DEVELOPMENT OF NANOSTRUCTURES BASED ON COPPER, ZINC, TITANIUM WITH APPLICABILITY IN VARIOUS ELECTROCHEMICAL SYSTEMS

PhD thesis - Abstract

for obtaining the scientific title of doctor from

Politehnica University Timișoara

in the doctoral field of CHEMICAL ENGINEERING

author

ing. Mina-Ionela POPESCU căs. MORARIU

scientific coordinator Conf.univ.dr.ing. Narcis-Mihai DUȚEANU

September 2025

CUPRINS

PURPOSE, OBJECTIVES AND STRUCTURE OF THE DOCTORAL THESIS

Currently, we're living in the era of modern technology where development of devices generates various benefits in all existing field. This industry becomes the pillar of the society; were the growth of services and products can be covered by the development of technologies.

The use of electronic devices has an increasing trend in today's society living standards and this was the reason of developing systems that are capable of storing and releasing electrical energy constantly.

Original contributions:

The first objective of PhD thesis was based on production of electrodes for energy storage application, called supercapacitors materials (SC). As a results, two electrodes were development with a nanowire structure, one of which in hybridized form, being functionalized with reduced graphene oxide (rGO). *The following advantages were highlighted:*

Reduced production costs, lack of use of truly hazardous substances, obtaining a nanocomposite structure that develops the potential rate of conductive properties, but especially, the use of a metallic substrate such as copper wire or zinc foil, which for production of supercapacitors is a favorable approach both in terms of improving electrical properties and as a result of the simplicity of material design. The choice of metallic substrates offers promising advantages especially for pseudocapacitors (Chapter 3 of PhD thesis).

The second objective of PhD thesis involves the fabrication of hybrid electrodes for electrochemical applications.

Electrodes decorated with titanium nanowires were developed to degrade an emerging pollutant, such as doxorubicin (DOX), but also electrodes with a mesoporous structure improve the absorbing properties of the material for detection of the same pollutant. Both electrodes were activated with rGO, their experimental study was detailed in Chapter 4 of the PhD thesis.

The PhD thesis is structured in 2 parts, 5 chapters, over 155 pages and presents a multidisciplinary orientation, because the research addresses two different directions of nanowire development on different metal supports (foils or meshes) generated through phase transitions of metal oxides.

The doctoral thesis is written in Romanian language and includes 18 tables, 98 figures, 373 bibliographical references and is structured in 5 chapters, as follows:

CHAPTER 1. THEORETICAL CONSIDERATIONS OF MATERIALS WITH CONTROLLED PROPERTIES

Chapter 1 presents: (i) a brief history of materials with controlled properties; (ii) the classification of nanomaterials (NM); (iii) methods used to grow nanowire structures, respectively the development of metal-oxide structures by integrating rGO; (iv) mechanisms of electrooxidation (EO) and photo-electrooxidation (FEO); (v) general information about the pollutant doxorubicin (DOX) - a powerful chemotherapeutic drug, which is part of the anthracycline class; (vi) a brief classification of supercapacitors (SC), the materials used for construction of electrodes and specific applications of SC.

1.1. Brief about history of development use and integration of materials with controlled properties in electrochemical processes for pollutant removal and energy storage applications

In the last decade, the synthesis and fabrication of particles with directed properties have led to the development of nanomaterials, implicitly nanotechnologies, which have been widely studied, due to the abundance of precursors used and the accessibility of consumable elements in various fields**.**

NM develop exponentially applications for wastewater treatment. Nanostructured materials with metal-oxide composition such as TiO_2, ZrO_2, Al_2O_3; but also materials such as Fe^{3+}, Ga^{3+}, La^{3+} ions, are often used as materials for the construction of electrodes for the degradation of emerging compounds. These artificially manufactured NMs can possess interesting antibacterial, optical, electronic and selectivity properties with high absorption capacity for pollutant removal [1].

Moreover, most studies have also focused on the spectacular development of high-performance nanomaterials of the supercapacitor (SC) industry, respectively, advances in the development of nanotechnology for electronic devices on metal substrates such as stainless steel [2], nickel [3], titanium [4], copper [5].

To improve the modern energy infrastructure of the 21st century, energy storage plays an important role in satisfying the global economy.

Currently, the development of the SC market materials and electrodes for energy storage is stimulated by the development of all fields, especially hybrid vehicles, smartphones and renewable energies.

1.2. Nanowire growth on Ti, Zn, Cu metal substrate

The growth behavior of nanowires is influenced by a number of factors such as: temperature, type of atmosphere, duration, chemical composition of the base material, methods of obtaining and other processes that are involved. Nanowires can offer advantages such as: surface growth, increasing reaction zones, good charge conductor, forming conductive channels, etc. and can be used in the development of sensors.

a) Titanium

It is known that the most stable form of TiO_2 is the rutile structure, Jian Shi and Xudong Wang [6] synthesized rutile nanowires using the layer deposition technique (ALD), using $TiCl_4$ and H_2O precursors, at a temperature of 650ºC. Researcher Jyh-Ming Wu [7] used the thermal evaporation method, using temperatures up to 1050ºC to grow NW. Nanowires were also obtained by the PVD technique, at a temperature of 850ºC, in a controlled atmosphere with argon flow, for 3h [8].

b) Zinc

Zhang-Wei Lu's collaborators [9] fabricated nanofilaments and nanowires using thermal oxidation in Ar atmosphere. The study was based on temperature influence and random growth of NWs, suggesting their applicability for the fabrication of laser devices and UV detectors. On the other hand, researcher Miles and his collaborators [10] demonstrated for the first time the growth of nanowires by anodization, using different types of bicarbonates. The experimental approach tells us that temperature, time and electrolyte concentration influence the growth rate of nanowires. The authors suggest that the implementation of the structures is suitable for photovoltaic, photocatalytic and sensing processes.

c) Copper

Mingji Chen [11] demonstrates that the driving force depends on the compressive stress, caused by the formation of CuO layers by increasing the temperature. A different method that induces defects in structure is epitaxial growth which is using an atmospheric pressure plasma jet in the thermal oxidation process. Technically, the method to obtain NWs is fast (5 minutes), but has quite a few disadvantages [12]. An interesting approach is the wrinkling and growth of NWs, developed in the study of Fa-chun Lai and his collaborators [13]. The study presents a time influence (0.5-10 h), using assisted thermal oxidation and describes also the mode and direction of growth.

1.3. Integration of rGO into metal-oxide structures

The hydrothermal method proved to be the easiest approach to obtain the TiO_2/rGO catalyst. Also, Yan Liu [14] developed nanocomposites based on GO and $TiCl_4$ with different ratios using a solution composed of ethanol and water as a solvent. The study demonstrated the anatase crystalline layered structure of TiO_2 and dispersed on the surface of freshly formed rGO. The final goal is given by the photocatalytic activity of the catalyst in order to degrade methyl orange.
The microwave-assisted (MW) hydrothermal method is known to be one of the most efficient methods for the formation of hybrid materials. In this case Aura S Merlano and his collaborators [15] obtained the rGO/ZnO composite. The study presented several variations in time irradiation and influences of Zn precursor concentrations.

1.4. Elimination of doxorubicin thru EO and FEO

The study by Mireia Sala et al. [16] demonstrated that the use of the photo-electrooxidation process FEO for textile effluents reduced the color by 85% and the chemical oxygen demand (COD) by 58% by generating radicals. Their research also focused on the use of both processes (EO and FEO) for degradation of the RB5 (nitrogen) and RB7 (phthalocyanine) groups. Thus, very good yields were demonstrated, of approximately 90% decolorization rate but with the risk of haloform formation if electrooxidation EO is used. Thus, photo-electrooxidation FEO was used as a system that can prevent apparition of chloroform.

1.5. Capacitors and supercapacitors

In the past, studies on conventional capacitors focused on classic ceramic materials, various types of glass and dielectric polymers[17]. However, with evolution of technologies and the need for their use in various industries, development is aimed to materials with higher capacity and specific energy like carbon-based materials that were developed in early instance followed by conductive polymers and transition metal oxides. This process was debated by researchers and has derived from chemical behavior proprieties and storage mechanisms and they reached the "hypothesis" that these electrode materials work almost like a battery [18].

CHAPTER 2. DEPOSITION TECHNIQUES, METHODS OF OBTAINING AND CHARACTERIZATION OF ELECTRODES BASED ON COPPER, ZINC AND TITANIUM

Chapter 2 is dedicated to experimental solution deposition techniques and methods for obtaining, respectively physico-chemical characterization of the obtained materials and the developed electrodes.

2.1. Overview

For the first time, the spin-coated method was used for coating paints. This technique has been widely used to deposit thin films with thicknesses in the micro and nanometer range. Currently, it ranks among the first as a functional technology, as it is widely used due to its developed properties of low cost, energy saving, short usage time and pollution reduction [19,20].

2.2. Methods for obtaining electrodes with ZnO, CuO, TiO_2 structure

To obtain the (rGO)-TiO_2 nanowire composite, Xinrui Cao and co-workers [21] used an in-situ method followed by calcination. Using a slightly adjusted hydrothermal method, the TiO_2/rGO nanowire nanocomposite was formed. The method proved to be effective in terms of charge separation, developing high photocatalytic performances [22].

In the scientific work of Chengzhen Wei and co-workers [23], mesoporous zinc oxide and nickel oxide architectures were obtained by annealing/calcination and hydrothermal methods, respectively. The sample exhibits a specific capacitance of 2498 F/g at a current density of 2.6 A/g. The electrode exhibited a loss rate of 3% over 2000 cycles, making it feasible for SC.

2.3. Electrode characterization based on Ti, Zn, Cu

a. morpho-structural methods

X-ray diffraction is considered a non-destructive and indispensable technique for the study of crystalline nanomaterials. It is a method that provides structural information about the crystallinity of all materials, including metal oxides (CuO, ZnO, TiO_2), structures (Zn-ZnO, $Cu/Cu_2O/CuO$), and formed electrodes (Zn-ZnO-rGO, Ti-TiO_2(NW)/rGO).

Scanning electron microscopy is important for the morpho-structural characterization of sample surfaces, being mandatory in the field of materials science. It illustrates the most beautiful structures, textures, and morphologies of all solid samples obtained and detailed in the experimental part (hybrid electrodes decorated with NW).

Atomic force microscopy is a method that can provide atomic-scale investigation, being a mechanical instrument that measures the topographies, the adhesion of three-dimensional structures of nanomertic materials (e.g.: simple titanium foil and the electrode with developed mesoporous structure).

The Brunauer-Emmett-Teller method is used to characterize materials such as catalysts, powders or materials with porous structure. The method was used for the mesoporous TiO_2 compound, by using a device.

b. optical methods

The UV-Vis method involves obtaining spectra in UV or Vis, formed as a result of light absorption by chemical substances. The materials (CuO, Zn-ZnO-rGO, Ti-TiO_2(NW)/rGO) will go through numerous excitation phases, thus, the processes of absorption, reflection and transmission take place depending on the interaction of light with the sample used.

In experimental studies, Raman analysis was used for structures with GO, respectively with rGO, where the ratios between the bands (I_D/I_G) are also reported.

c. electrochemical methods

Cyclic voltammetry was used to observe the behavior of materials developed for the SC storage applications industry.

Galvanostatic charge-discharge electrochemical tests were performed to observe the character of the material and calculate the storage capacity which is detailed according to each electrode (Cu-Cu_2O-CuO(NW), respectively Zn-ZnO(NW)-rGO.

Impedance spectroscopy was used to calculate the specific parameters: charge transfer (Rp), ohmic resistance (Rs) and Warburg resistance that are detailed in the chapters containing the original contributions.

CHAPTER 3. DEVELOPMENT OF ELECTRODES FOR ENERGY STORAGE APPLICATIONS

3.1. Development and characterization of copper oxide-based electrodes with nanowires for energy storage applications

This study focuses on the growth of Cu_2O/CuO nanowires by one-step thermal oxidation using a flexible copper mesh at oxidation temperatures range of 300 to 600 °C in a controlled atmosphere of mixed-flow Ar and O_2 gases.

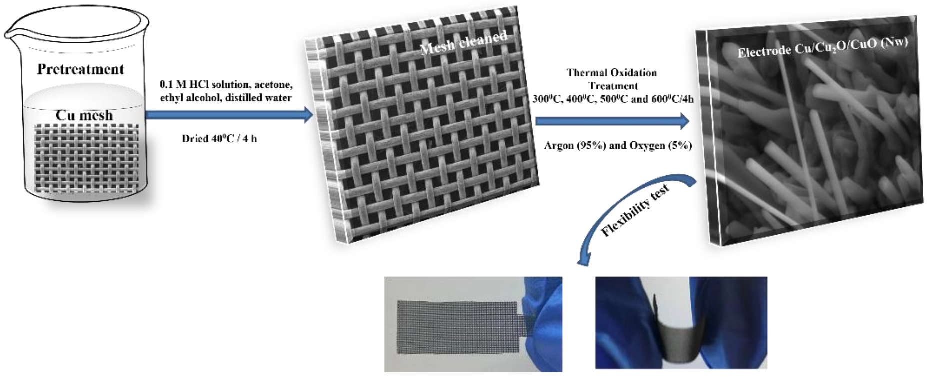

Figure 1. Schematic diagram of the synthesis protocol for development of the $Cu/Cu_2O/CuO$ (NW) electrode [24]

• We achieved the production of oxide nanowires on a metal support, using a material with a relatively low production cost, named copper mesh.

• We developed the electrodes through a very simple method, by thermal oxidation, in a single step. It is an innovative method for obtaining metal oxides on a large scale.

• We adapted this process according to the experimental data, using a temperature range between 300 and 600ºC, in a controlled atmosphere. The transitions between the metallic phases of copper and the oxide (Cu-Cu_2O-CuO) could be achieved in the presence of argon (95%) and oxygen (5%).

• The applied heat treatment influenced the crystallinity of the phases. Like this we showed the presence of two cubic crystal structures and one monoclinic, from X-ray diffraction, XRD, data, which were compared with specialized studies and implicitly with the program databases.

• We observed that the temperature of 300ºC limits the growth of crystallites, this denotes that Cu_2O with cubic structure presents a limited number of nanowires.

• Through the X-Pert HighScore software we defined the amount of Cu_2O respectively of CuO approximately, using the Profile Fitting function.

• The data obtained from the calculation of the crystallite size using the Debye-Scherrer equation, show that, for the compound Cu_2O they are much larger (23-110nm) compared to CuO (13-62 nm). This difference is due to the transient process between phases.

• We optimized the process by adjusting the temperature and time to improve the appearance of the nanowires respectively to have a control of their agglomeration.

• We demonstrated that for each temperature, our material has a different morphology. In an additional study described in subchapter 3.1. we detailed the morphology at different temperatures and times, the data that was in that study is not registered in the ISI article.

• From SEM images we calculated the average width of the nanowires for the CuO phase, where it ranged from 29nm (300ºC) to 437nm (600ºC). The oxidation method aimed to increase the density of nanowires. From scanning electron microscopy, SEM resulted in a 15x increase in the thickness of the nanowires in particular.

• Following cyclic voltammetry, we demonstrated that the electrodes are favorable to the positive domain and are stable. The non-uniform and rectangular curves highlighted the pseudo-capacitance of the $Cu/Cu_2O/CuO$ (NW) electrodes.

• From cyclic voltammetry, VC we proved that the electrode formed at the lowest temperature (300 ºC) has the highest storage capacity of 26.158 mF/cm^2, recorded for the lowest scan rate (5mV/s).

• From another electrochemical analysis CDG we calculated the specific capacity and observed that for the same electrode, it was 21.198 mF/cm^2, also recorded at the lowest current density (0.5 mA/cm^2). Which means that the storage capacity is much higher for electrodes that do not present agglomeration of nanowires.

• We also showed that the maximum achieved regarding the retention rate after 400 cycles was for the electrode obtained at 400 ºC, where it presented a percentage of 156.52%. The maximum number of cycles presented in the study was 500, this also representing the life of the electrode. The electrode obtained at 600ºC presented the lowest retention rate (96.98%).

• From the galvanostatic charge-discharge, CDG, we observed that increasing the current density induces the reduction of redox reactions in the system, so that the electrode obtained at 300º C is best suited as a material for supercapacitors.

• From the electrochemical impedance spectroscopy, EIS, we proved that the electrodes obtained between temperatures 300-600ºC have a favorable capacitive character, obtaining the best conductivity for the 300ºC $Cu/Cu_2O/CuO$ (NW) electrode.

• At the same time, we demonstrated the flexibility of the electrodes (this is an important parameter for applicability in the field of supercapacitors) and we observed that the surface area increased directly proportionally to the bending angles for the tested 300ºC $Cu/Cu_2O/CuO$ (NW) electrode.

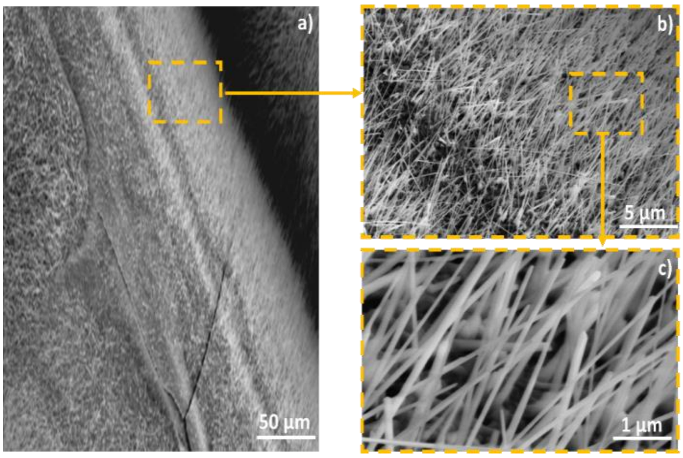

Figure 2. SEM morphologies for the $Cu/Cu_2O/CuO$(NW) electrode obtained at a temperature of 400°C a) 50µm, b) 5µm, c) 1µm

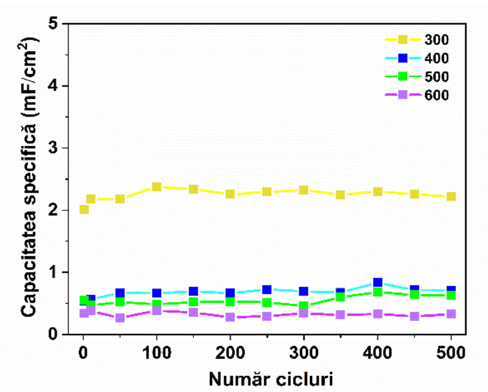

Figure 3. Specific capacitance of $Cu/Cu_2O/CuO$ (NW) electrodes over a period of 500 cycles at a current density of 8 mA/cm^2 [24]

3.2. Development and characterization of hybrid electrodes based on zinc oxide with nanowires functionalized with reduced graphene oxide for energy storage applications

In subchapter 3.2, the development of the zinc oxide nanowire electrode a process similar to the study of the Cu mesh, but activated with rGO, by the microwave hydrothermal method is presented, the structure is evolving towards a hybrid system. The technique of reducing and depositing graphene oxide by the microwave-assisted hydrothermal method (MW) on ZnO(NW) supports represents the novelty of the work, which aims to form the electrodes "in-situ".

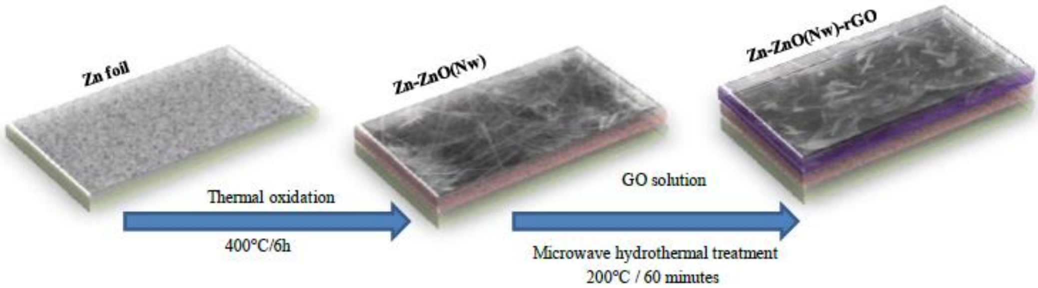

Figure 4. Schematic representation of the development of the hybrid electrode by the microwave-assisted hydrothermal method [25]

• ZnO nanowires were made using cheap supports called zinc foils/plates, which have certain properties of easy handling, flexibility and thermal conductivity.
• The development of the electrode structure was based on the same principle of thermal oxidation (400ºC) as the study mentioned above. The difference is that a longer calcination time (6h) was chosen, in the presence of Ar and O_2, to obtain the desired conformation.
• The final electrode was "functionalized" with reduced graphene oxide by the hydrothermal method in a microwave field (in-situ). We observed that this method is the most efficient in terms of depositing and reducing graphene oxide, simultaneously.
• We observed from X-ray diffraction, XRD that the Zn-ZnO(NW) nanowire support presents a hexagonal structure. We also showed that rGO was integrated into the final structure of the formed electrode.
• From the SEM images we concluded that rGO produced structural changes and at the same time the random growth of zinc nanowires took place. The average width of the Zn oxides for the support and the electrode was similar in the cross sections (1.61-1.75µm).
• From the UV-Vis spectra we demonstrated the enhancement of the spectrum for the hybrid electrode Zn-ZnO(NW)-rGO, as well as the increase of the band gap by 0.8eV, due to the presence of carbon through graphene oxide.
• Also, from Raman spectroscopy, following the I_D/I_G ratio we showed that the final electrode (in reduced form) has a value higher than 1.34x compared to the nanowire structure (functionalized with GO) which explains the defects or structural changes in the SEM analysis.
• From the voltametric tests we demonstrated that the electrode is favorable to the negative domain. The non-ideal rectangular shape confirmed that the Zn-ZnO(NW)-rGO electrode functions as a pseudo-capacitor.
• From cyclic voltammetry, VC, we showed that the highest storage capacity is 395.79 mF/cm^2 recorded at the lowest scan rate (5 mV/s).

• In contrast, from the galvanostatic charge-discharge, CDG, it resulted that the maximum specific capacity 145.59 mF/cm^2 was reached at a density of 2 mA/cm^2. Which means that the graphene in contact with the solution electrolyte played an important role.

• The life span of the Zn nanowire electrode was tested at a no. of 250 cycles, using cyclic voltammetry, VC, demonstrating a nonlinear behavior and a retention capacity of 107.36%. The maximum reached is 118.28% after 120 cycles.

• From the galvanostatic charge-discharge, CDG, we demonstrated that the retention rate after 250 cycles was 120.86%.

• From electrochemical impedance spectroscopy, EIS we can conclude that there is an electrochemically efficient interface due to the low value of the ohmic resistance Rs= 3.77Ω, but with a poor electrical conductivity of the charge transfer which presents a high value of Rp=95 Ω. At the same time, the slope at 45^0 suggests a good capacitive behavior. These characteristics are favorable for energy storage applications such as batteries or supercapacitors.

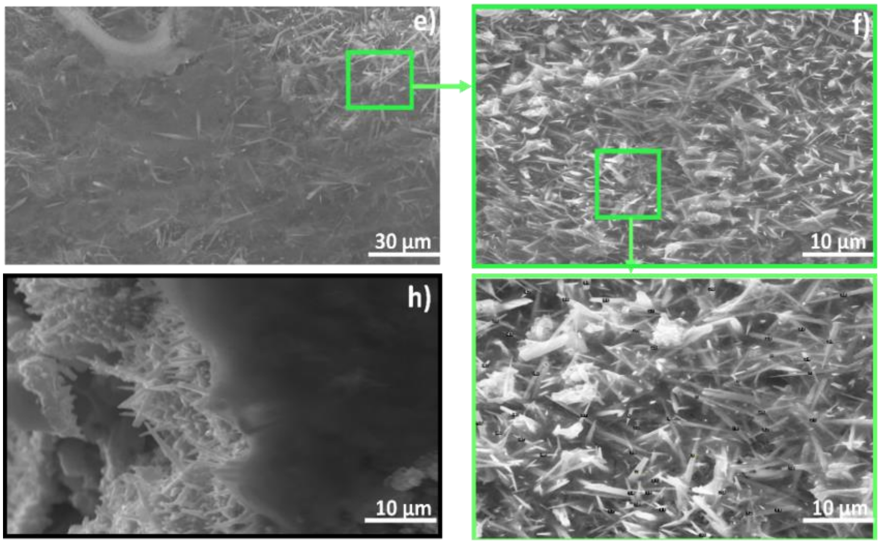

Figure 5. SEM morphologies for e) Zn-ZnO(NW)-rGO electrode at 30 µm, f) Zn-ZnO(NW)-rGO electrode at 10 µm, g) reference points for calculating the average width of Zn oxide nanowires for the electrode, h) cross-section for Zn-ZnO(NW)-rGO

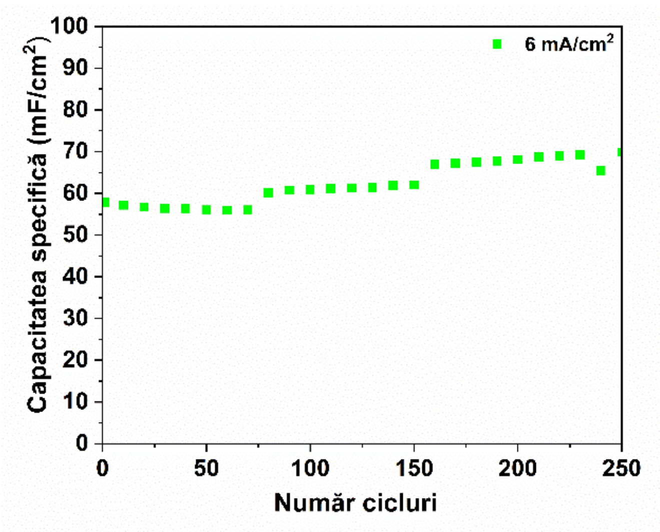

Figure 6. Specific capacitance of the electrode at a current density of 6 mA/cm^2[25]

CHAPTER 4. DEVELOPMENT OF ELECTRODES FOR POLLUTANT REMOVAL PROCESSES

4.1. Development and characterization of electrodes based on titanium oxide nanowires functionalized with reduced graphene oxide for the removal of doxorubicin through electrooxidation and photo-electrooxidation processes

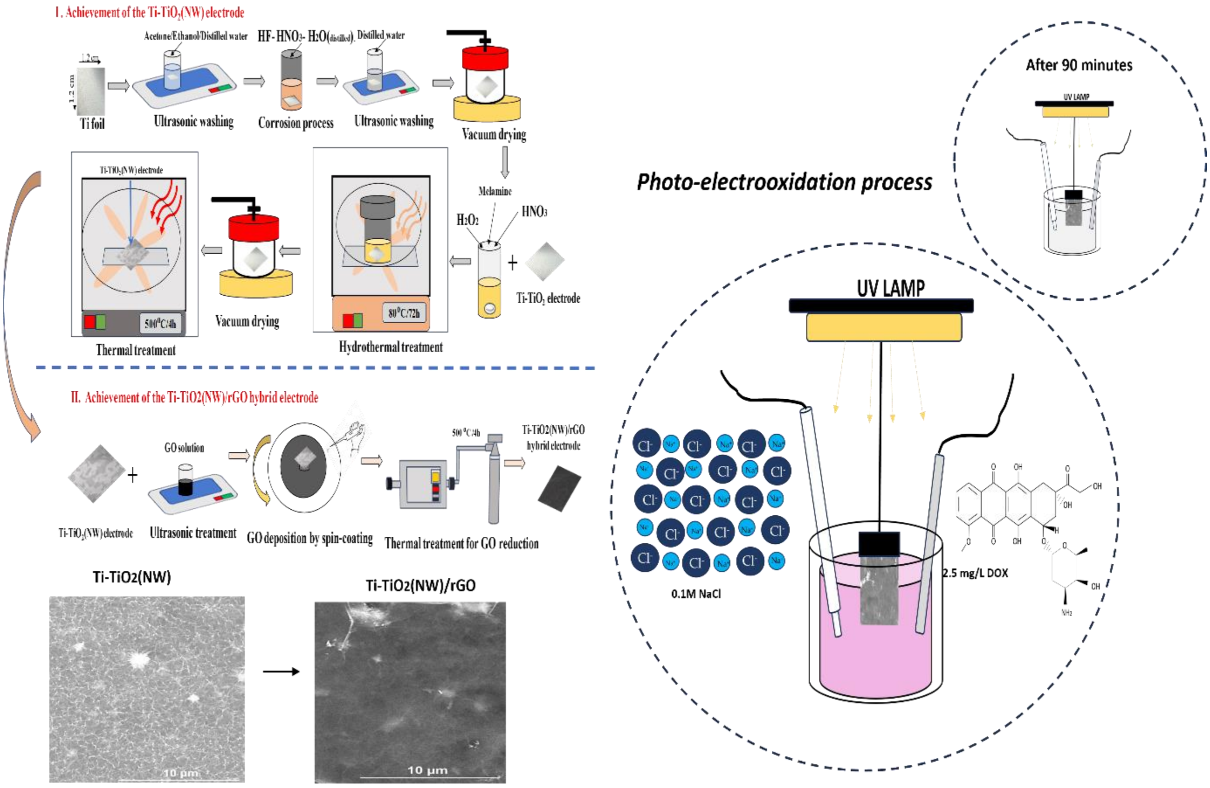

Figure 7. Development of the Ti-TiO2(NW)/rGO hybrid electrode on titanium substrate for FEO [26]

The Ti-TiO2(NW)/rGO hybrid nanowire electrode was developed through several steps: hydrothermal treatment, followed by spin-coating and thermal oxidation in a controlled nitrogen (N) atmosphere. The principle of obtaining the nanowires (NW) is based on the application of titanium foil corrosion, using a mix of acids and implicitly the use of a melamine "template".

• To make this electrode, we introduced the melamine template into the structure, in association with the hydrothermal treatment. This helps to form the nanowire structure by obtaining 3 crystalline phases: anatase, brookite, rutile. All this phases are obtained at 500ºC. A novelty is the brookite phase which, compared to another study that used a melamine template and a similar experimental protocol, only disclosed the obtaining of two phases at a higher temperature (650ºC).

• We calculated the size of the crystallites and it resulted that the rutile phase presents the largest nanocrystallites (24.2 nm). Following X-ray diffraction, XRD we showed that the reduction of rGO took place.
• During the experiments we observed that the corrosion time is an important factor. Thus, the time of 10 minutes was considered optimal in terms of this process. It is worth mentioning that the corrosion is slightly preferential, meaning that there is no absolute control on the surface of the support. We have noticed that the corrosion time influences the layer thickness. A long corrosion time implies a thick layer upon deposition.
• We performed spin-coated deposition and observed that adding a large number of layers has the disadvantage of electrode exfoliation.
• From scanning electron microscopy, SEM, we showed that the structure may have small channels caused by acid corrosion (HF and HNO_3) which helps in deposition of layers in the structure. We observed that the growth of nanowires in the form of islands was randomly performed around these cracks.
• Also, the advantage was the rGO layer that hid all the imperfections, resulting in a uniform coating over the entire electrode surface. The average nanowires in the SEM images for the simple unfunctionalized Ti-TiO_2(NW) structure was 0.0548µm.
• From Raman spectroscopy we demonstrated that the band ratio for the Ti-TiO_2(NW)/rGO electrode is similar (I_D/I_G= 1.15) to previous studies (Zn-ZnO(NW)-rGO I_D/I_G= 1.18)
• We used two electrochemical degradation methods and observed that the most efficient was electrochemical photo-oxidation, FEO.
• Following the absorption spectra we observed that the processes under UV irradiation showed a degradation efficiency of 80% in a time of 90 minutes using the lowest concentration in the calibration curve of 2.5 mg DOX /L. This concentration was chosen due to the small size of the electrode 0.5x0.8 cm in the electrolyte solution.

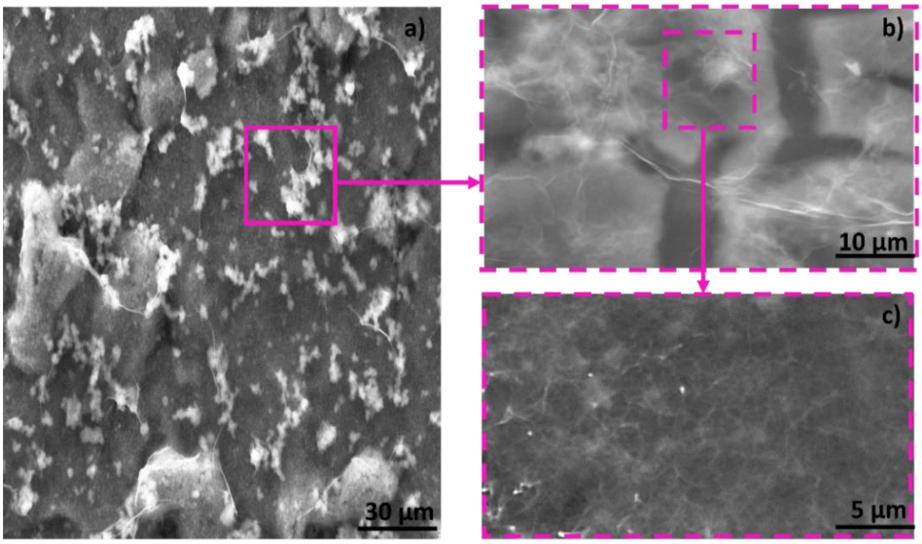

Figure 8. SEM images for the Ti-TiO_2(NW)/rGO electrode at a)30 µm, b) 10 µm, c) 5 µm

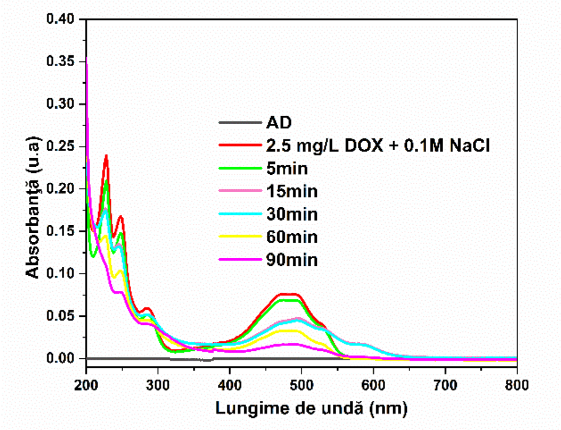

Figure 9. Absorption spectrum after FEO process of Ti-TiO_2(NW)/rGO electrode [26]

4.2. Development and characterization of electrodes based on titanium oxide with mesoporous structure functionalized by reduced graphene oxide for the detection of doxorubicin

In the current research, mesoporous TiO_2 was chosen due to its large specific surface area which can improve the stability of the composite material deposited on the Ti foil, together with rGO. The mix of mesoporous titanium dioxide and reduced graphene oxide was deposited on a titanium (Ti) foil, which was previously chemically corroded, thus determining a higher reaction and a faster electron transfer of the redox system.

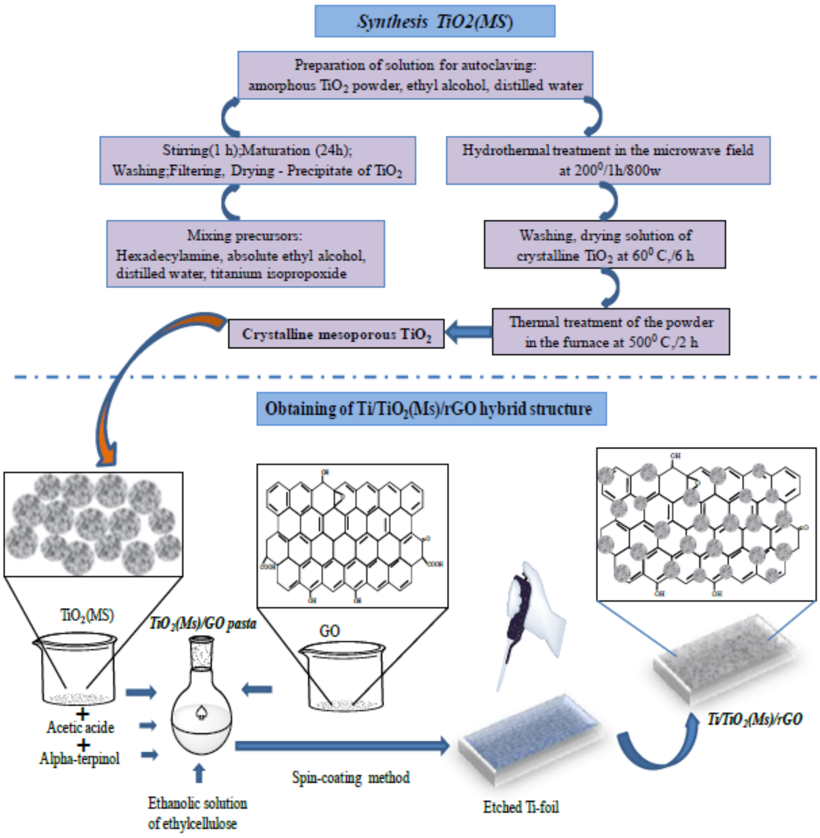

Figure 10. Development of the electrode with mesoporous structure Ti/TiO_2(Ms)/rGO[27]

• As in the previous study, the development of the Ti/TiO_2(Ms)/rGO electrode happened on titanium support (foil type) with an area of 1.1x1.5 cm.

• At the same time, to obtain the final shape of the electrode, the following steps were necessary: synthesis of amorphous TiO_2 powder, obtaining crystalline TiO_2, production of TiO_2(Ms) paste with GO and construction of the electrode by depositing 6 layers of GO, which were subsequently transformed into rGO.

• The titanium foil was subjected to the corrosion process as in the other studies, but this time using 0.5M HF, to destabilize, at the same time to increase the adhesion of the layers upon deposition and to increase the electron transfer in the redox system.

• We used a mesoporous structure with a large specific surface area of $140m^2/g$ to increase the electroactive surface. Thus, in this study a significantly larger surface area (2.3x) than the geometric surface mentioned above resulted.

• From the AFM micrographs we showed that the layer deposition was regular over the entire electrode surface. From the SEM analysis we showed the globular shape of the TiO_2(Ms) powder. Following the EDAX we confirmed the purity of the materials.

• Subsequently, we calculated the crystallite size of the mesoporous powder and they were quite large with a value of 8.43 nm.

• In this work we chose the controlled thermal treatment of obtaining rGO in an atmosphere different from N, compared to previous studies where Ar was used.

• From UV-Vis spectroscopy we showed that the band gap had a considerable decrease of 1.75 eV (compared to titanium foil that had 3.0 eV).

• Raman spectroscopy was also consistent with previous studies.

• We demonstrated that the synergistic properties of rGO improve the electrode structure through several analyses.

• The electrode with a large electroactive surface area opens new perspectives in the detection of emerging pollutants.

• From voltametric testing we demonstrated that the electrode has the ability to detect DOX in a concentration range of 1-7mg/L.

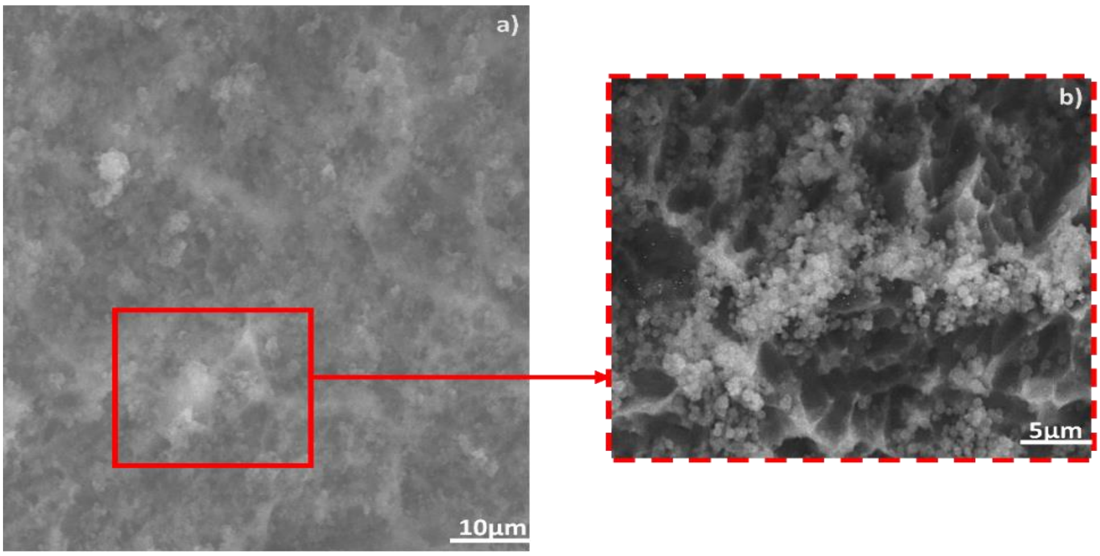

Figure 11. SEM morphologies for the corroded support at a) 10µm, b) 5µm

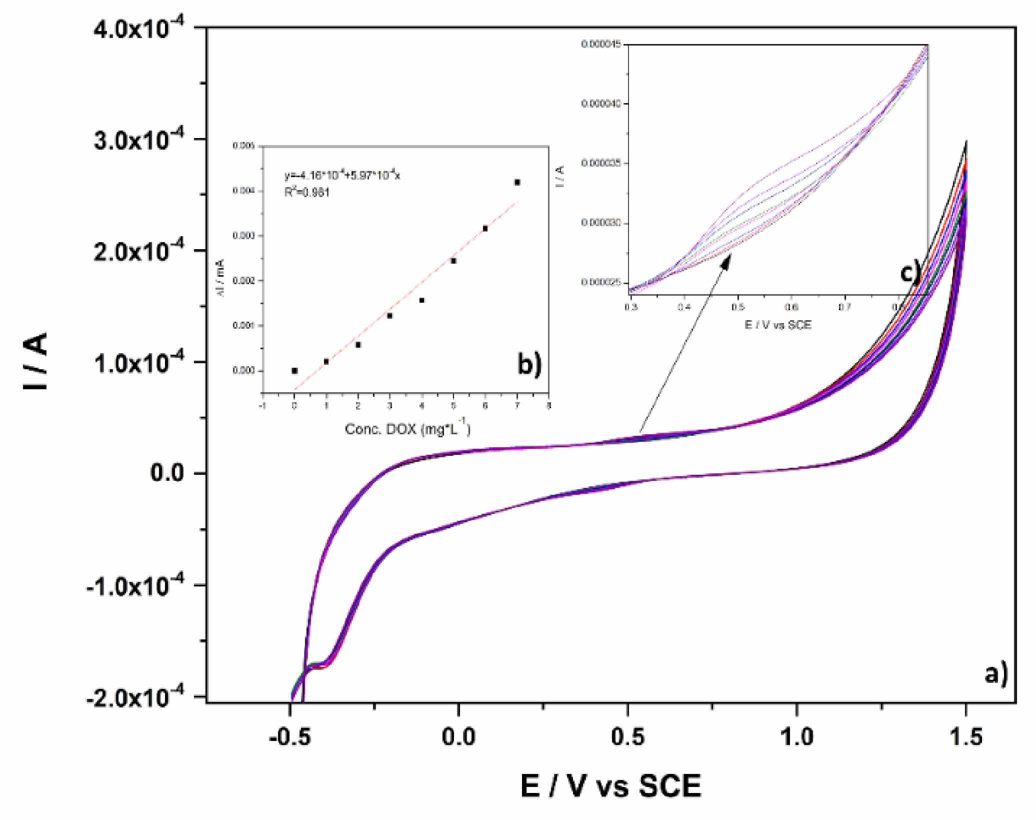

Figure 12. Cyclic voltammograms recorded a) in the presence of 1-7 mg DOX/L, at a scan rate of 50 mV/s for the three-dimensional electrode, b) the linear relationship between DOX concentrations and the anodic current peak, c) the detailing of the anodic peaks [27]

CHAPTER 5. GENERAL CONCLUSIONS, ORIGINAL CONTRIBUTIONS AND FUTURE RESEARCH TRENDS

Chapter 5 includes the final conclusions of all the experimental results obtained and carried out in the previous chapters, highlighting the original contributions made, as well as the presentation of future research trends.

Following the results of the PhD thesis, we have shown that this field is a current and interesting one due to some essential properties of producing electrodes by simple methods and at the same time with a low production cost, having a very wide range of applicability including SC materials. For example, future studies will aim to: research trends for electrodes dedicated to energy storage applications and research trends for electrodes dedicated to electrochemical pollutant removal, applications:

- Testing electrodes on zinc and copper metal supports for the detection of emerging pollutants: doxorubicin and capecitabine or pharmaceutical pollutants: paracetamol and ibuprofen. I believe that these nanowire electrodes have the potential to detect or degrade these pollutants because in the following study I developed a titanium electrode on a metal support with a NW structure and found that it had very good efficiencies in both the detection and degradation of the pollutant DOX.

- Testing other compounds for degradation, including: pharmaceutical compounds such as analgesics or hormones that represent an imminent danger to wastewater, as well as pesticides that destroy natural ecosystems.
- Using water from Timisoara wastewater stock and deploying in a large-scale facility that degrade emerging pollutants.

Selective bibliography

[1]. Al Miad, A.; Saikat, S.P.; Alam, M.K.; Sahadat Hossain, M.; Bahadur, N.M.; Ahmed, S. Metal oxide-based photocatalysts for the efficient degradation of organic pollutants for a sustainable environment: a review. *Nanoscale Advances* **2024**, *6*, 4781-4803, doi:10.1039/D4NA00517A.

[2]. Kim, D.Y.; Ghodake, G.S.; Maile, N.C.; Kadam, A.A.; Sung Lee, D.; Fulari, V.J.; Shinde, S.K. Chemical synthesis of hierarchical NiCo2S4 nanosheets like nanostructure on flexible foil for a high performance supercapacitor. *Scientific Reports* **2017**, *7*, 9764, doi:10.1038/s41598-017-10218-z.

[3]. Ahmad, R.; Shah, M.A. Hydrothermally synthesised nickel oxide nanostructures on nickel foam and nickel foil for supercapacitor application. *Ceramics International* **2023**, *49*, 6470-6478, doi:https://doi.org/10.1016/j.ceramint.2022.10.179.

[4]. Rahman, M.A.; Haque, M.A.; Shaikh, M.A.A.; Roy, C.K.; Reaz, A.H.; Shawon, M.T.A.; Baksi, P.K.; Yasmin, S.; Kabir, M.H.; Won, S.H.; et al. Titanium sulfide thin film coated titanium foil for high-performance symmetric supercapacitor. *Journal of Energy Storage* **2024**, *99*, 113205, doi:https://doi.org/10.1016/j.est.2024.113205.

[5]. Chiam, S.L.; Lim, H.N.; Hafiz, S.M.; Pandikumar, A.; Huang, N.M. Electrochemical Performance of Supercapacitor with Stacked Copper Foils Coated with Graphene Nanoplatelets. *Scientific Reports* **2018**, *8*, 3093, doi:10.1038/s41598-018-21572-x.

[6]. Shi, J.; Wang, X. Growth of Rutile Titanium Dioxide Nanowires by Pulsed Chemical Vapor Deposition. *Crystal Growth & Design* **2011**, *11*, 949-954, doi:10.1021/cg200140k.

[7]. Wu, J.-M.; Shih, H.C.; Wu, W.-T.; Tseng, Y.-K.; Chen, I.C. Thermal evaporation growth and the luminescence property of TiO2 nanowires. *Journal of Crystal Growth* **2005**, *281*, 384-390, doi:https://doi.org/10.1016/j.jcrysgro.2005.04.018.

[8]. Xiang, B.; Zhang, Y.; Wang, Z.; Luo, X.; Zhu, Y.W.; Zhang, H.; Yu, D. Field-Emission Properties of TiO2 Nanowire Arrays. *Journal of Physics D: Applied Physics* **2005**, *38*, 1152, doi:10.1088/0022-3727/38/8/009.

[9]. Wu, Z.-W.; Tyan, S.-L.; Lee, C.-R.; Mo, T.-S. Bidirectional growth of ZnO nanowires with high optical properties directly on Zn foil. *Thin Solid Films* **2017**, *621*, 102-107, doi:https://doi.org/10.1016/j.tsf.2016.11.052.

[10]. Miles, D.O.; Cameron, P.J.; Mattia, D. Hierarchical 3D ZnO nanowire structures via fast anodization of zinc. *Journal of Materials Chemistry A* **2015**, *3*, 17569-17577, doi:10.1039/C5TA03578C.

[11]. Chen, M.; Yue, Y.; Ju, Y. Growth of metal and metal oxide nanowires driven by the stress-induced migration. *Journal of Applied Physics* **2012**, *111*, 104305, doi:10.1063/1.4718436.

[12]. Dey, A.; Ghosh, P.; Chandrabose, G.; Damptey, L.A.O.; Kuganathan, N.; Sainio, S.; Nordlund, D.; Selvaraj, V.; Chroneos, A.; St J. Braithwaite, N.; et al. Ultrafast epitaxial growth of CuO nanowires using atmospheric pressure plasma with enhanced

electrocatalytic and photocatalytic activities. *Nano Select* **2022**, *3*, 627-642, doi:https://doi.org/10.1002/nano.202100191.
[13]. Lai, F.c.; Lin, S.z.; Chen, Z.g.; Hu, H.l.; Lin, L.m. Wrinkling and Growth Mechanism of CuO Nanowires in Thermal Oxidation of Copper Foil. *Chinese Journal of Chemical Physics* **2013**, *26*, 585-589, doi:10.1063/1674-0068/26/05/585-589.
[14]. Liu, Y. Hydrothermal synthesis of TiO2–RGO composites and their improved photocatalytic activity in visible light. *RSC Advances* **2014**, *4*, 36040-36045, doi:10.1039/C4RA06342B.
[15]. Merlano, A.S.; Pérez, F.R.; Cabanzo, R.; Mejía, E.; Hoyos, L.M.; Salazar, Á. Chemical and morphological analysis of formation of rGO/ZnO composite obtained by microwave-assisted hydrothermal method. *Journal of Physics: Conference Series* **2020**, *1541*, 012015, doi:10.1088/1742-6596/1541/1/012015.
[16]. Sala, M.; López-Grimau, V.; Gutiérrez-Bouzán, C. Photoassisted Electrochemical Treatment of Azo and Phtalocyanine Reactive Dyes in the Presence of Surfactants. *Materials* **2016**, *9*, doi:10.3390/ma9030211.
[17]. Sun, J.; Luo, B.; Li, H. A Review on the Conventional Capacitors, Supercapacitors, and Emerging Hybrid Ion Capacitors: Past, Present, and Future. *Advanced Energy and Sustainability Research* **2022**, *3*, 2100191, doi:https://doi.org/10.1002/aesr.202100191.
[18]. Kim, S.J.; Koh, H.-J.; Ren, C.E.; Kwon, O.; Maleski, K.; Cho, S.-Y.; Anasori, B.; Kim, C.-K.; Choi, Y.-K.; Kim, J.; et al. Metallic Ti3C2Tx MXene Gas Sensors with Ultrahigh Signal-to-Noise Ratio. *ACS Nano* **2018**, *12*, 986-993, doi:10.1021/acsnano.7b07460.
[19]. Meyerhofer, D. Characteristics of resist films produced by spinning. *Journal of Applied Physics* **1978**, *49*, 3993-3997, doi:10.1063/1.325357.
[20]. Sahu, N.; Parija, B.; Panigrahi, S. Fundamental understanding and modeling of spin coating process: A review. *Indian Journal of Physics* **2009**, *83*, 493-502, doi:10.1007/s12648-009-0009-z.
[21]. Cao, X.; Tian, G.; Chen, Y.; Zhou, J.; Zhou, W.; Tian, C.; Fu, H. Hierarchical composites of TiO2 nanowire arrays on reduced graphene oxide nanosheets with enhanced photocatalytic hydrogen evolution performance. *Journal of Materials Chemistry A* **2014**, *2*, 4366-4374, doi:10.1039/C3TA14272H.
[22]. Hu, J.; Li, H.; Wu, Q.; Zhao, Y.; Jiao, Q. Synthesis of TiO2 nanowire/reduced graphene oxide nanocomposites and their photocatalytic performances. *Chemical Engineering Journal* **2015**, *263*, 144-150, doi:https://doi.org/10.1016/j.cej.2014.11.007.
[23]. Wei, C.; Pang, H.; Cheng, C.; Zhao, J.; Li, P.; Zhang, Y. Mesoporous 3D ZnO–NiO architectures for high-performance supercapacitor electrode materials. *CrystEngComm* **2014**, *16*, 4169-4175, doi:10.1039/C3CE42567C.
[24]. Morariu, M.-I.; Nicolaescu, M.; Hulka, I.; Duţeanu, N.; Orha, C.; Lăzău, C.; Bandas, C. Fabrication of Cu_2O/CuO Nanowires by One-Step Thermal Oxidation of Flexible Copper Mesh for Supercapacitor Applications. *Batteries* **2024**, *10*, doi:10.3390/batteries10070246.
[25]. Bandas, C.; Nicolaescu, M.; Popescu, M.I.; Orha, C.; Căprărescu, S.; Lazau, C. One-Step Microwave-Assisted Hydrothermal Preparation of Zn-ZnO(Nw)-rGO Electrodes for Supercapacitor Applications. *Materials* **2023**, *16*, doi:10.3390/ma16134536.
[26]. Morariu, M.-I.; Nicolaescu, M.; Orha, C.; Lăzău, C.; Duteanu, N.; Bandas, C. Heterostructure Based of Ti-TiO_2(NW)/rGO Hybrid Materials for Electrochemical Applications. *Inorganics* **2025**, *13*, doi:10.3390/inorganics13020031.
[27]. Bandas, C.; Popescu, M.I.; Orha, C.; Nicolaescu, M.; Pop, A.; Lazau, C. Development of Hybrid Electrodes Based on a Ti/TiO_2 Mesoporous/Reduced Graphene Oxide Structure for Enhanced Electrochemical Applications. *Coatings* **2023**, *13*, doi:10.3390/coatings13081359.