Journal of Composites and Compounds 4 (2022) 178-181

Available online at www.jourcc.com

Journal homepage: www.JOURCC.com

Journal of Composites and Compounds

Synthesis and Characterization of CuO@PANI composite: A new prospective material for electrochemical sensing

Hicham Meskher [a], Fethi Achi [a], Hakim Belkhalfa [b]*

[a] *Laboratory of Valorization and Promotion of SaharianRessources (VPSR), Kasdi-Merbah University, Ouargla, 30000, Algeria.*
[b] *Scientific and Technical Research Center in Physicochemical Analysis, Bou-Ismail, Tipaza, Algeria*

ABSTRACT

Herein, one-step oxidation-chemical polymerization in situ to prepare a composite of copper oxide nanoparticles doped with polyaniline(CuO@PANI) was investigated in order to check the electrochemical properties.The influence of the synthetic approach, the doping effectiveness of copper oxide nanoparticles, as well as the structure of the as-synthesized composite, were all studied. The synthesized compositewas characterized by field emission SEM and XFR. The results showed favorable interaction between PANI and CuO NPs. The electron microscopy analysis of the composite indicates that CuO is well dispersed and agglomerated in the PANI matrix as can be seen clearly in X-ray fluorescence analysis. Moreover, X-ray assessment indicated that the amount of CuO NPs strengthens the crystallinity of PANI. Moreover, to investigate the electrochemical performance of CuO@PANI, the composite was drop-casted on a glassy carbon electrode surface and its electrocatalytic activity was examined via a potentiostate in presence of catechol. As a result, the electrical conductivity of the synthesized hybrid was found to be drastically increased (around 60 %) as compared to that of pure PANI at room temperaturedue to the formation of conducting path between CuO and PANI surface. Hence, through this work we highly recommend to use this hybrid for future electrochemical sensing applications.

Peer review under responsibility of UGPH.

ARTICLE INFORMATION

Article history:
Received 02 October 2022
Received in revised form 11 November 2022
Accepted 26 December 2022

Keywords:
Chemical Polymerization
Composite
Polyanaline
Electrochemical sensing
Electrocatalytic activity

1. Introduction

Because of their unique properties and qualities, nanoparticles are being employed in a wide range of scientific and technological applications [1-7]. Due to their excellent physical and catalytic characteristics, nanoparticles (NPs) such as metal oxide have been used in electrochemistry to increase their electro-catalytic efficiency [8-10]. In addition, the high surface area [11], antibacterial activity [12] and drug delivery [13] make such materials effective substrate for fabrication of novel composites material for various fields[14-16]. In addition, Nanomaterials and their nanocomposites with unique atomic thickness are promising materials for various applications including tissue engineering [16], energy storage [17, 18], water related applications [18] and catalytic industries [20-22] due to their outstanding properties such as high mechanical strength, large surface area, good chemical and thermal stability, ease of functionalization, and hydrophilic surface.

For instance, Benmoussa et al., proposed a novel electrochemical biosensor to detect cancer biomarker (lactic acid) based on organic-inorganic composite coupled with a molecularly imprinted polymer to create a highly sensitive and selective electrochemical biosensor where a limit of detection around 0.726 µM has been determined [14]. Hence, The NPs-modified electrode enhanced signal responsiveness, sensitivity, and repeatability [23-27], and it has several bioscience applications.

Furthermore, the characteristics of composite materials are determined by the morphology of the phases, which must be regulated across many length scales [25-28]. As a result, the creation of such materials is a “land of multidisciplinarity”, requiring chemists, physicists, material scientists, and engineers to collaborate together.

CuO NPs have been popular in bio-electrochemical and electrochemical operations in recent years due to their capacity to promote electron transmission in various types of sensors [29-32] and update the electrode surface in batteries and supercapacitors[33-36]. CuO NPs can be used in electronics, coatings, ceramics, catalysis, petrochemical products, and a variety of other applications. Polyaniline (PANI) was found to have similar features such as exceptional electrical conductivity, more oxygen-containing functional groups, strong water solubility, a wide surface area, and a higher platform for improved electrochemical sensor performance[37-41]. However, the electrochemical examination of bare PANI is restricted due to its poorer electro-catalytic activity than metal oxide based PANI nano-hybrid (CuO@PANI). The combination of PANI and metal oxide nanoparticles resulted in a high sensitivity for

* *Corresponding author: Hicham Meskher; E-mail: hicham.meskher@gmail.com, hicham.meskher@g.enp.edu.dz*

https://doi.org/10.52547/jcc.4.4.1

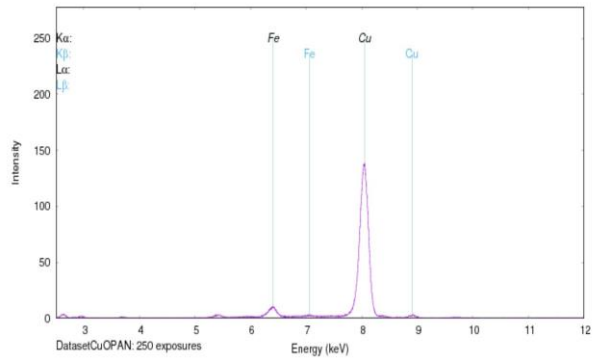

Fig. 1. XRF of synthesized nanocomposites CuO@PANI.

target molecule analysis[42,43].

In this work, we offer a novel in situ polymerization technique for the easy and fast synthesis of PANI and CuO dispersed PANI composite materials. X-ray diffraction (XRD) and scanning electron microscopy were used to analyze the produced nanocomosites (SEM). The prepared organic-inorganic was also studied for electrochemical applications.

2. Methods and Materials

2.1. Reagents

Sigma-Aldrich provides monosodium and disodium phosphate, catechol (CC), aniline, sodium hydroxide, chloride acid HCl (1M), ammonium peroxySulfat (APS), copper sulfate ($CuSO_4$), sodium hydroxide (NaOH)and deionized water.

2.2 Instrumentation

The electrochemical studieswere examined using BIOLOGIC Instrument. A conventional three electrode electrochemical system was applied for the electrochemical monitoring of CC, which incorporated of GCEas working electrode, Platine electrode as counter electrode and aqueous saturated calomel electrode (SCE) as reference electrode. The synthesized CuO@PANI and PANI were confirmed and characterized by XFR (OLYMPUS BTX-716) and their surface morphology was studied using SEM analysis (ZEISS Ultra-55).

2.3 Chemical synthesis of polyaniline(PANI)

To synthesis polyaniline, 20 ml of chloride acid HCl (1M) was slowly added to 3.1 ml of aniline (0.15 M) in 190 mland kept under stirring for 15 minutes in closed beaker. Meanwhile, another solution was prepared by adding 7.5 g of Ammonium PeroxySulfat (APS) to 10 ml of deionized waterand thenwas added to the first solution wisely for 2 hours. Dark green particles were obtained indicating successful formation of polyaniline. The masse obtained wastreatmed with 20 ml of exceed ammonia to remove chloride acid from the synthesized PANI. The quantity of PANI precipitated washed several times with ethanol and water and then dried in vacuum for 12 hours.

2.4 Synthesis of CuO@PANInano-hybrid

CuO@PANInano-hybridwas synthesized by preparing a mixture of polyaniline (PANI), copper sulfate ($CuSO_4$) and sodium hydroxide (NaOH). Firstly, 100 mg of PANI was added to $CuSO_4$ solution (10 mg/ml) under ultrasonication and stirring for 2 hours at 60°C. Secondly, the NaOH solution (0.25mol/l) was added to the prepared mixture to produce $Cu(OH)_2$. Similarly, the mixture was followed by ultrasonication and stirring for 1 hour at 80°C. Finally, a dark blue precipitation was appeared, hence, the mass was collected by filtration and washed three times with deionized water and dried for 2 hours at 80°C.

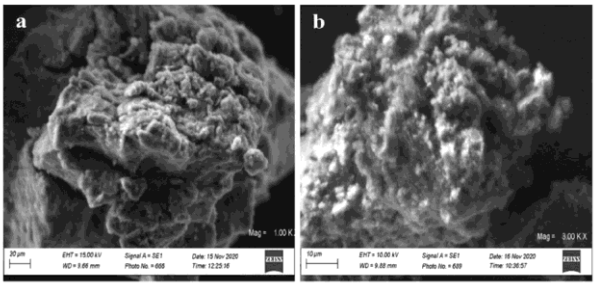

Fig. 2. SEM analysis of (a) PANI and (b) CuO@PANI.

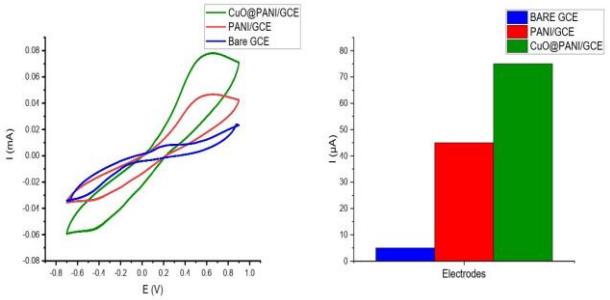

Fig. 3. CVs of 5 mMK3[Fe(CN)6]/K4[Fe(CN)6] at different modified GCE in the presence of 0.1 M PBS contains 0.1M KCL at sweep rate of 0.1 V/s.

2.5 Preparation of modified glassy carbon electrodes

Before and after any experiment, the bare and the modified GCE was primarily burnished by Alumina pouder (50µm Al_2O_3) in a circular motion to clean its surface and in same time the electrode moved smoothly through drawing number eight to avoid creating grooves in its mirror surface, and then cleaned with deionized water to wash it from any trace of Al_2O_3 or any other nanomaterial.

Afterward, 15 mg of each synthesized nanomaterials were dispersed in 5 mL of ethanol by ultrasonication for 20 min to obtain a 3 mg/ml homogeneous colloidal solutions. Finally, a micro volume of each suspension liquid were dropped onto the bare GCE surface and dried at room temperature to manufacture modified electrodes.

3. Results and Discussion

3.1. Characterization of the synthesized nanomaterials

The chemical structures of PANI and CuO@PANInano-hybrid were characterized using X-ray fluorescence (XRF)and scanning electron microscopy (SEM). As seen in **figure 1**, the XRF of CuO@PANI reveals that the CuO nanoparticles has successfully coated over the surface of PANI.

The morphological characterizations of the synthesized PANI and CuO@PANI nano-hybrid were examined by SEM. It shows that the prepared PANI is significantly exfoliated and porous crumbled spheres like-structure as depicted in **figure 2.a.** It is observed from **figure 2.b** that the soft white patches on the surface of PANI shows that CuO NPs have been well incorporated on the PANI surface. Hence, CuO nanoparticles are well dispersed onto PANI agglomerations which are closely in contact with each other.

3.2. Electrochemical study of the prepared nanomaterials

The electrochemical performance of prepared nanomaterials was carefully investigated at the bare GCE, PANI and CuO@PANI modified GCE using cyclic voltammetry (CV). The CV experiments were carried out in 15 ml PBS (0.1 M, pH 7.0). Sweep rate for all CV measurements was selected as 100 mV/s. Figure 3 shows the CV responses

of bare GCE (blue curve), PANI/GCE (red curve) and CuO@PANI/GCE (green curve) in the presence of 0.1 M KCl solution containing 5 Mm K3[Fe(CN)$_6$]/K4[Fe(CN)$_6$] (1:1) and the results were plotted in the form of CVs with a potential ranging from -0.7 V to 1.0 V. All potentials were measured and reported versus the SCE potential.

As can be seen in figure 3, the bare GCE can barely detect the presence of $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$. When compared to the bare GCE, PANI/GCE exhibits a redox peak with lower peak currents, suggesting that the oxidation peak of $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ may be separated with a low electrochemical response. On the other hand, the CuO@ PANI/GCE (green curve) exhibits a well-defined oxidation peak with a greater peak of separation, suggesting that the $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ redox process is quasi-reversible. The boost on the response of the GCE may due incorporation of CuO NPs on the surface of PANI which to improve the active surface of the synthesized composite and improved the electron transfer rate at the GCE active surface. Furthermore, the synthesiwed composite displays a significant synergistic impact due to the inter-constituent interactions between CuO NPs and PANI, resulting in improved high electron transfer with better electrochemical performance.

4. Conclusions

The present study reported a fast single step synthesis procedure of a novel organic-inorganic composite based on PANI and CuO nanoparticles. The porous structure, morphology and the successful incorporation of CuO NPs into the surface of PANI has been determined by SEM while FRX has been used to investigate the metallic properties of the synthesized composite. The electron transfer ability of CuO NPs and PANI, and their catalytic activity along with the syngeric effect of these materials when combined with each other improve the GCE electrochemical performance. Hence, the CuO@PANI composite may find an excellent application in electrochemical detection of electroactive molecules such as phenolic compounds and biomolecules such as glucose.

Ethical Approval

Not applicable.

Acknowledgments

The authors thank the Laboratory of Valorization and Promotion of Saharian Ressources (VPSR), Kasdi-Merbah University and Scientific and Technical Research Center in Physicochemical Analysis (Algeria) for financial support of this work.

REFERENCES

[1] S. Azadmehr, M.J. Taftreshi, S. Alamdari, Synthesis, Characterization and Scintillation Response of $ZnWO_4$-GO Nanocomposite, Journal of s and Compounds 4(12) (2022) 158-162.

[2] F.E. Ab Latif, A. Numan, N.M. Mubarak, M. Khalid, E.C. Abdullah, N.A. Manaf, R. Walvekar, Evolution of MXene and its 2D heterostructure in electrochemical sensor applications, Coordination Chemistry Reviews 471 (2022) 214755.

[3] H. Meskher, F. Achi, A. Zouaoui, S. Ha, M. Peacock, H. Belkhalfa, Simultaneous and Selective Electrochemical Determination of Catechol and Hydroquinone on A Nickel Oxide (NiO) Reduced Graphene Oxide (rGO) Doped Multiwalled Carbon Nanotube (fMWCNT) Modified Platinum Electrode, Analytical Letters 55(9) (2022) 1466-1481.

[4] Y.S. Prasanna, S.S. Deshmukh, Significance of Nanomaterials in solar energy storage applications, Materials Today: Proceedings 38 (2021) 2633-2638.

[5] H. Meskher, F. Achi, S. Ha, B. Berregui, F. Babanini, H. Belkhalfa, Sensitive rGO/MOF based electrochemical sensor for penta-chlorophenol detection: a novel artificial neural network (ANN) application, Sensors & Diagnostics 1(5) (2022) 1032-1043.

[6] I. Ahmed, M.M.H. Mondol, M.J. Jung, G.H. Lee, S.H. Jhung, MOFs with bridging or terminal hydroxo ligands: Applications in adsorption, catalysis, and functionalization, Coordination Chemistry Reviews 475 (2023) 214912.

[7] J. Guo, Y. Wang, Y. Cai, H. Zhang, Y. Li, D. Liu, Ni-doping Cu-Prussian blue analogue/carbon nanotubes composite (Ni-CuPBA/CNTs) with 3D electronic channel-rich network structure for capacitive deionization, Desalination 528 (2022) 115622.

[8] G. Maduraiveeran, M. Sasidharan, W. Jin, Earth-abundant transition metal and metal oxide nanomaterials: Synthesis and electrochemical applications, Progress in Materials Science 106 (2019) 100574.

[9] A.R.C. Bredar, A.L. Chown, A.R. Burton, B.H. Farnum, Electrochemical impedance spectroscopy of metal oxide electrodes for energy applications, ACS Applied Energy Materials 3(1) (2020) 66-98.

[10] D. Aurbach, I. Weissman, Y. Gofer, E. Levi, Nonaqueous magnesium electrochemistry and its application in secondary batteries, The Chemical Record 3(1) (2003) 61-73.

[11] P. Fallahazad, M. Sharifi, N. Naderi, M.J. Eshraghi, A comparison of optical properties of ZnO nanorods and ZnO nanotips for improving light absorption in rGO/ZnO nanostrctures, Journal of Composites and Compounds 4(11) (2022) 74-76.

[12] M. Karimi, E. Sadeghi, S.K. Bigdeli, M. Zahedifar, Synthesis, feasibility study of production of singlet oxygen and hydroxyl radical and performance in antibacterial activity of ZnS: Eu QDs, Journal of Composites and Compounds 4(11) (2022) 77-82.

[13] F. Sharifianjazi, M. Irani, A. Esmaeilkhanian, L. Bazli, M.S. Asl, H.W. Jang, S.Y. Kim, S. Ramakrishna, M. Shokouhimehr, R.S. Varma, Polymer incorporated magnetic nanoparticles: Applications for magnetoresponsive targeted drug delivery, Materials Science and Engineering: B 272 (2021) 115358.

[14] F.B. Moussa, F. Achi, H. Meskher, A. Henni, H. Belkhalfa, Green one-step reduction approach to prepare rGO@ AgNPs coupled with molecularly imprinted polymer for selective electrochemical detection of lactic acid as a cancer biomarker, Materials Chemistry and Physics 289 (2022) 126456.

[15] A. Nouri, B. Faraji Dizaji, N. Kianinejad, A. Jafari Rad, S. Rahimi, M. Irani, F. Sharifian Jazi, Simultaneous linear release of folic acid and doxorubicin from ethyl cellulose/chitosan/g-C_3N_4/MoS_2 core-shell nanofibers and its anticancer properties, Journal of Biomedical Materials Research Part A 109(6) (2021) 903-914.

[16] S. Askari, Z.A. Bozcheloei, Piezoelectric composites in neural tissue engineering: material and fabrication techniques, Journal of Composites and Compounds 4(10) (2022) 37-46.

[17] T. Lu, S. Dong, C. Zhang, L. Zhang, G. Cui, Fabrication of transition metal selenides and their applications in energy storage, Coordination Chemistry Reviews 332 (2017) 75-99.

[18] V. Salarvand, M. Abedini Mohammadi, F. Ahmadian, F. Rajabi Kouchi, M. Saghafi Yazdi, A. Mostafaei, In-situ hydrothermal synthesis of NiCo(X)Se compound on nickel foam for efficient performance of water splitting reaction in alkaline media, Journal of Electroanalytical Chemistry 926 (2022) 116929.

[19] A. Ali, F. Long, P.K. Shen, Innovative Strategies for Overall Water Splitting Using Nanostructured Transition Metal Electrocatalysts, Electrochemical Energy Reviews 6(1) (2023) 1-30.

[20] P. Mialane, C. Mellot-Draznieks, P. Gairola, M. Duguet, Y. Benseghir, O. Oms, A. Dolbecq, Heterogenisation of polyoxometalates and other metal-based complexes in metal–organic frameworks: from synthesis to characterisation and applications in catalysis, Chemical Society Reviews 50(10) (2021) 6152-6220.

[21] H. Meskher, H.C. Mustansar, A.K. Thakur, R. Sathyamurthy, I. Lynch, P. Singh, T.K. Han, R. Saidur, Recent trends in carbon nanotube (CNT)-based biosensors for the fast and sensitive detection of human viruses: a critical review, Nanoscale Advances (2023).

[22] F. Ahmadian, V. Salarvand, M. Saghafi, M.T. Noghani, A. Yousefifar, Production and characterization of high-performance cobalt–nickel selenide catalyst with excellent activity in HER, Journal of Materials Research and Technology 15 (2021) 3942-3950.

[23] S.P. Usha, H. Manoharan, R. Deshmukh, R. Álvarez-Diduk, E. Calucho, V.V.R. Sai, A. Merkoçi, Attomolar analyte sensing techniques (AttoSens): a review on a decade of progress on chemical and biosensing nanoplatforms, Chemical Society Reviews 50(23) (2021) 13012-13089.

[24] M. Hicham, A. Fethi, S. Ha, B. Khaldoun, Antifouling double layers of functionalized-multi-walled carbon nanotubes coated ZnO for sensitive and selective electrochemical detection of catechol, Fullerenes, Nanotubes and Carbon Nanostructures 30(3) (2022) 334-347.

[25] T. Ören Varol, O. Hakli, U. Anik, Graphene oxide–porphyrin composite nanostructure included electrochemical sensor for catechol detection, New Journal of Chemistry 45(3) (2021) 1734-1742.

[26] M. Pirzada, Z. Altintas, Nanomaterials for virus sensing and tracking, Chem-

ical Society Reviews 51(14) (2022) 5805-5841.
[27] M. Saghafi, S.A. Hosseini, S. Zangeneh, A.H. Moghanian, V. Salarvand, S. Vahedi, S. Mohajerzadeh, Charge storage properties of mixed ternary transition metal ferrites MZnFe oxides (M =Al, Mg, Cu, Fe, Ni) prepared by hydrothermal method, SN Applied Sciences 1(10) (2019) 1303.
[28] E.H. Jazi, R. Esalmi-Farsani, G. Borhani, F.S. Jazi, Synthesis and Characterization of In Situ Al-$Al_{13}Fe_4$-Al_2O_3-TiB_2 Nanocomposite Powder by Mechanical Alloying and Subsequent Heat Treatment, Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry 44(2) (2014) 177-184.
[29] Z. Xu, W. Deng, X. Wang, 3D hierarchical carbon-rich micro-/nanomaterials for energy storage and catalysis, Electrochemical Energy Reviews 4(2) (2021) 269-335.
[30] B. Ates, S. Koytepe, A. Ulu, C. Gurses, V.K. Thakur, Chemistry, structures, and advanced applications of nanocomposites from biorenewable resources, Chemical Reviews 120(17) (2020) 9304-9362.
[31] V.K. Thakur, R.K. Gupta, Recent progress on ferroelectric polymer-based nanocomposites for high energy density capacitors: synthesis, dielectric properties, and future aspects, Chemical reviews 116(7) (2016) 4260-4317.
[32] H. Meskher, F. Achi, Electrochemical Sensing Systems for the Analysis of Catechol and Hydroquinone in the Aquatic Environments: A Critical Review, Critical Reviews in Analytical Chemistry (2022) 1-14.
[33] F. Fazl, M.B. Gholivand, High performance electrochemical method for simultaneous determination dopamine, serotonin, and tryptophan by ZrO_2–CuO co-doped CeO_2 modified carbon paste electrode, Talanta 239 (2022) 122982.
[34] S. Nithya, A. Dutta, Superior dual mode electrochemical sensing of NH_3 using Ni_2+ doped CuO anode with lanthanum gallate based electrolyte, Sensors and Actuators B: Chemical 361 (2022) 131731.
[35] K. Wang, Y. Sun, W. Xu, W. Zhang, F. Zhang, Y. Qi, Y. Zhang, Q. Zhou, B. Dong, C. Li, Non-enzymatic electrochemical detection of H_2O_2 by assembly of CuO nanoparticles and black phosphorus nanosheets for early diagnosis of periodontitis, Sensors and Actuators B: Chemical 355 (2022) 131298.
[36] E. Niknam, H. Naffakh-Moosavy, M. Ghahraman Afshar, Electrochemical performance of Nickel foam electrode in Potassium Hydroxide and Sodium Sulfate electrolytes for supercapacitor applications, Journal of Composites and Compounds 4(12) (2022) 149-152.
[37] S. Li, J.-H. Lee, S.M. Hwang, J.-B. Yoo, H. Kim, Y.-J. Kim, Natural Activation of CuO to $CuCl_2$ as a Cathode Material for Dual-Ion Lithium Metal Batteries, Energy Storage Materials 41 (2021) 466-474.
[38] M. Karami, M.A. Akhavan-Bahabadi, S. Delfani, M. Raisee, Experimental investigation of CuO nanofluid-based direct absorption solar collector for residential applications, Renewable and Sustainable Energy Reviews 52 (2015) 793-801.
[39] F. Chang, M. Xiao, R. Miao, Y. Liu, M. Ren, Z. Jia, D. Han, Y. Yuan, Z. Bai, L. Yang, Copper-based catalysts for electrochemical carbon dioxide reduction to multicarbon products, Electrochemical Energy Reviews 5(3) (2022) 1-35.
[40] B. Fakić, A. Kumar, M. Alipour, A. Abbas, E. Ahmadi, N. Nikzad, P. Shafiee, Carbon-based materials and their composites as anodes: A review on lithium-ion batteries, Journal of Composites and Compounds 4(11) (2022) 124-139.
[41] H. Khalilpour, P. Shafiee, A. Darbandi, M. Yusuf, S. Mahmoudi, Z. Moazzami Goudarzi, S. Mirzamohammadi, Application of Polyoxometalate-based composites for sensor systems: A review, Journal of Composites and Compounds 3(7) (2021) 129-139.
[42] A. Yadav, H. Kumar, R. Sharma, R. Kumari, Influence of polyaniline on the photocatalytic properties of metal nanocomposites: A review, Colloid and Interface Science Communications 40 (2021) 100339.
[43] E. Saeb, K. Asadpour-Zeynali, Facile synthesis of TiO_2@ PANI@ Au nanocomposite as an electrochemical sensor for determination of hydrazine, Microchemical Journal 160 (2021) 105603.
[44] Y. Shen, Z. Qin, T. Li, F. Zeng, Y. Chen, N. Liu, Boosting the supercapacitor performance of polyaniline nanofibers through sulfonic acid assisted oligomer assembly during seeding polymerization process, Electrochimica Acta 356 (2020) 136841.
[45] T. Liu, Y. Guo, Z. Zhang, Z. Miao, X. Zhang, Z. Su, Fabrication of hollow CuO/PANI hybrid nanofibers for non-enzymatic electrochemical detection of H2O2 and glucose, Sensors and Actuators B: Chemical 286 (2019) 370-376.
[46] Y. Zhao, B. Liu, L. Pan, G. Yu, 3D nanostructured conductive polymer hydrogels for high-performance electrochemical devices, Energy & Environmental Science 6(10) (2013) 2856-2870.