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A Different Approach to Graphene-Doped MnO Supercapacitor Production: Synthesis with Different Solvents

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STRACT

Supercapacitors fill the performance gap between traditional capacitors and batteries. Due to their higher energy density than traditional capacitors and higher rapid charge/discharge and cycle life than batteries, supercapacitors offer a versatile solution for storing and transferring high-density energy obtained at variable times within seconds and integrating into energy transfer lines, unlike renewable energy sources. . In this study, graphene oxide (GO), which will be used to produce materials with supercapacitive properties, was synthesized by the Modified Hummers method. The produced graphene oxide (GO) was reinforced into metal oxide (MnO) solutions synthesized by the sol-gel method. As a result of the characterization processes of the obtained samples, the effects of graphene oxide (GO) and different solvents on the composite materials were examined by XRD, SEM, FT-IR, DTA-TG, UV-vis and cyclic voltammetry (CV) methods.

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1.Introduction

Supercapacitors fill the performance gap between traditional capacitors and batteries. They exhibit higher energy density than conventional capacitors and higher power density than batteries. The energy storage mechanisms of supercapacitors do not involve slow electron transfer reactions as in batteries and are completely electrostatic. Therefore, supercapacitors can provide long cycle life and very high-power density, but their energy density is low. Due to their higher energy density than traditional capacitors and higher rapid charge/discharge and cycle life than batteries, supercapacitors offer a versatile solution for storing and transferring high-density energy obtained at variable times within seconds and integrating into energy transfer lines, unlike renewable energy sources. [1]. Besides energy transfer lines, supercapacitors also find a place in high-tech products such as portable electrical devices, electric and hybrid vehicles, and flexible electronic devices [2, 3]. Supercapacitors, according to the way they store charge; They are divided into three basic groups: electrical double-layer capacitors, pseudo capacitors and hybrid (mixed) capacitors. Each group has a different cargo storage system, and these cargo storage systems specific to each group are; It consists of the combination of these two systems, faradaic and non-faradaic. In the Faradaic operating system, charge exchange occurs between the electrolyte and the electrode, as in oxidation-reduction reactions. In the non-faradaic system, there is no chemical mechanism as in the faradaic system, that is, there is no charge exchange between the electrolyte and the electrode. In this system, load distribution occurs physically [4]. Hybrid capacitors; They are supercapacitors produced to achieve higher performances by using the unique properties of electrical double layer capacitors and pseudo capacitors. In hybrid supercapacitors, the electrodes designated as cathode and anode consist of various combinations. In hybrid supercapacitor configuration; Electrodes whose main material is carbon are generally preferred as cathodes, and non-fardaic electrostatic charge storage occurs with the cathode. Metal oxide material is generally preferred as the anode and reduction-oxidation reactions occur through the anode. Thus, hybrid supercapacitors have the characteristics of pseudo capacitor and electrical double layer capacitor. Since both non-faradaic and faradaic systems are operational, the power and energy densities of hybrid supercapacitors are higher than electrical double layer capacitors. On the other hand, the higher stability of hybrid supercapacitors compared to pseudo capacitors allows the conversion cycle to be higher. For this reason, hybrid capacitors with higher cycle life than pseudo capacitors and higher capacitance and energy density than electrical double layer capacitors have been obtained. There are three types of hybrid capacitors: asymmetric, battery type and composite: Asymmetric hybrid supercapacitors; It is obtained by combining fardaic pseudo capacitors with non-faradaic electrical double layer (EDLC) electrode. In battery type hybrid supercapacitors, the supercapacitor electrode and battery electrode are combined. With this configuration, high power density batteries and high energy density supercapacitors can be created [54]. In composite supercapacitors; metal oxides, conductive polymers or carbon-based materials are used together. While specified carbon materials provide high surface area and capacitive double layer charge, pseudocapacitive materials enable the capacitance of the capacitor to increase due to reduction-oxidation reactions [5]. In battery and supercapacitor mechanisms, the electrode material is the basic component that determines the performance of the system. Improving the electrode surface by optimizing variables such as material components, conductivity, porosity, surface area, etc. plays an important and major role in the production and development of new generation energy storage devices with high storage capacity and high performance. Carbon and its derivatives (graphene, graphene oxide, CNT) are used in supercapacitors as the basic electrode material due to their large surface area and high electrical conductivity. Carbon-based materials store energy in the electrical double layer formed as a result of the electrostatic separation of charges at the electrode/electrolyte interface. However, the capacitance value of the electrical double layer is limited by the surface area. Supercapacitors are categorized into three groups. These; electrochemical double layer capacitors (EDLC), pseudo capacitors (pseudo) and mixed (hybrid) capacitors, and this grouping can be sorted according to the preferred electrode type and how it stores energy (Faradaic or non-Faradaic) [6]. In order to develop new generation capacitors with high power and energy density, it is necessary to improve the electrical double layer capacitance by using materials with a pseudo-capacitive energy storage mechanism that stores energy through fast and reversible redox reactions occurring on the electrode surface. Carbon-based materials create a high surface area matrix that increases the contact between the electrolyte and the active material in the composite structure, while pseudo-capacitive materials increase the specific capacitance with faradaic reactions [7]. In order for composite electrodes to become widespread and commercialized, there is a need to produce new generation composite materials with cheap methods using environmentally friendly materials. Recently discovered graphene is seen as a ray of hope in this regard [8]. Graphene has a large surface area. The surface area of 1 gram of graphene is measured to be approximately 2600 m^2. Theoretically, a supercapacitor with a value of 550 F/g can be made using 1 gram of graphene. In some studies, values of 90-130 F/g were reached. In practice, when the value of 380 F/g is reached, the current capacity of lithium-ion batteries is reached. Moreover, if metal oxide compounds are used together with graphene oxide, which is a graphene derivative, it seems possible to increase this theoretical value many times. In summary, it can be said that the current energy density of supercapacitors is close to the energy density of lithium-ion batteries, but has not yet exceeded it. Most of the studies on this subject are commercial in nature and kept confidential [9]. In this study, graphene oxide (GO), which will be used to produce materials with super capacitive properties, was synthesized by the Modified Hummers method. The produced graphene oxide (GO) was reinforced into metal oxide (MnO) solutions synthesized by the sol-gel method. A pressing process was applied to the produced composites. As a result of the characterization processes of the obtained samples, the effects of graphene oxide (GO) and different solvents on composite materials were examined.

2. Material and Method

In this study, Graphene oxide and MnO powders were prepared separately in different solvents. The modified Hummers method was used in the synthesis of graphene oxide (Figure 1.) and the Sol-Gel method (Figure 2.) was used in the preparation of MnO powders. Graphene oxide powders were dissolved in 4 different solvents used in the preparation of MnO powders and added to the MnO solutions prepared with the same solvent, 6 hours of sonication and 24 hours of magnetic stirring were applied. Then, the resulting composite mixture was dried and subjected to grinding. As the final processing step, pelletization was performed and the samples were made ready for analysis (Figure 3.).

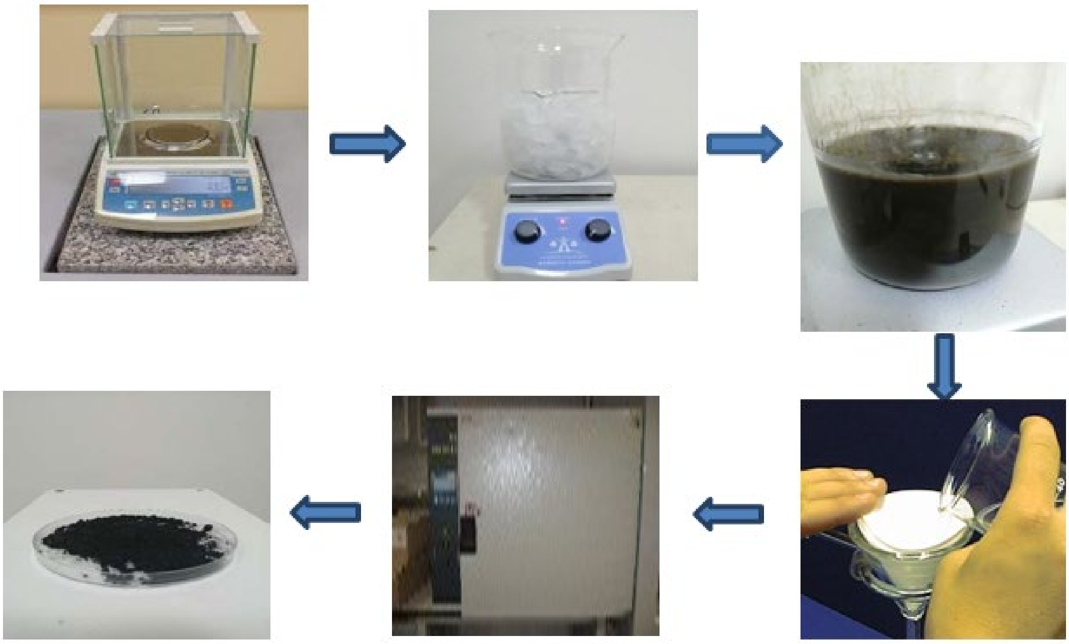


Figure 1. Graphene oxide production scheme

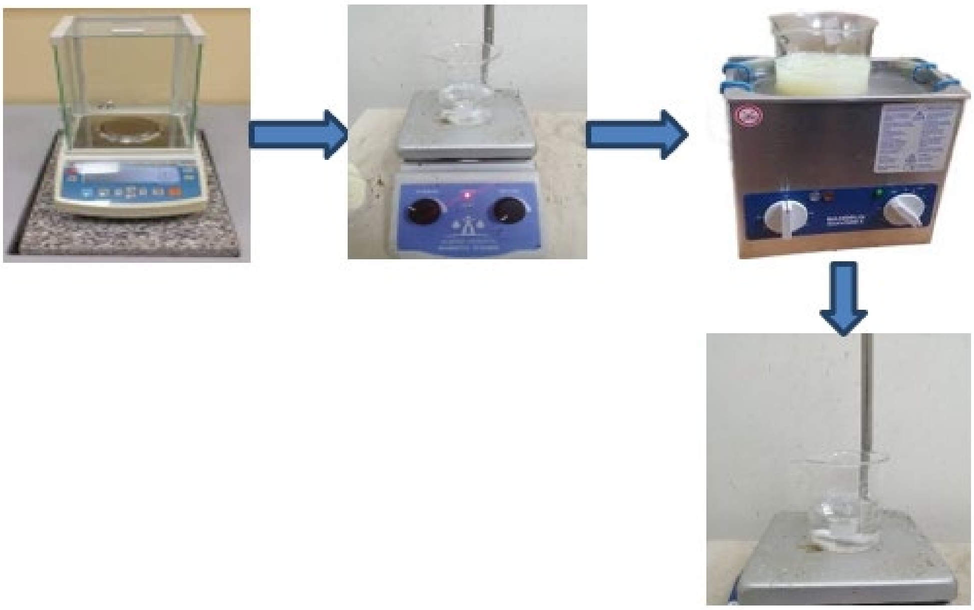


Figure 2. Scheme of metal oxide production.

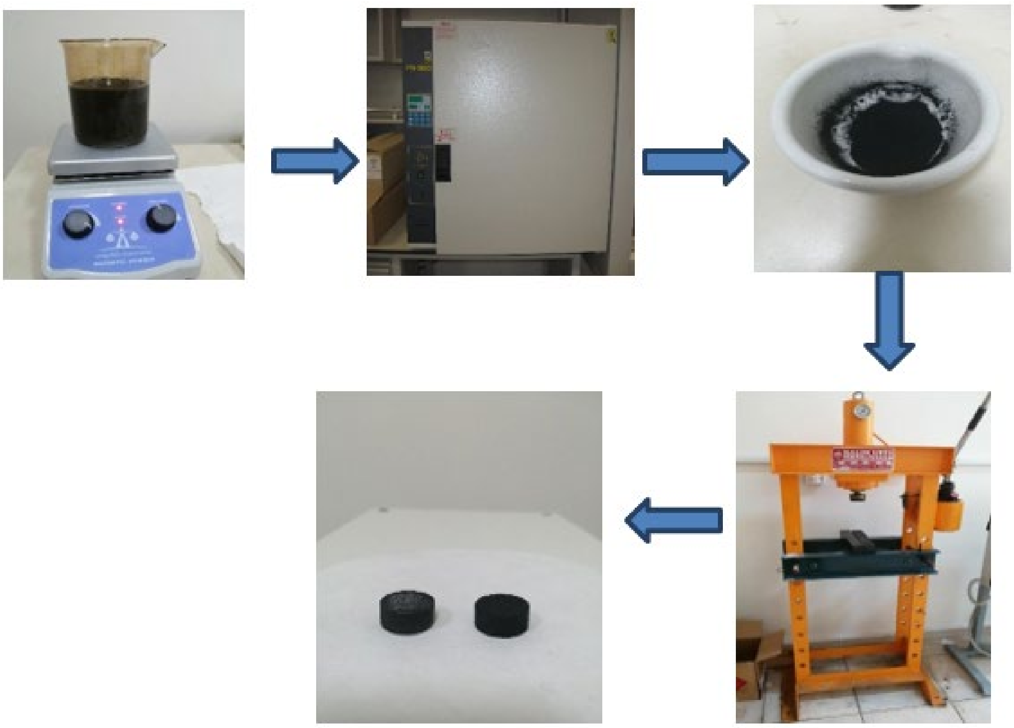
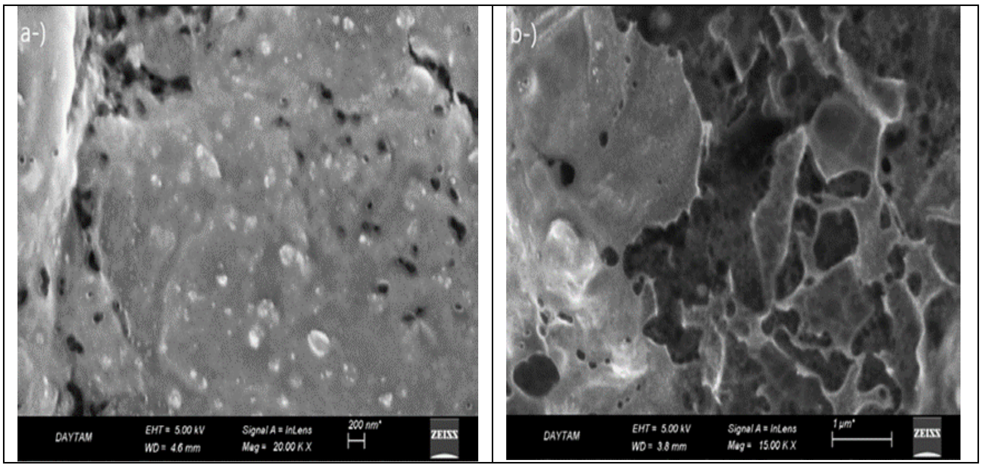


Figure 3. Composite sample production.

3. Results and Discussions

The surface structure and morphologies of the prepared films were examined with a scanning electron microscope (ZEISS SIGMA 300). Characterization of the crystal structure and properties of the samples was carried out using Cu Kα (λ=0.15406 nm) radiation at a scanning speed of 0.02° with a PANalytical Empyrean X-ray diffraction device (XRD). Reflectance R(λ) measurements of the films were taken with a Shimadzu UV-VIS-NIR 3600 model spectrometer in the wavelength range of 200-900nm. Thermo Scientific Nicolet iS5 brand FT-IR was used to determine the chemical bonding between particles in the samples. Mass changes (TG) that will occur in nano composites depending on temperature and exothermic or endothermic changes (DTA) that occur as a result of crystallization, melting and sublimation in the sample were made with the (Shimadzu DTG-60AH) brand automatic simultaneous TG/DTA Device.



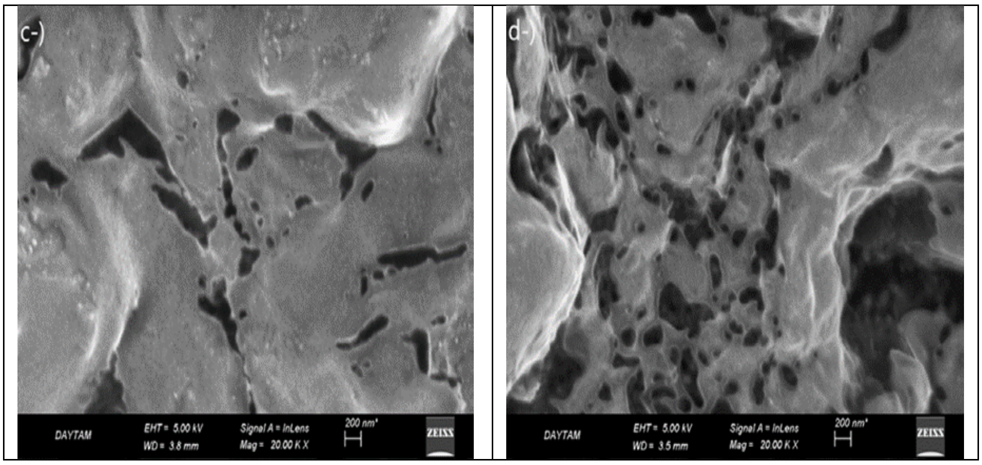


Figure 4. SEM micrographs of NiO/GO nanoelectroceramics a) Acetone, b) 2-Methoxyethanol, c) Ethyl alcohol d) Pure water

When the images are examined, it is clearly seen that the MnO and graphene oxide layers are generally separated from each other successfully, without any plate breakage, and that these layers have a monolayer structure with their transparent structure. As a result of SEM examination, it was determined that the thickness of the layers of the plates was at nano level. In addition, the agglomerated plates in the starting powder were successfully dispersed, and objectives such as deagglomeration, dispersion and grain reduction were successfully achieved.

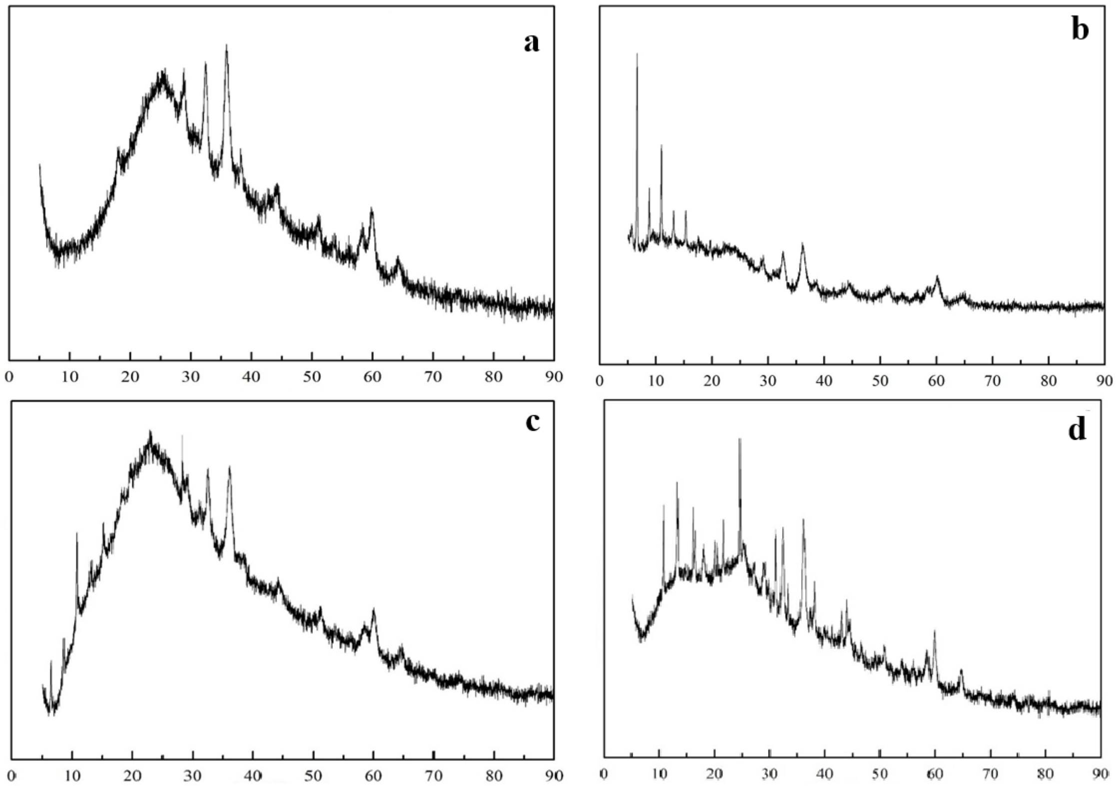


Figure 5. XRD patterns of GO-containing MnO electroceramics a) Acetone, b) 2-Methoxyethanol, c) Ethyl alcohol d)Pure water

XRD patterns of GO/MnO composite are shown in figure 5. The diffraction peaks of graphene oxide do not appear much, which clearly indicates that the content of oxygen groups in graphene oxide is significantly reduced. Various other peaks are considered MnO, which are now integrated with each other. Moreover, the strong peaks of the GO/MnO composite are consistent with the standard literature.

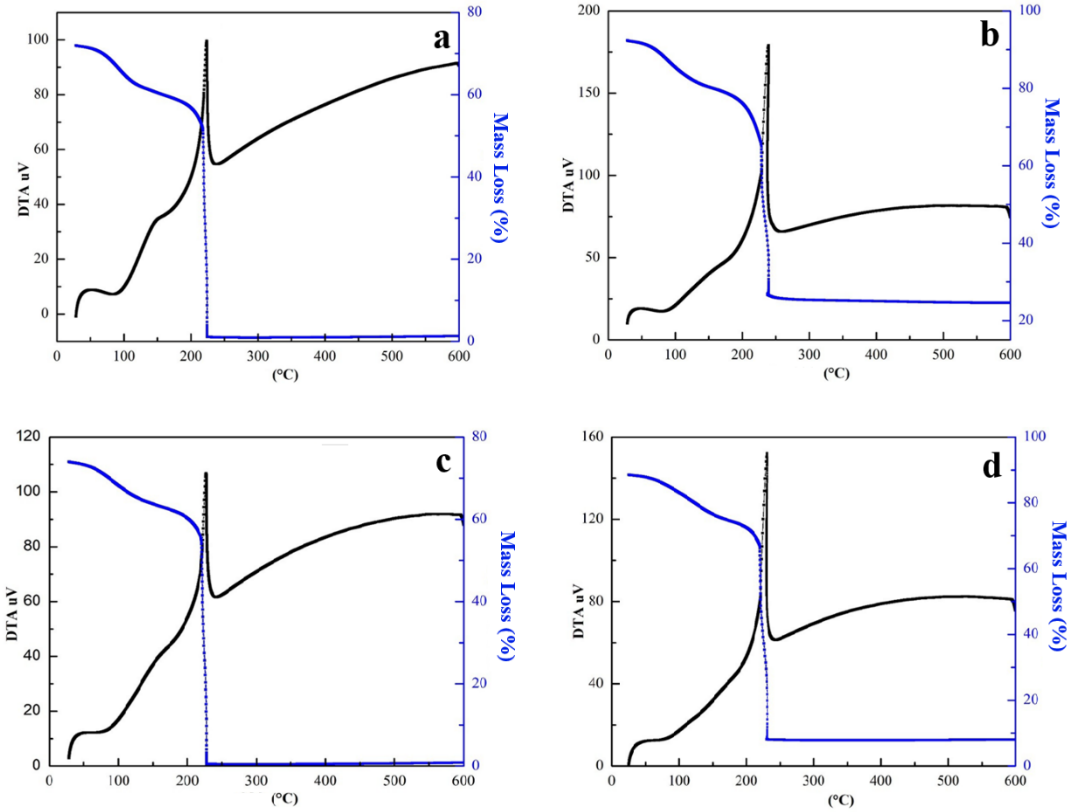


Figure 6. DTA and TGA curves of the as-produced MnO/GO samples a) Acetone, b) 2-Methoxyethanol, c) Ethyl alcohol d) Pure water

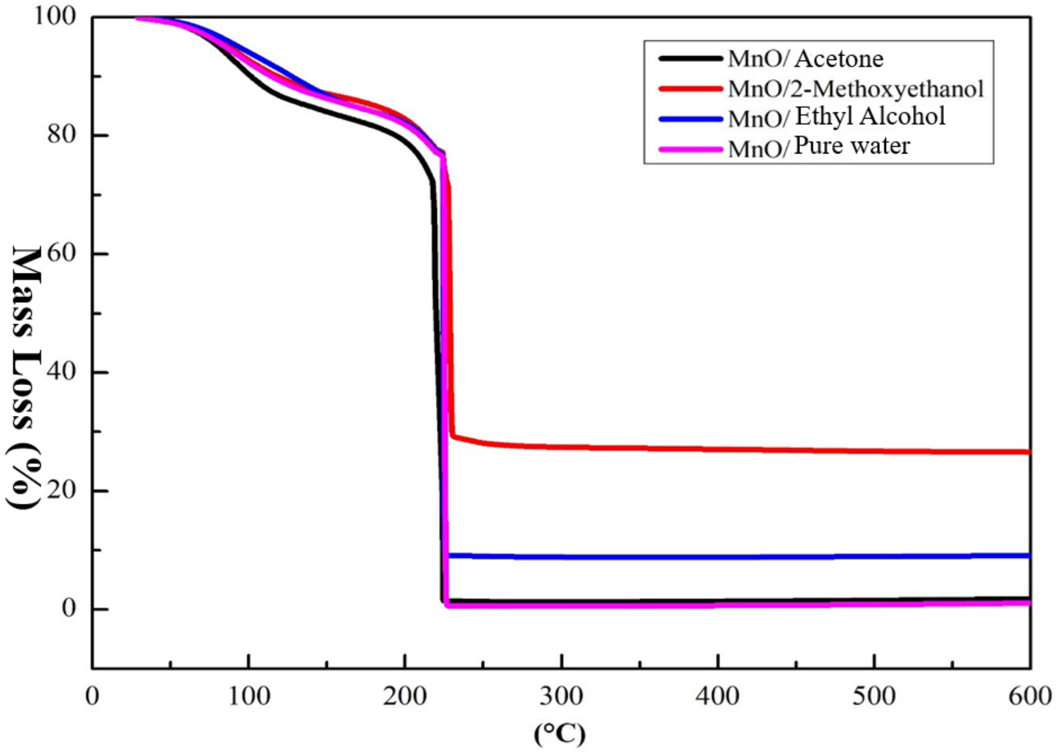


Figure 7. DTA-TG graphs of MnO/GO sample dissolved with different solvents.

Thermal stability of MnO nanoparticles by thermal gravimetric (TG) and differential thermal analysis (DTA) shows the TGA / DTA behavior of MnO/GO nanoparticles at 50 to 600 ^{o}C. The actual content of each ingredient in the samples is determined by the TGA. The first weight loss at 31-135 °C is related to the dehydration of MnO/Graphene Oxide nanoparticles. The second weight loss in the range of 135-315, 315-400 and 400-525 °C may be related to the removal of water molecule from MnO nanoparticles. However, the small weight loss in the range of 525– 590 °C observed in the TGA thermogram could be attributed to the removal of oxygen from the manganese oxide lattice due to the phase transition of Mn0. TGA analysis of MnO shows a sharp mass loss between 315-400 ^{o}C related to the evaporation of surface-adsorbed water from the materials. This is consistent with the DTA results, where the endothermic peak corresponding to the phase transition of layered tunneled MnO was observed at 145 ^{0}C. FTIR spectra reveal the chemical information and major functional groups present in GO/MnO materials. The broad band observed at 3442 cm^{-1} can be explained as the symmetric stretching vibration of hydroxyl groups in GO. The two narrow and strong absorption bands at 632 and 522 cm are assigned to the coupling mode between MnO stretching modes of tetrahedral and octahedral regions of GO/MnO composite samples. For GO/MnO composite, the band density increases and narrows. Increasing band density indicates an increase in their number. Functional groups indicating good quality of GO/MnO composite film. The absorption peaks at 1615 and 1402 cm are related to the vibration mode of C O aromatics and C O carboxy groups in GO. Additionally, the absorption bands around 1231 and 1043 cm^{-1} in the composite material were assigned to the presence of CO epoxy and CO alkoxy group. These characteristic bands confirm the formation of GO/MnO composite samples

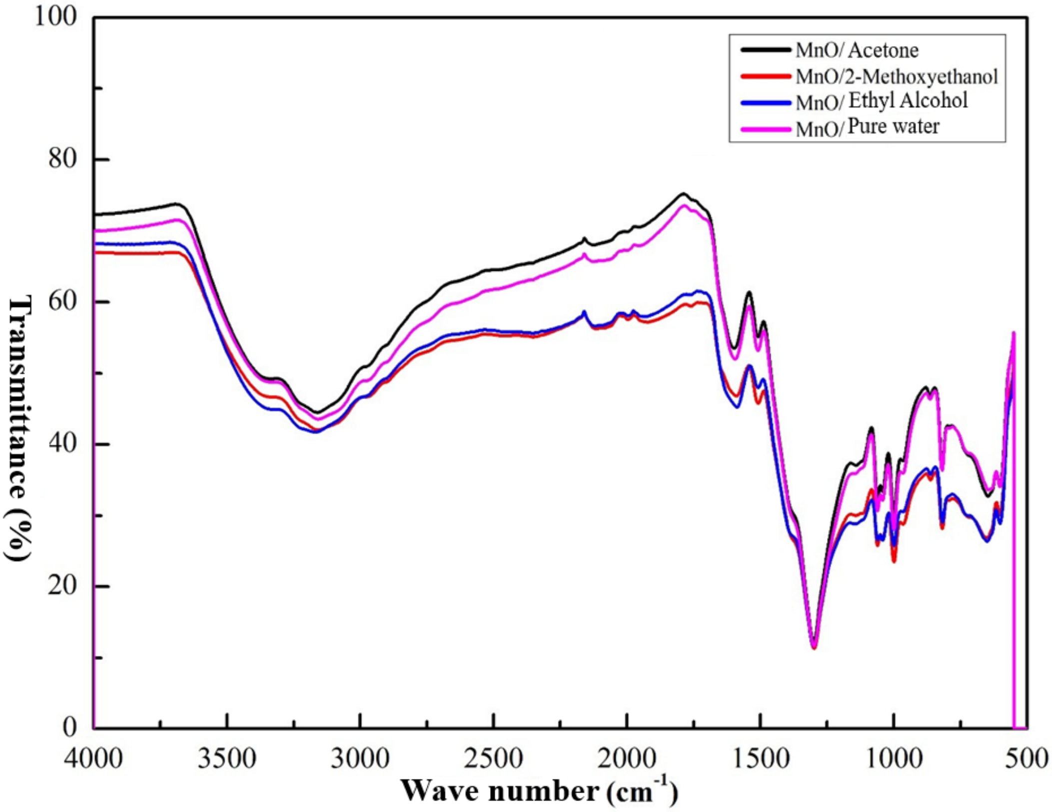


Figure 8. FTIR spectra of the as-prepared samples

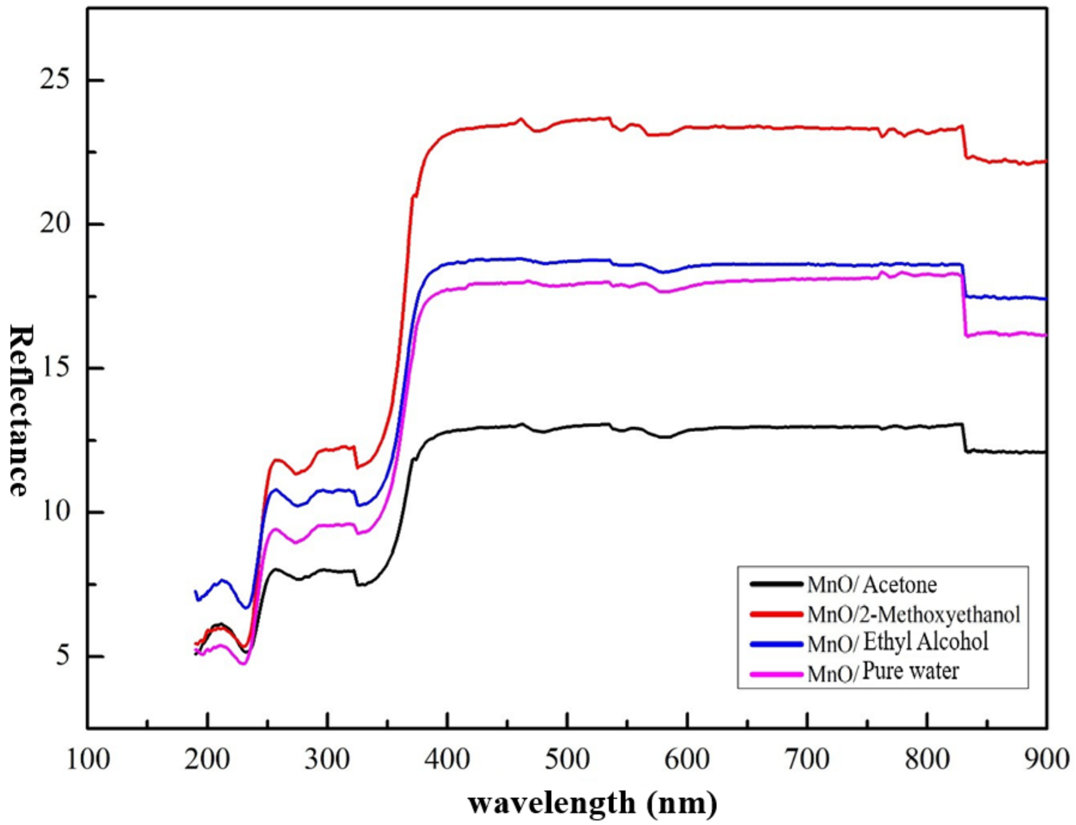


Figure 9 The diffuse reflectance as a function of the wavelength

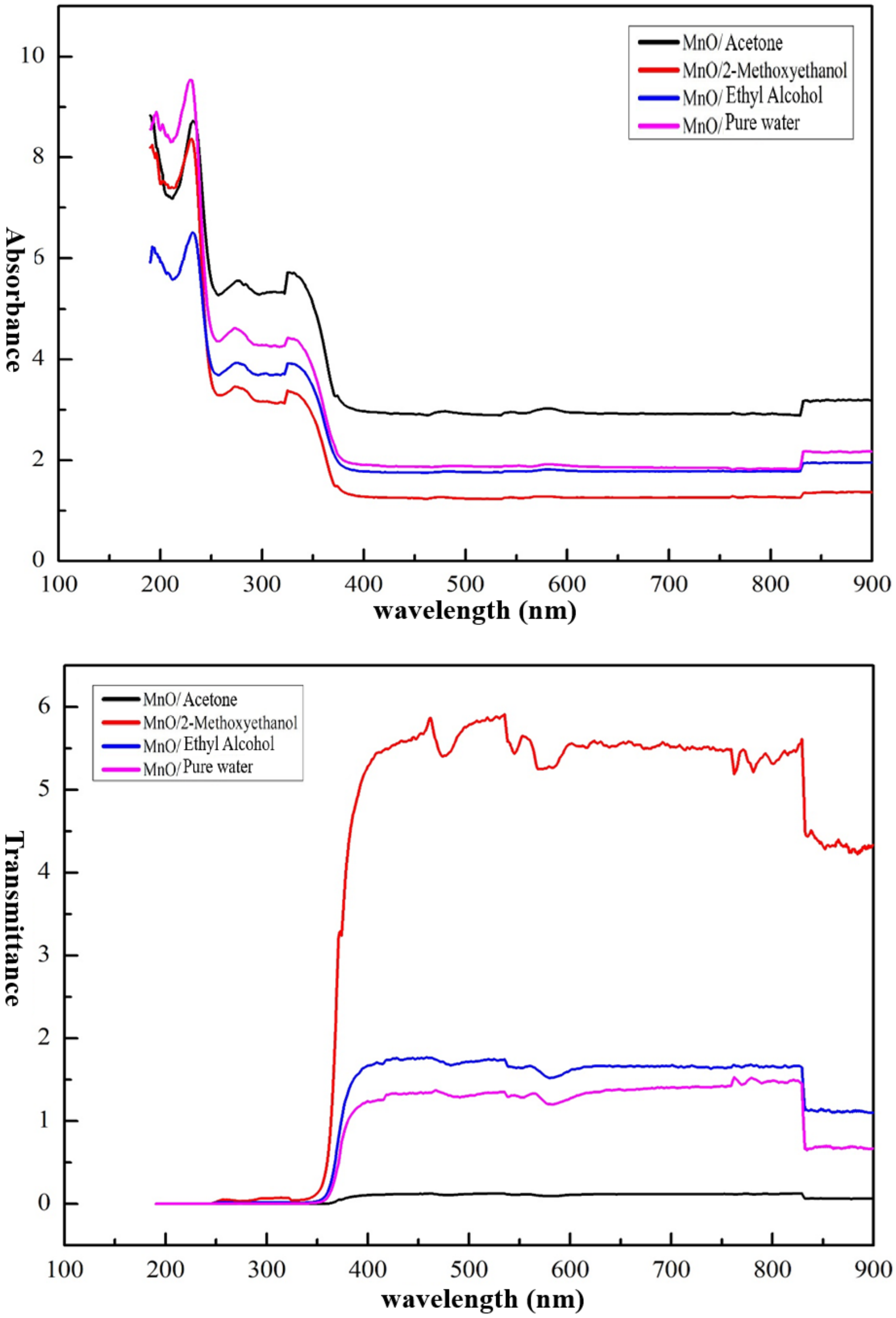


Figure 10-11. Absorbance and Transmittance spectra of the as-prepared samples

Examination of MnO/GO spectra reveals that the sample absorbs electromagnetic radiation in the UV wavelength range of 100-400 nm. The absorption maximum (λ_{max}) of MnO/GO was found to be 352 nm. The difference spectrum of the samples shows a hump in the UV region, supporting a strong interaction between GO and MnO.

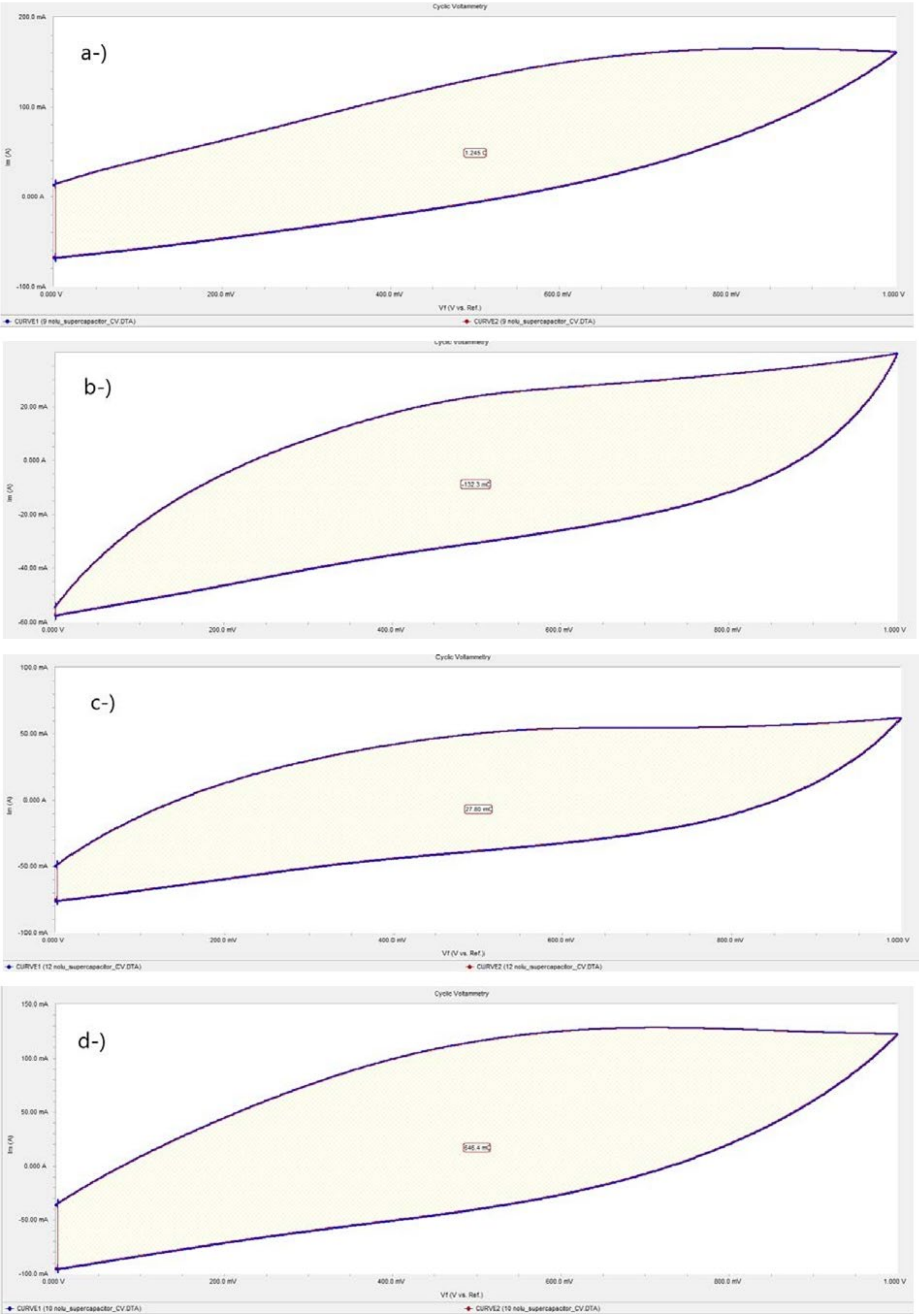


Figure 12. dissolved with different solvents CV plots of MnO/GO samples.

Electrochemical analyzes of the prototype hybrid supercapacitor were carried out in the 0-1 V potential range. CV analysis was performed at different scan speeds, from low scan speed to high scan speed. Figure 12. shows the CV curves of MnO/GO samples dissolved with different solvents. The curves show the supercapacitor with both storage mechanisms. It means storage. The highest capacitance value was detected in the sample dissolved with acetone.

Sample	Capacitance Value (F g^{-1})
MnO/Acetone/GO	19.93
MnO/2-Methoxyethanol/GO	1.50
MnO/Ethyl Alcohol/GO	0.43
MnO/pure water/GO	7.50

Conclusions

In this study, graphene oxides (GO) with supercapacitive properties were synthesized using the Modified Hummers method. The resulting graphene oxide (GO) was then reinforced with MnO solutions, synthesized using different solvents through the sol-gel method. The resulting microstructure showcases a hierarchical formation, with primary particles organized in layered configurations.These thermal analysis results harmonize with the insights gained from XRD analysis. Findings from capacitance-voltage measurements underscore the impact of solvent selection on the electrochemical performance of GO/MnO supercapacitors and highlight the superior capacitance achieved with pure water as the dissolution medium.

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