





Research Article

Fabrication of MnO₂ Nanocomposite on GO Functionalized with Advanced Electrode Material for Supercapacitors

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A new strategy for supercapacitor formation was carried out in the study using electrodes made of graphene oxide (GO) and manganese dioxide (MnO₂) nanocomposites. To the present knowledge, only a few investigations have been carried out concerning the synthesis of GO-MnO₂-based nanocomposites and their electrochemical properties, with varying mass ratios, as well as the change in electrochemical properties of their components as MnO₂ and GO were tested individually for the enhanced stability and performances. A synthetic method was performed successfully to manufacture MnO₂/GO nanocomposites. The findings of the present study show that the composites have a lot of potential as an effective conduction property. A composite of graphene oxide supported manganese dioxide nanocomposites fabricated with the simple soft chemical route. As-prepared nanocomposites can be improved in performance by the interactions between GO and MnO₂.

1. Introduction

In the last few decades, the importance of nanomaterials was enormously increased due to their unique features and mechanical properties. Various approaches have been implemented to develop a vast number of nanomaterials

through the dedicated synthesis methods of top-down and bottom-up methods which are considered as the most common and commercial techniques for nanomaterial synthesis. Nanofragmentation is considered as one of the effective and most promising methods in the field of nanotechnology to generate and tune the nanomaterials into different unique

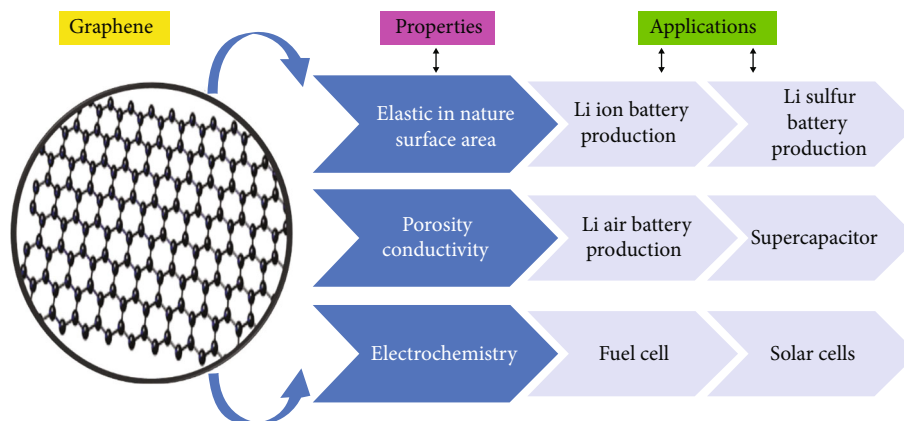


FIGURE 1: Mechanical and electrical properties and their applications of graphene.

nanostructures like nanotubes, nanofibers, and nanorods. This makes them valuable for real-world applications concerning its property which have also been discussed in Figure 1 with the various phenomena. Energy is considered to be one of the most significant needs in today's world, and it is used in various forms [1, 2]. Nonetheless, rising energy demand causes natural issues and the exhaustion of petroleum derivatives such as fossil fuels. Therefore, a serious examination of energy stockpiling and conversion has gotten a great deal of consideration as far as future innovation advancement. Due to its powerful thickness, long cycle life, and quick charging rate, supercapacitors are increasingly being used to supplement or even replace batteries in a variety of applications [2, 3]. The M_{30} electrode has the largest specific capacitance; they can be credited in the form of joined concepts to make MnO_2 as a redox potential of pseudocapacitance and reduced graphene oxide (rGO) as an electrical twofold layer capacitance. The M_{30} electrode's further developed performance could also be attributed to its high graphene carbon content, which helps in diminishing the cationic way into the terminal network that is electrode matrix and bringing down move obstruction which is transfer resistance.

There is a large demand for both conventional and non-conventional energy resources as there is a sudden rise in population and also an increase in living standards. There is a need for nonconventional renewable energy sources due to the increase in greenhouse gas and the depletion of fossil fuels. Therefore, electrochemical energy systems are found to be the alternative for this problem [4]. Recently, electrochemical capacitors like supercapacitors have been introduced over conventional energy stockpiling because of their powerful thickness and energy density when compared to the conventional and recent batteries in Figure 2. They have been used in dc motor drives, robots, electric vehicles, and even UPS (uninterruptable power supply) systems. Due to the charge capacitance, the storage of supercapacitors is subdivided into three different types such as electrical double-layer capacitors (EDLCs), pseudocapacitors, and hybrid or mixed electrodes; recent advancements in the supercapacitance are discussed in Figure 3. The best supercapacitors are the ones that should possess maximum energy

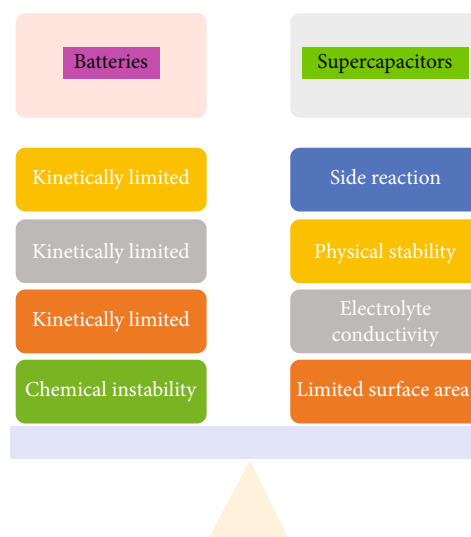


FIGURE 2: Comparison of batteries' and supercapacitors' performances.

storage capacitance. The supercapacitor capacitance value is decided by two storage principles, which both grant indivisibly to the total capacitance [5].

As an alternative to ruthenium oxide (RuO_2) (which is widely used in metal oxide supercapacitors), manganese oxide (MnO_2) offers the advantage in terms of high hypothetical capacitance, cost proficiency, and less toxicity as well as environmental safety [6, 7]. MnO_2 has been used for lithium batteries, sensors, catalysts, and alkaline Zn/MnO_2 cell applications; under ambient settings, MnO_2 is perhaps considered as the most steady manganese oxides, with remarkably strong physical and excellent compound properties. These mixtures' high polymorphism and underlying adaptability have given them a wide scope of uses, including catalysis, biosensors, and energy stockpiling. MnO_2 electrodes have set up themselves as a conceivably ideal terminal material for replacing RuO_2 in supercapacitors because of their high explicit capacitance, natural similarity, and cost viability [8–11].

The main concerns regarding for advancement of active materials in supercapacitor development were underlying

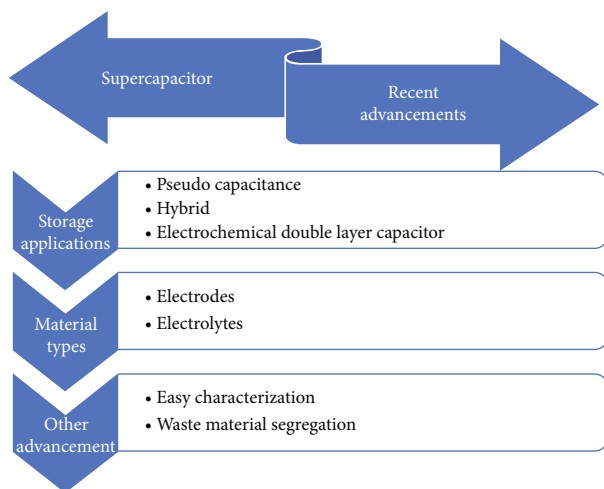


FIGURE 3: Recent advancements in supercapacitor.

adaptability and dependability, quick cation dissemination under high charge-release rates, high reversible capacitance, and natural friendliness. In general, manganese is a change metal component that can exist in different types of stable oxides, viz, MnO , Mn_3O_4 , Mn_2O_3 , and MnO_2 , and crystallizes in different types of crystal structures [12, 13]. Usually, MnO_2 is amorphous. Deposition of Fe does not change the amorphous nature of MnO_2 but changes its surface morphology that results in increased porosity, increasing the pseudocapacitive performance of MnO_2 [1, 14, 15]. Both active and inert electrodes may be used in high surface area, conductive materials for capacitive supercapacitors that utilize infinitesimal charge partition, or quick, reversible redox responses in the active materials for pseudocapacitance [16, 17].

Graphene is a 2D (dimensional) single-layer hexagonal lattice closely packed by sp^2 carbon molecules with a carbon-based nanostructure, namely, carbon-carbon distances of 0.142 nm between the atoms. Over the most recent days, the emergence of graphene-mediated materials is used for the fabrications of graphene-based composites which are made a lot of consideration in the field of science and technology because of their novel properties like high mechanical strength, great thermal and electrical conductivity, innate adaptability, and good optical and electrochemical features. It is the first crystal that is steady at normal temperature conditions, especially at room temperature [17–20].

Since its experimental discovery in 2004 [18], graphene has been utilized in a variety of applications. In light of its uniqueness, it has piqued the interest and imagination of scholars. It has high surface region, great conductivity, and other unique qualities the ease with which it may be functionalized, the mechanical qualities that it has, and as a result, graphene nanosheets have gained a lot of attention. There is a lot of excitement about the possible applications in a variety of technology fields, nanoelectronics, batteries, and supercapacitors, to name a few sensors and field-effect transistors [21–23].

Graphene has high conductivity and surface area that can be considered as an ideal choice for use in supercapacitors because of its capacitance values in the selected mate-

rials which are directly proportional to its surface area. As surface area increases, its energy storage value also increases. The capacitance value of graphene materials varies and depends on how they have been stacked. If the surface area of the graphene sheet increases, it can easily be accessible to electrolytes and contributes to the capacitance. So improper stacking of graphene also leads to less capacitance. Hence, avoiding the inner or outer sheet restacking can help graphene in increasing the performance of energy storage. Thus, graphene-based nanomaterials provide an ideal platform to develop various potential materials in the branches of electronics, energy storage devices, and biosensors. The electrons are generally delocalized on either side of the single graphene sheet layer sheet which acts as a barrier and prevents the sheet from restacking; at the same time, these electrons can be useful for identifying other surfaces to bind. Oxidation and shedding of graphite lead to the development of hydrophilic graphite oxide known as graphene oxide. The single-layer oxide of graphene possesses several oxygen species in its structure and aids in various chemical modifications. Hence, numerous graphene-based functional nanomaterials can be generated according to their chemical modifications.

Graphene oxide possesses good mechanical stability and can act as appropriate support for stacking manganese oxide in electroactive materials for supercapacitor applications [24]. The single-layered graphene oxide gives a high surface region for the deposition of MnO_2 nanosheets without any restocking and helps in adhesion to other nanostructures. With the high surface region and high stacking effectiveness of the MnO_2 -GO composite, the particular capacitance value increases [25].

The present study focuses on the development of a MnO_2 -GO-based supercapacitor that should attain good electric conductivity. MnO_2 and MnO_2 -GO composite can be synthesized by a simple and economical electrodeposition method.

2. Materials and Methodology

2.1. Synthesis of MnO_2 -GO Nanocomposites. Advanced Hummers and Offeman's method was used to synthesize GO. Approximately 10 milligrams of graphene oxide with MnO_2 was added and processed using an ultrasonicator after dispersion, after which the reaction mixture was boiled under the microwave; then, the reaction mixture was mixed into the solution of 10 ml of FeCl_3 and 1 M H_2SO_4 ; this solution was added for about 2 hours using the syringe. The sample mixture was then emptied into 20 ml of double-distilled water added after stirring. Centrifugation was used to obtain MnO_2 /GO nanocomposites, which were then washed several times with water. The overall process has been schematically represented in Figure 4 [26–28].

2.2. Fabrication of MnO_2 -GO Supercapacitor (SC). MnO_2 -GO nanostructures were deposited on current collector substrates by the electrodeposition method by constant potential mode. The stainless steel (SS) substrate was cut and polished into 1×1 cm and then washed by ultrasonication for 15 min in deionized water. Electrodeposition was carried

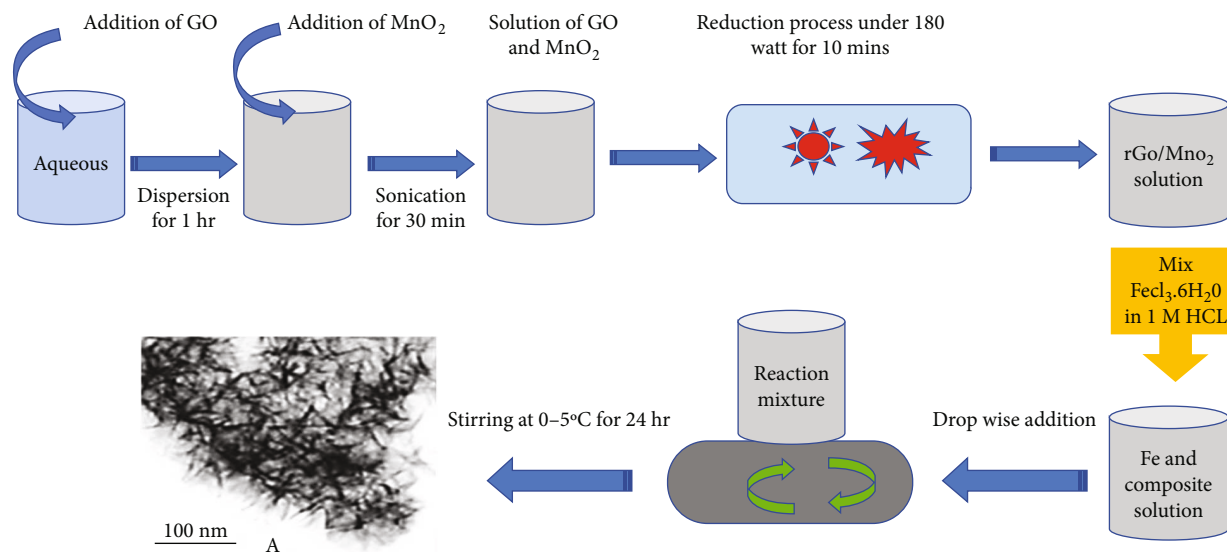


FIGURE 4: Schematic overview of nanocomposite formation under controlled conditions.

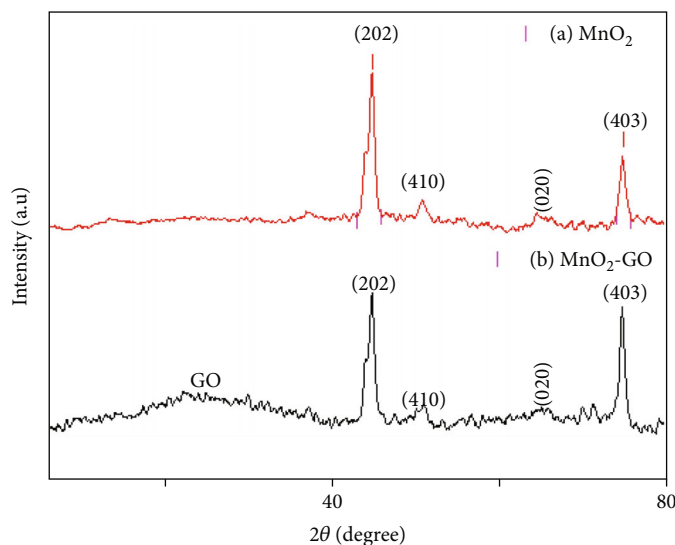


FIGURE 5: (a) MnO_2 and (b) MnO_2 -GO substrate.

potentiostatically at 0.8 V for 30 min using the as-prepared SS substrate considering it as the testing electrode. Platinum and silver/silver chloride terminals were utilized as counter electrodes (reference). The electrolyte was prepared by 20 mg of GO mixed with 25 ml deionized water and dispersed by ultrasonication; then, 0.1 M of MnSO_4 arrangement was added. The pH of the arrangement was made to 10 by adding 1 M NaOH. The resulting films were rinsed in deionized water and dried at room temperature [14, 27, 29].

2.3. Substrate Characterization. The construction of fabricated nanocomposite thin films was portrayed by powder XRD (Skillet logical XPert Pro MRD diffractometer, Amsterdam, Netherland), worked at 40 kV and 30 mA, and furnished with Cu radiation at a wavelength of 0.15406 nm. The functional groups of electrodeposited MnO_2 -GO nanocomposites were analyzed by FTIR-ATR. The local type of

functional groups in the nanocomposite was recorded in the scope of $3000\text{-}500\text{ cm}^{-1}$ (Fourier transform infrared spectrometer, Shimadzu, Japan).

2.4. Transmission Electron Microscopic Analysis. Transmission electron microscopy was utilized to inspect the morphologies of as-obtained products to determine their shape, size, and dimensions (TEM). All experiments were conducted utilizing a three-anode framework comprising of a functioning electrode made of exposed or modified glassy carbon (GCE, 3 mm in width), a reference electrode made of saturated calomel (SCE), and an assistant electrode made of platinum wire.

3. Result and Discussion

3.1. XRD Analysis. Figure 5 shows the XRD pattern for the MnO_2 and MnO_2 -GO deposited films, Figure 5(a)

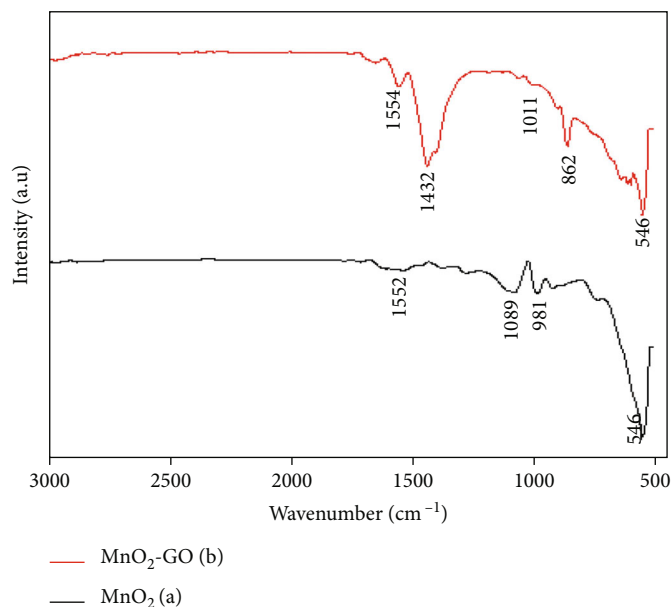


FIGURE 6: (a) MnO_2 and (b) $\text{MnO}_2\text{-GO}$.

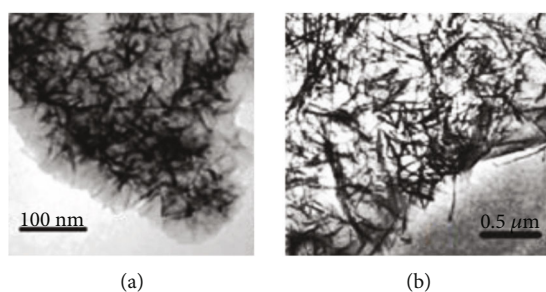


FIGURE 7: TEM micrograph of nanocomposite morphology: (a) 100 nm magnification of nanostructure; (b) 500 nm-based magnification of nanostructure.

represents MnO_2 , and Figure 5(b) represents $\text{MnO}_2\text{-GO}$ substrate. All the diffraction peaks for the MnO_2 thin film have good agreement with the reference JCPDS (no. 65-1298), further indexed to orthorhombic MnO_2 (orthorhombic crystal structure). The sharp peak tends to the small grain size found as 12 nm by Scherer's formula. The diffraction pattern of $\text{MnO}_2\text{-GO}$ composite also exhibits the same as MnO_2 except for the peak around 26° which is due to the presence of GO. It affirms the presence of MnO_2 and GO in the composite. The top at 26° weak and broad peak is referred from the research article of [24]. The average XRD patterns and Raman spectra of chemically synthesized GO- MnO_2 nanocomposites were investigated when the MnO_2/GO feeding ratio was varied. As indicated by the report of the most concentrated GO peak around the 2θ $10, 2^\circ$, the (001) reflection is comparative, and because of the introduction of oxygen-containing functional groups on the graphite sheets, the interlayer dividing (0.87 nm) was a lot bigger than the interlayer of pristine graphite (0.34 nm).

3.2. FTIR Analysis. FTIR analysis was carried out for SS modified MnO_2 and $\text{MnO}_2\text{-GO}$ thin films; as shown in Figure 6, the results show several transmittance peaks for

MnO_2 thin films; it represents Figure 6(a) MnO_2 and Figure 6(b) $\text{MnO}_2\text{-GO}$. The strong peak at 546 cm^{-1} is given to the Mn-O stretching vibration of MnO_2 , and the peaks at 981, 1089, and 1552 are due to the vibration of O-O and OH bending vibrations. For $\text{MnO}_2\text{-GO}$ film, the peak at 546 cm^{-1} for MnO_2 and the peaks around 1554 cm^{-1} , 1432 cm^{-1} are also found which are attributed to the C=C vibrations and O-H vibration of graphene oxide. It clearly shows the presence of MnO_2 and GO in the $\text{MnO}_2\text{-GO}$ film. The functional group peaks of MnO_2 and GO have been crosschecked from the research publication of [30].

3.3. TEM Analysis. Image of graphene oxide nanosheets were viewed by transmission electron microscopy. The as-synthesized GO sheet is discovered to have a smooth surface. With generally high magnification, the manganese oxide nanoparticles were covered with nanosheets of graphene oxide nanoparticles, and more insights concerning the morphology of nanocomposites were investigated, in which GO nanosheets are made out of several layers and the length of each MnO_2 nanoparticle is cut formed as slice with scales going from 30 to 50 nm. Moreover, MnO_2/GO arrangement of nanocomposites can be ultrasonicated in ethanol for

about an hour with little deficiency of MnO_2 from GO, demonstrating that MnO_2 adsorption on the outside of GO is steady. These recently mentioned properties are those of manufactured MnO_2/GO nanocomposites.

TEM was used to examine GO/MnO_2 -based nanocomposites, which were prepared straight from the reaction mixture with no contamination of the surface coating. The surface of the graphene oxide sheet was disordered. The dissolved nanoneedles are less ordered or unbounded as a result of the crystallization process. The sample's morphology was observed as heterostructure nanocomposites in Figure 7 with diameters ranging from 20 to 500 nm. Figure 7(a) shows the resolution of composites at 100 nm scale range where the clear observations of the nanostructure are observed. In Figure 7(b), the structure of nanocomposites was observed with a 500 nm scale range for the comparison in the morphology and shapes of the composites, which was further corroborated with [17, 26, 31]. According to the report of [27, 32], the less arranged precursors on GO sheets rapidly evaporated with the development of extra nanoneedles through a dissolution crystallization mechanism as the reaction advanced from 1 to 10 minutes. The morphology of samples with a more extended response time of 30 minutes showed no discernible differences, implying that the crystal formation process was nearly complete after that time [33, 34].

In this study, $\text{MnO}_2/\text{graphene oxide}$ nanocomposites were effectively formed using a simple wet-chemical process. MnO_2 is completely covered on the outside of GO nanosheets, according to TEM investigations, and the elements and composition were confirmed by EDX and FT-IR. The content, as well as the crystal structure, was investigated using XRD.

4. Conclusion

In this work, pristine MnO_2 and MnO_2 -GO composites were successfully coated on SS by the electrodeposition method. The obtained coatings were homogeneous and showed a very good adhesion on the metal substrate. The coated substrates were characterized using XRD and FTIR. The primary properties were examined utilizing the X-beam diffraction method. From the outcomes, we discovered the orthorhombic structure of MnO_2 with a molecule size around 12 nm. Besides, we conclude with the presence of MnO_2 and graphene sheets in the composite. FTIR spectrum confirmed the presence of Mn-O stretching vibration and bending vibration of graphene oxide in the composite.

Graphene has a distinct chemical makeup and a wide range of properties, including exceptional electrical, optical, thermal, and mechanical capabilities. To meet the increased demand for thin-film processing, composite-mediated integration has evolved in recent technologies, and a number of synthetic techniques, including chemical and physical methodologies, have been created for device integration as well. Graphene has been composited with polymers, semiconductor nanoparticles, metals, metal oxides, sulphides, alloys, carbon nanotubes, organic molecules, and other materials. The enhancement of the properties of these

composited materials is based not only on the individual components but also on their interaction.

In this study, authors are experiencing the advantage of making novel and an innovative supercapacitor (SC) which was made out of nanocomposites, which had excellent advantages over other conventional capacitors and other electronic devices. The advantages include the following: they are most commonly used in electric hybrid vehicles, military types of machinery, communication devices for uninterrupted power supply in mobiles, and laser devices.

There are certain challenges to overcome; the supercapacitors are cost-effective and highly dense in energy. Recently, many initiatives have been started to overcome the problems associated with the low energy density developed by the SCs which are developed from nanostructure-mediated electrodes with enhanced capacitance. Higher operating voltages can help you save money on your energy bills. The energy density increases as the working potential window widens, needing less material, separator, and electrolyte to store the same amount of energy. A high cell voltage means that fewer cells must be connected in series to form a specific voltage system, reducing the load on external voltage-balance circuits, which are now widely utilized. Last but not least, electrode materials for SCs have sparked a lot of attention in recent years as a way to create cost-effective and high-performing energy storage devices. Waste materials are a cost-effective way to make supercapacitor electrodes for this purpose, albeit they still need a lot of work (fabrication methods, electrolyte selection, etc.) before they can be sold as raw electrode material in the commercial market.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare no potential conflict of interest.

Acknowledgments

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