langer J.J. – Comparative XPS surface study of polyaniline thin films, *Solid State Ion.*, **179** (2008) 2234–2239. <https://doi.org/10.1016/j.ssi.2008.08.004>.
28. Ogawa S., Tsuda Y., Sakamoto T., Okigawa Y., Masuzawa T., Yoshigoe A., Abukawa T., Yamada T. – Evaluation of doped potassium concentrations in stacked Two-Layer graphene using Real-time XPS, *Appl. Surf. Sci.*, **605** (2022) 154748. <https://doi.org/10.1016/j.apsusc.2022.154748>.

29. Ahuja P., Ujjain S. K., Arora I., Samim M. – Hierarchically grown NiO-decorated polyaniline-reduced graphene oxide composite for ultrafast sunlight-driven photocatalysis. *ACS Omega*, **3** (2018) 7846–7855. <https://doi.org/10.1021/acsomega.8b00765>.
30. Dupin J.-C., Gonbeau D., Vinatier P., Levasseur A., – Systematic XPS studies of metal oxides, hydroxides and peroxides, *Phys. Chem. Chem. Phys.*, **2** (2000) 1319–1324. <http://doi.org/10.1039/A908800H>.
31. Tiwary P., Chakrabarty N., Edwards H.J., Dhanak V.R., Kar A., Mahapatra R., Chakraborty A.K. – Hydrothermally grown uniform sized nickel hydroxide/oxyhydroxide hexagonal nanoprisms exhibiting room temperature ethanol sensing properties, *Appl. Surf. Sci.*, **570** (2021) 151090. <https://doi.org/10.1016/j.apsusc.2021.151090>.
32. Menezes P. W., Yao S., Beltrán-Suito R., Hausmann J. N., Menezes P. V., Driess M. – Facile access to an active γ -NiOOH electrocatalyst for durable water oxidation derived from an intermetallic nickel germanide precursor. *Angew. Chem. Int. Ed.*, **60** (2021) 4640–4647. <https://doi.org/10.1002/anie.202014331>.
33. Jayababu N., Poloju M., Shruthi J., Reddy M. V. R. – Synthesis of ZnO/NiO nanocomposites for the rapid detection of ammonia at room temperature. *Mater. Sci. Semicond. Process.*, **102** (2019) 104591. <https://doi.org/10.1016/j.mssp.2019.104591>.
34. Vuong N. M., Hien T. T., Han V. T., Hieu H. N., Van Nghia N. – Efficient performance acetone sensor based on squirrel-tail like Ni doped ZnO hierarchical nanostructure. *Mater. Charact.*, **180** (2021) 111388. <https://doi.org/10.1016/j.matchar.2021.111388>.
35. Abdel Hamid Z., Hasan Gomaa M., S. Abdel Rehim S., Abdel Hamid M., Ibrahim A. – Synthesis and characterization of nanostructured polyaniline thin films with superhydrophobic properties. *Coatings*, **9** (2019) 748. <https://doi.org/10.3390/coatings9110748>.
36. Thi Kim Ngan N., Thi Thom N., An N. N. X., Hai L. V., Thi Nam P., Le Thanh Nguyen H., Van Viet P., Thi Thu Trang N., Hoang N. T., Tran D. L. – Design of NiOOH/PANI-Gr and NiOOH/PANI-CNTs interfaces for sensitive and selective methanol electrochemical sensors. *J. Electrochem. Soc.*, **168** (2021) 107509. <https://doi.org/10.1149/1945-7111/ac2d44>.
37. Miao Y., Ouyang L., Zhou S., Xu L., Yang Z., Xiao M., Ouyang R., – Electrocatalysis and electroanalysis of nickel, its oxides, hydroxides and oxyhydroxides toward small molecules, *Biosens. Bioelectron.*, **53** (2014) 428–439. <https://doi.org/10.1016/j.bios.2013.10.008>.
38. Cao H., Si S., Xu X., Li J., Xia Y. – Acetate as electrolyte for high performance rechargeable Zn-Mn-deposited Zn/Ni foam-supported polyaniline composite battery. *J. Electrochem. Soc.*, **166** (2019) A1266. <https://doi.org/10.1149/2.1271906jes>.
39. Zhang J., Li J. – The oxygen vacancy defect of ZnO/NiO nanomaterials improves photocatalytic performance and ammonia sensing performance. *Nanomaterials*, **12** (2022) 433. <https://doi.org/10.3390/nano12030433>.
40. Liu C., Yang F., Schechter A., Feng L. – Recent progress of Ni-based catalysts for methanol electrooxidation reaction in alkaline media. *Adv. Sens. Energy Mater.*, **2** (2023) 100055. <https://doi.org/10.1016/j.asems.2023.100055>.