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Synthesis, Morphological and Structural Properties of Graphene Oxide Based Hybrid Supercapacitive GO/Sn Nanocomposites with Different Solvents

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ABSTRACT

The need for efficient energy storage and clean energy alternatives is one of the biggest concerns in the modern world. The need can be met through the application of energy storage devices such as supercapacitors, batteries, fuel cells and other energy storage devices. Supercapacitors are devices dedicated to energy storage.

In this study, graphene oxide/SnO composite materials were obtained by using acetone, ethyl alcohol, 2- Methoxyethanol, pure water solvents. SnO nanoparticles salts used in making composite materials were produced using the sol-gel method. Graphene oxide (GO) used to obtain the composite material was synthesized using the Hummers method. XRD, SEM, FT-IR, analyzes were applied to the obtained samples. Electrode construction was carried out for supercapacitor applications by using metal oxide and graphene oxide doped composite materials obtained by using different solvents. Electrochemical measurements of the produced electrodes were performed by cyclic voltammetry (CV) and the capacitance curves and impedance spectrometers of the electrodes were determined.

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1. INTRODUCTION

In parallel with the increase in the world population, economic development also increases.(1) With this increase, an ever-increasing energy demand occurs in direct proportion. Fossil fuels maintain their place in meeting this demand and are still the primary energy source. Greenhouse gases released as a result of the use of fossil fuels as a resource cause climate changes. To ensure energy security and a sustainable life, the share of non-fossil energy sources, such as wind, renewable solar, wave, biomass, etc., in electrical energy production is rapidly increasing(2). However, renewable resources provide energy in variable amounts and at certain intervals depending on natural conditions. Due to this disadvantage, there are problems in integrating them into energy transfer lines that require continuous energy, and energy storage systems with both high power density and high energy density are needed. Considering these problems and demands, supercapacitor energy storage systems offer solutions for variable energy needs(3).

Supercapacitors; They are energy storage materials that can store higher and larger amounts of charge than known capacitors. Other names for supercapacitors are electrochemical capacitors or ultracapacitors. Supercapacitors, which are improved versions of classical capacitors, have similar main features to classical capacitors(4). Classical capacitors consist of two conductive electrodes kept separate from each other by an insulating material. When voltage is applied to the capacitor, the opposite charge accumulates on the surface of both electrodes. An electric field is created through the charges kept separate by the insulating material, thus enabling the capacitor to store energy. Ability of capacitors to store electric charge; It is equivalent to the stored positive charge divided by the voltage(5).

Nowadays, nano supercapacitors have become quite common. Many features such as less raw material, less energy consumption, more affordable prices, and more comfortable transportation come to the fore in applications in obtaining nanosized materials(6). Mechanical properties, melting point, magnetic properties and chemical composition of materials can be easily controlled and intervened at nanometer levels. These new and high-level properties have led to an increase in the use of nanomaterials by playing an important role in space, telecommunications and all engineering applications(7).

The usage area of nanoparticles depends not only on their structural properties but also on their production methods. Many of the production methods preferred to obtain metal oxide nanoparticles are also preferred for nanomaterial production (8). The method of producing nanoparticle-sized materials is one of the most important variables in terms of the structural and magnetic properties of the materials. The most suitable method preferred for production may vary depending on the type of material to be produced (9). Effective variables such as the production method, the chemicals determined for production, equal homogeneous mixing and the ability of oxide materials to react are of great importance in terms of synthesizing nanoparticle-sized materials in the desired sizes. For the production of nanoscale size metal oxide particles; Various methods such as hydrolysis of inorganic salts, microemulsion and hydrothermal method, ultrasonic technique, using polar and non-polar solvent systems and sol-gel are known (10). The synthesis of metal oxide particles with nanoscale crystal structure is achieved at very high temperatures.

The sol-gel method, also known as the chemical solution method, is a wet-chemical technique widely used in materials science and nanomaterial production(11). This technique is also called "wet-chemical process". The sol-gel method consists of two steps: First, a Sol structure is obtained, and the second step is the conversion of Sol into Gel.

2. Material and Method

2.1. Graphene Oxide Production

The modified Hummers method, one of the chemical methods, was preferred to obtain graphene oxide from graphite powder. When graphite layers are oxidized, the layers are opened thanks to oxide derivatives, and the opened layers are separated from each other by sonication. In this way, graphene oxide layers are formed. In this study, graphite powder, sodium nitrate ($NaNO_3$) and sulfuric acid (H_2SO_4) were mixed in an ice bath. In the second stage, potassium permanganate ($KMnO_4$), a strong oxidant, was slowly added to the solution and mixed at 35 °C. In the third stage, deionized water was added to the mixture and mixing was continued. Finally, hydrogen peroxide (H_2O_2) with a concentration of 30% was added to the mixture and mixing was continued. At the end of these processes, the mixture was washed with deionized water until pH: 7 and filtered. After the filtering process, the material was dried in an oven at 50 °C for 24 hours. At the end of this period, GO was obtained in powder form(12).

2.2. Metal Oxide Production

The process of preparing the pure metal oxide solution;

a) 10 ml of solvent and 2 M metal oxide powders were placed in the test bottles, which were washed with de-ionized water and allowed to dry, and were mixed in a magnetic stirrer at 500 rpm at 60 °C for 15-20 minutes.

b) It was observed that the color of the new mixture formed after the mixing process was completed was white.

c) 0.3 ml monoEthanolamine solution, which is a stabilizer, was added to the mixture and mixed again with a magnetic stirrer at 500 rpm at 60°C for 2 hours and with an ultrasonic mixer for 1 hour.

d) After the mixing process was completed, it was observed that the color of the white mixture became transparent. These processes were carried out separately for metal oxide powder (SnO) with different solvents (Deionized water, Acetone, Ethyl alcohol, 2-Methoxyethanol) and the metal oxide solution was obtained(13).

2.3. Composite Sample Production

Graphene oxide powders obtained by the modified Hummers method were dissolved separately with deionized water, 2-methoxy ethanol, acetone and ethyl alcohol and sonicated. 1 g of graphene oxide powder was dissolved in 10 ml of different solvents, this solution obtained was;

- It was added to the metal oxide solutions obtained by the sol-gel method and mixed in a magnetic stirrer for 24 hours.
- Then, the resulting composite mixture was dried at 175 °C for 6 hours.
- The composite structure, which was dried and turned into a solid form, was subjected to the grinding process.
- The powders obtained by grinding were brought into the desired shape with the help of a press to make pellets, and as a result, GO/SnO, composite electrodes were obtained(14).

3. Results and Discussions

When the images are examined, it is clearly seen that the SnO 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(15).

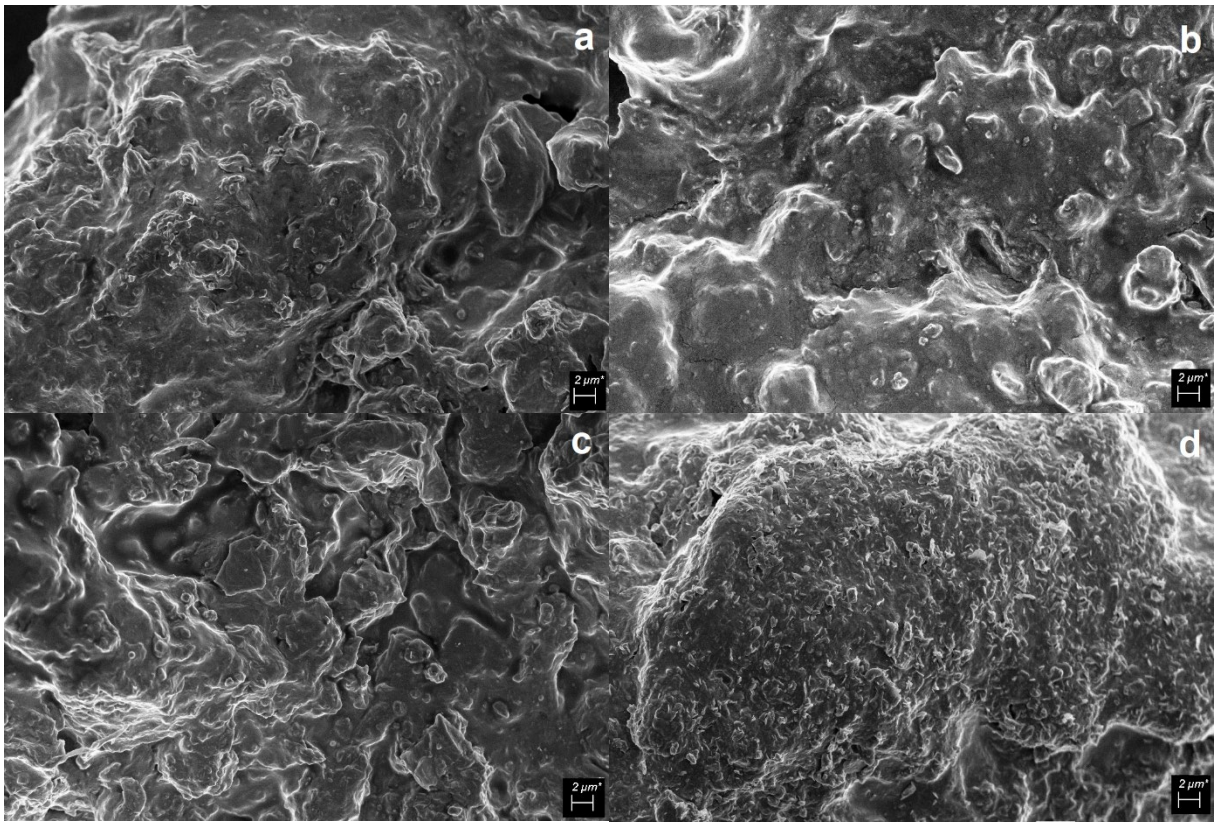

Figure 1 The SEM images of the a) Acetone, b) 2-Methoxyethanol, c) Ethylalcohol and d) Pure water Hybrid Supercapacitive GO/Sn Nanocomposites

When the X-ray diffraction patterns of the obtained composite samples are examined, peak intensities and widths reveal differences between the solvents used. Peaks with high intensities and narrow widths mean that crystallization is good, while peaks with low intensities and wide widths mean that crystallization is not good. The figures show the x-ray diffraction patterns of the samples obtained using different solvents. Various peaks with different intensities and widths are observed in the resulting diffraction pattern. All samples were obtained using solutions of the same molarity. The only difference is the solvents used. When the peaks were examined according to the x-ray diffraction pattern analysis of the samples, it was determined that there were crystal structures in the (110), (101), (200), (211) and (220) planes and peaks belonging to the tetragonal rutile SnO crystal structure were observed. When the X-ray diffraction patterns of my samples are examined using different solvents, it is seen that the change in solvents affects the peak intensity. The preferential orientation of all samples is in the (110) plane. The fact that the intensity of the SnO/GO material obtained using pure water is higher and the peak width is narrower than the others means that crystallization is good at this temperature(2).

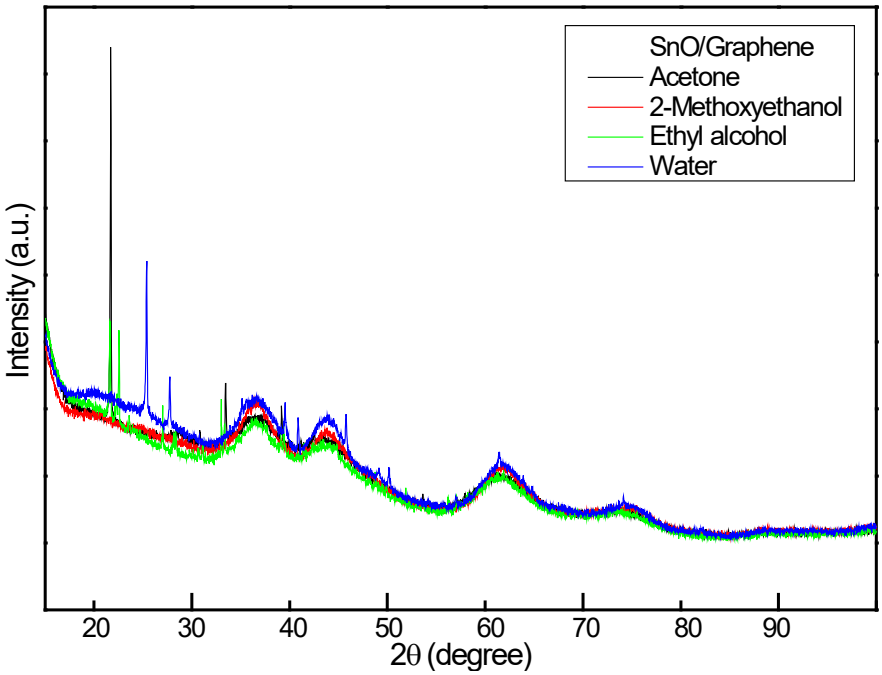

Figure 2 XRD patterns of SnO/GO nanopowders

For graphene oxide, peaks of small intensity were observed at 3438 cm-1 due to the stretching vibrations of the hydroxyl groups of the residual interlayer water. C=O in carboxyl groups (– COOH) is observed at 1742 and 1707 cm-1, respectively. Skeletal νC=C vibrations of unoxidized graphite domains are observed around 1645 cm-1. The bands at 1448 and 1050 cm correspond to OC–H deformation and C–O stretching vibrations (alkoxy groups), respectively. The peaks of graphene were detected at 1723, 1449, 1098 cm-1 for C=O, O–C–O and C–O, respectively. The absorption peak at 545 cm-1 is associated with the stretching vibrations of Sn-O. Additionally, the wide absorption band around 3303 cm-1 indicates the presence of the OH functional group resulting from the washing process(3).

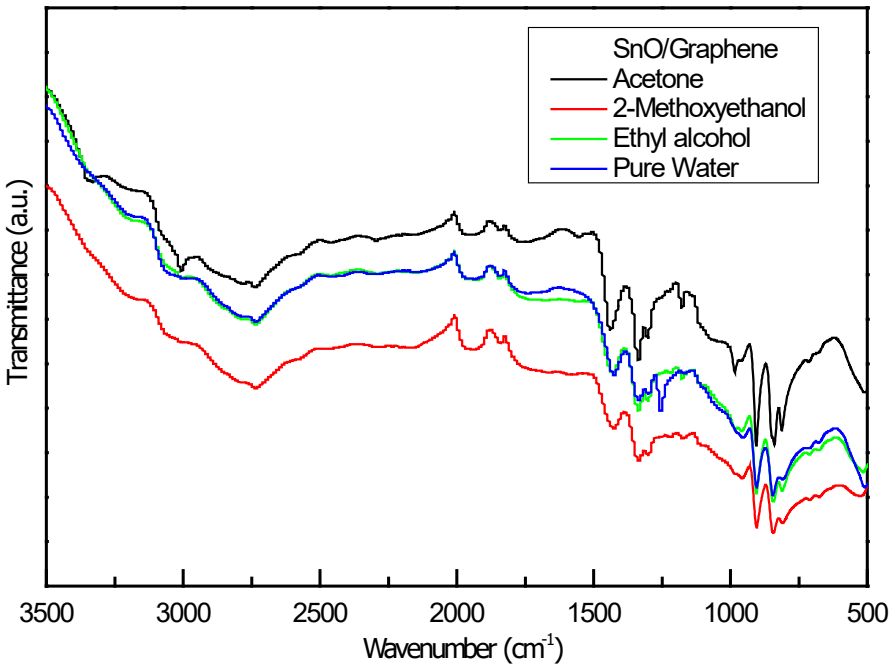

Figure 3 The transmittance spectra vs. wavenumber of the a) Acetone, b) 2-Methoxyethanol, c) Ethylalcohol and d) Pure water Hybrid Supercapacitive GO/Sn Nanocomposites

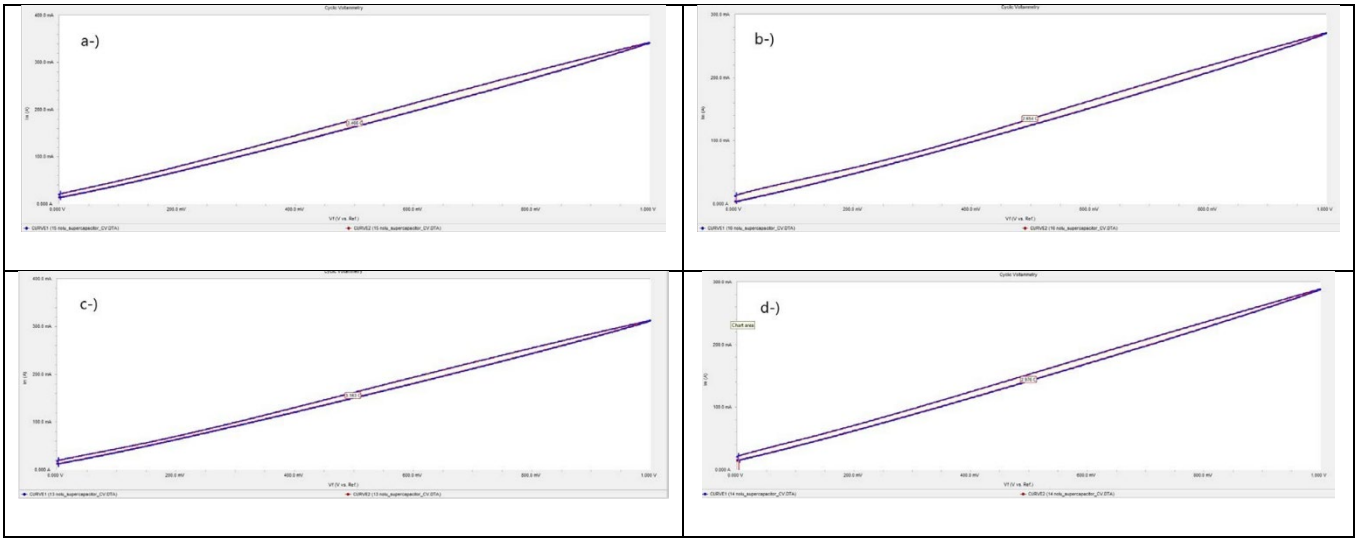

Figure 4. CV curves of SnO/GO samples dissolved with different solvents

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 4.24 shows the CV curves of SnO/GO samples dissolved with different solvents. The curves indicate that the supercapacitor stores with both storage mechanisms. The highest capacitance value was detected in the sample dissolved in ethyl alcohol.

These properties of the composite indicate that the specific capacitance increases due to the combined effect of EDLC and pseudo-capacitance of the composite. When electrochemical properties are studied in the range of potentials between -0.2 and 0.8 V, it is seen that the capacitance behavior between the electrode and electrolyte increases. Scanning speeds increase and current density increases due to the change of anodic and cathodic current towards the reversible reaction. In these CV experiments, the scanning speed As it increased, it also increased its electrochemical supercapacitor properties.

Therefore, the results obtained from CV measurements; It shows that at low scanning speeds, the charge storage and discharge phases occur quickly and reversibly, with behaviors close to parallelograms, and that the double layer formation on the electrode surface quickly reorganizes against potential changes. When the scanning speed increases, the voltammogram deviates from its quadrangular geometry as the interaction between ions and electrolyte decreases. This situation becomes evident until the scanning rate increases to 200 mV/s, but this situation is improved with graphene material. The capacity of the samples was also increased with the addition of GO

4. Discussion

In this study, SnO/GO composite samples were obtained using metal oxides obtained by the sol-gel method from the composition of different salts and GOs produced by the Hummers method. XRD, SEM, FTIR and CV analyzes of the produced samples were performed. How the crystal structure of the obtained composite samples changed depending on different solvents was determined by XRD and SEM analyses. The results obtained in this study are summarized below:

- When the SEM analysis images of the samples were examined, it was observed that they were in nano size. It is clearly seen from the images that graphene oxide structures are placed among the metal oxide powders obtained.
- When the XRD results of the samples obtained by combining graphene oxide powders with metal oxides obtained using solvents other than tin salts were examined, it was seen that they showed metal oxide and graphene oxide phases. The intensities and widths of the obtained peaks are due to differences between the solvents used.
- When the FT-IR analysis results were examined, bonds belonging to the graphene oxide structure were observed in the peaks. The solvents used, metal oxides and the presence of hydroxyl groups are also clearly seen in the spectra.
- Results obtained from CV measurements; It shows that at low scanning speeds, the charge storage and discharge phases occur quickly and reversibly, with behaviors close to parallelograms, and that the double layer formation on the electrode surface quickly reorganizes against potential changes. In this study, the role, importance and effect of different solvents were investigated. The effects of four different solvents on supercapacitor efficiency were compared and characterized along with the analyses.

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Competing interests

The authors declare that they have no competing interests.

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