ANNOTATION

dissertations for the degree of Doctor of Philosophy (PhD)
according to the educational program 8D07113 – «Nanomaterials and nanotechnology in chemistry»

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OBTAINING NANOPAPER BASED ON WASTE PLANT MATERIALS AND WOLLASTONITE

General characteristics of the work.

This dissertation focuses on the development of nanostructured paper with enhanced mechanical and electrochemical properties derived from plant waste materials (mown grass, rice husk, and walnut shell).

Relevance of the research topic.

In the context of global climate change, increasing demand for renewable energy sources, and the need to reduce environmental impact, utilizing plant waste to develop functional materials has become a priority in scientific research.

The relevance of this study is driven by the necessity to develop new, sustainable, and environmentally friendly materials, particularly nanopaper, by processing plant waste (mown grass, rice husks, and walnut shells). The modern market requires compact and long-lasting equipment for energy storage and conversion. To meet this demand, new technologies are being developed that utilize plant waste to create products with improved mechanical and electrochemical properties, particularly for high-performance supercapacitor electrodes.

Nanostructured paper composed of nanocellulose, activated carbon, and carbon nanotubes was successfully synthesized for binder-free electrodes used in high-performance energy storage systems. Optimizing the composition and fabrication conditions significantly enhanced the electrodes' specific capacitance, energy density, and durability under cyclic testing. This research, spanning from cellulose extraction from plant waste to nanocomposite formation and integration into electrochemical devices, presents a holistic strategy for the efficient utilization of biomass to develop advanced functional materials.

The aim of the work is develop nanostructured paper from nanocellulose, activated carbon, and carbon nanotubes with tailored electrochemical properties for energy storage applications.

Tasks of the work. To achieve the set goal, the following tasks were undertaken:

– Extraction of cellulose from plant waste via chemical-thermal processing and assessment of the effects of mineral fillers (wollastonite, diatomite, barium sulfate) on the mechanical properties of paper and cardboard.

– Synthesis of crystalline and fibrillar nanocellulose using acid hydrolysis and TEMPO oxidation methods, followed by structural and morphological characterization.

– Investigation of the effects of activation methods on the morphological and structural characteristics of activated carbon derived from plant waste.

– Fabrication of nanostructured paper based on nanocellulose, activated carbon, and carbon nanotubes, optimization of its composition for supercapacitor electrodes, and evaluation of its electrochemical properties using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) to assess its energy storage efficiency.

The object of the study is nanostructured paper based on nanocellulose, activated carbon and carbon nanotubes, obtained from recycled plant waste.

The subject of the study is the physicochemical and electrochemical properties of nanostructured paper.

Research methods. To solve the problems necessary to achieve the set goal, the following research methods were used: thermogravimetric analysis (TGA), elemental analysis (EDX), X-ray phase analysis (XRF), optical microscope, scanning electron microscopy (SEM), method of determining the specific surface area (BET), transmission electron microscope (TEM), galvanostatic and potentiostatic analysis, cyclic voltammetry (CVA), Infrared spectroscopy, Raman spectroscopy.

Scientific novelty of the research. During the research work the following results were obtained:

- cellulose was obtained from plant waste by the method of chemical-thermal treatment and the effect of mineral fillers (wollastonite, diatomite, barium sulfate and technological additives) on the mechanical properties of paper and cardboard made on the basis of the obtained cellulose was established. Paper and cardboard compositions with significantly improved strength and flexibility characteristics were developed due to the optimization of the ratio of cellulose from grass and the use of additives in the form of waste paper and wollastonite. The obtained cardboard composition has high indentation resistance strength up to 903 kPa and flexibility up to 91 times by the number of double folds;

– fibrillar nanocellulose synthesized by acid hydrolysis and TEMPO oxidation methods was obtained. It was found that the TEMPO oxidation method reduces the resistance to aggregation and decreases the fiber diameter to 20–40 nm;

– the effect of the activation method on the porous structure and spectroscopic characteristics of activated carbon was established. Chemical activation with KOH leads to a microporous structure with a high intensity ratio of the G/2D peaks (0.52–0.55), while physical activation with CO_2 promotes the formation of a mesoporous structure and a few-layer graphene structure with a lower G/2D ratio (0.45-0.49);

– nanostructured paper based on nanocellulose, activated carbon and carbon nanotubes was synthesized, its composition was optimized for use in supercapacitor electrodes and its electrochemical properties were determined using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) to evaluate its efficiency in energy storage systems. The developed electrodes for supercapacitors have a specific capacitance of up to 145 F/g and an energy density of up to 9.9 kWh.

The main provisions submitted for defense:

1. Paper and cardboard based on cellulose from mown grass, waste paper and wollastonite with an optimal component ratio of 40:40:20 with the addition of 2% rosin

glue, polyacrylamide and aluminum sulfate have increased strength (903 kPa) and flexibility (91 double fold);

2. Fibrillar nanocellulose obtained by acid hydrolysis methods has a fiber diameter of 10 to 69 nm and a zeta potential of 28.80±0.10 mV, while that obtained by TEMPO oxidation has a fiber diameter of 20-40 nm and a zeta potential of 20.50±0.36 mV.

3. Physical activation of CO_2 promotes the formation of a mesoporous structure and a few-layer structure graphene structure with a G /2D ratio of 0.45 (for carbonized rice husk) and 0.49 (for carbonized walnut shell).

4. Nanostructured paper based on nanocellulose, activated carbon and carbon nanotubes, used as electrodes of supercapacitors, has a high specific capacity of 145 F/g and improved electrochemical characteristics of 9.9 kW/h.

Theoretical significance.

The theoretical significance of the work lies in expanding knowledge about the processing of plant waste into functional materials with high added value. The results obtained deepen the understanding of the processes of obtaining cellulose, nanocellulose and activated carbon from plant waste, as well as the influence of their morphological and structural characteristics on the physicochemical, mechanical and electrochemical properties of composite materials.

Practical significance.

The practical significance lies in obtaining environmentally friendly and cost-effective materials for use in paper and cardboard products and energy storage systems. The implementation of this work contributes to the development of "green" technologies, reducing the burden on the environment and increasing the efficiency of using renewable resources.

The results obtained in the dissertation research can be used in the educational process when giving lectures and conducting elective courses in the specialty of nanomaterials and nanotechnology.

Relationship with research and development and government programs.

The work was carried out within the framework of grant funding projects:

• AP09057909 “Development of methods for producing composite electrodes based on carbon nanomaterials without the addition of polymer binders for use in electrochemical energy storage sources” (2021–2023).

• AP14871062 “Development of energy-dense composites based on nanocellulose and functionalized CNTs for improved energy storage systems” (2022–2024).

• AP13068375 “Production of cellulose materials based on waste plant materials and mineral additives” (2022–2024).

The author's personal contribution consists of setting up and conducting experiments, summarizing and interpreting the results, writing articles and reports. The aim and objectives, planning of experiments, discussion of results and main provisions for defense were discussed with both scientific advisers.

Publications

As a result of research on the topic of the dissertation, 12 scientific papers were published, including4 articles in journals included in the Web of Science database, 5 articles in publications recommended by the Committee for Control in the Sphere of Education and Science of the Republic of Kazakhstan, and 3 patents for a utility model were received.

Articles published in journals included in the international scientific database Web of Science and Scopus:

1 **Taurbekov A.** et al. Investigations of Activated Carbon from Different Natural Sources for Preparation of Binder-Free Few-Walled CNTs/Activated Carbon Electrodes (2023), Journal of Composites Science, 7 (11), art. no. 452 (https://doi.org/10.3390/jcs7110452 , Scopus – CiteScore – 4.5, percentile 74%, Q2).

2 **Taurbekov A.** et al. Biomass Derived High Porous Carbon via CO_2 Activation for Supercapacitor Electrodes (2023), Journal of Composites Science, 7 (10), art. no. 444 (https://doi.org/10.3390/jcs7100444 , Scopus – CiteScore – 4.5, percentile 74%, Q2).

3 **Taurbekov A.** et al. Valorization of Grass Clipping Waste: A Sustainable Approach to Cellulose Extraction and Paper Manufacturing (2024), Applied Sciences (Switzerland), 14 (15), art. no. 6680 (https://doi.org/10.3390/app14156680 , Scopus – CiteScore – 5.3, percentile 79%, Q1).

4 **Taurbekov A.** et al. Nanocellulose and carbon nanotube composites: a universal solution for environmental and energy challenges (2024), Journal of Environmental Chemical Engineering, P. 113262 (https://doi.org/10.1016/j.jece.2024.113262 , Scopus – CiteScore –11.4, percentile 85%, Q1).

5 articles in scientific publications recommended by the Committee for Scientific and Technical Education of the Ministry of Education and Science of the Republic of Kazakhstan:

1 Atamanova T.S., Yeleuov M., **Taurbekov A.,** Atamanov M.K. Development of flexible electrodes without the use of polymer binders based on activated carbons and carbon nanotubes // Combustion and Plasma Chemistry. - 20. - (2022). - 239-246 .

2 Prikhodko N.G. , Yeleuov M.A., Askaruly K., Tolynbekov A.B., **Taurbekov A.T.,** Abdisattar A.A., Atamanov M.K. Study of the initial plant biomass for the bulk production of graphene-like structures // Combustion and Plasma Chemistry. - 20. - (2022). - 221-231 .

3 **Taurbekov A.T.,** Kaidar B.B., Chernoglazova T.V., Mansurov Z.A. Obtaining cellulose fibers from fallen elm leaves // Combustion and Plasma Chemistry. - 18. - (2020). - 141-148 .

4 Prikhodko N.G. , Yeleuov M.A., Abdisattar A.A., Askaruly K., Tolynbekov A.B., **Taurbekov A.T.** Study of the properties of carbon materials obtained from plant biomass by hydrothermal carbonization as initial precursors for obtaining graphene-like structures // Combustion and Plasma Chemistry. - 22. - (2023). - 13-26 .

5 Baltabay A.S., **Taurbekov A.T.,** Imash A.A., Kaidar B.B., Smagulova G.T., Ko W.B., Mansurov Z.A. Extraction of cellulose from rice husk waste // Combustion and Plasma Chemistry. – 2023. – T. 21. No. 3. – pp. 181-189

Patents for utility models have been received :

1 Patent No. 6900 RK. Method of manufacturing cardboard / **Taurbekov A.T.,** Mansurov Z.A. , Chernoglazova T.V. – Published. 02.25.2022. Bulletin No. 8.

2 Patent No. 8721 RK. Method for producing nanofibrillar cellulose / Atamanov M.K., **Taurbekov A.T.,** Kaidar B.B., Atamanova T.S., // – Publ. 12/15/2023.

3 Patent No. 9573 RK. Method for producing cellulose fibers from plant raw materials / Smagulova G.T., **Taurbekov A.T.,** Baltabay A.S., Imash A.A., Kaidar B.B., Keneshbekova A.M., Mansurov Z.A. // – Publ. 09/20/2024

Reliability and validity of the results obtained

The reliability of the results is confirmed by data consistency obtained through modern physicochemical research methods. The research was conducted at Al-Farabi Kazakh National University, the Institute for Combustion Problems, and the Jean Lamour Institute (France).