ANNOTATION

to the dissertation work of Dana Kanzhigitova on the topic "Development of novel functional hybrid materials based on conducting polymers", submitted for the degree of Doctor of Philosophy (PhD) in the specialty 8D05301-Chemistry.

The dissertation work is presented in the form of a *series of articles* published by the doctoral student in accordance with the requirements of paragraph 5-1 of the rules for awarding academic degrees, approved by the order of the minister of Science and higher education of the Republic of Kazakhstan No. 7 dated 09.01.2023.

The relevance of research. Due to their many potential uses, conducting polymers have attracted a lot of attention in the last several decades. The electrical, optical, and distinctive nanostructures of conducting polymers like PEDOT, polypyrrole (PPY), polyaniline (PA), and polythiophene (PT) have attracted a lot of interest. Nanostructured conducting polymers can be successfully fabricated using techniques such as self-assembly, phase separation, emulsion polymerization, and crosslinking of micelles. The interesting characteristics of conducting polymers have led to the development of a wide range of nanostructures, and several synthetic methods have been employed to create these structures. Recent studies have shown that the dimensionality of conducting polymer nanostructures is an important parameter for tuning its distinct electrical properties, which became apparent with the discovery of conducting polymers. On the other hand, 2D nanosheet production methods are either too complicated or too expensive. The electrical characteristics and device performance of polymer chains are further restricted by the random or disordered structure of the chains created through traditional synthesis methods. By revealing new methods for conducting polymer nanostructures during synthesis, the work has important consequences for materials science. The innovative combination of structure-directing agents, inorganic templates, and bicontinuous microemulsion systems improves our material opportunities while also contributing to our fundamental understanding of nanostructure design.

Research goal. The primary goal of this research is to investigate fundamental scientific issues in conducting polymers by enhancing conductivity through structural modifications. This will involve synthesizing novel materials and examining the relationships between their structure, morphology, and sensing properties for hydrogen gas detection. The key research goal is to develop innovative methods to create nanomaterials within a bicontinuous system, emphasizing the impact of the oxidant-to-monomer ratio on morphology. Additionally, the study aims to fabricate organized conducting polymer chains using an inorganic crystal template to understand the relationship between ordered polymer chains, improved charge carrier mobility, and enhanced hydrogen gas sensing capabilities. Lastly, the goal is to manipulate a structure directing agent to fabricate diverse conducting polymer structures like nanoparticles, bowl shapes, and 2D films.

Achieving this goal involves solving the following tasks:

1. To examine the impact of four different bicontinuous reactors, particularly pure, nonionic, cationic, and anionic interfaces, on the structure and properties of conducting polymer structures. To design and produce 3D polypyrrole (PPY) and their composites by incorporating certain linkers in the bicontinuous reactor system.
2. To design and synthesis of composites of conducting polymer/V_2O_5 via intercalation and assembly approaches. Additionally, explore the impact of doping on the structural properties of the conducting polymer composite. Furthermore, investigate the influence of doping on the structural characteristics of the conducting polymer composite. To understand the relationship

between the structure/morphology and sensing properties of the above fabricated materials and finding the relationship between carrier mobility and hydrogen detection performance.
3. To synthsize 3,3'-(octane-1,8-diylbis(oxy))dianiline (3AP-C8), an aniline derivative monomer, through bicontinuous microemulsion technique and to study the impact of doping on the resulting conducting polymer.

Research object. Hybrid composite materials based on conducting polymers and V_2O_5 templates, monomers of conducting polymers and modified functional monomers and their polymers.

Research methods. The study employed interfacial polymerization techniques, which involved manipulating the oxidant-to-monomer ratios to control the form and characteristics of the polymers. Moreover, comprehensive material characterization universally involves the application of advanced techniques such as Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Confocal Microscopy, Energy-Dispersive X-Ray Spectroscopy (EDS), and Four-point probe characterization analysis. The synthesis processes were modified to produce customized nanostructures by strategically employing structure-directing agents such as p-toluene sulfonic acid (p-TS).

Research hypothesis:

1. The use of a bicontinuous microemulsion system will provide the strategic synthesis of 2D and 3D conducting polymers and nanocomposites. This approach will offer a high level of control over the morphologies and electrical properties of the conducting polymer materials. The control of the interfaces, such as their nature, thickness, monomer/oxidant ratios, and doping level, is anticipated to be important.

Moreover, the use of specifically created linkers and the incorporation of special components during the production of nanocomposites will improve the characteristics of the resulting conducting polymer materials.

2. The addition of p-TS to the hybrid thin films of Vanadium pentoxide and polypyrrole will result in improved hydrogen gas sensing properties. This enhancement can be explained by the ordered structure of the composites as well as the increased charge carrier mobility.

3. The bicontinuous microemulsion reactor will control the synthesis of polyaniline-based nanomaterials and offer creation of various nanostructures of conducting polymers (such as bowl, hollow 2D films), and the key factors such as the concentration of monomers and oxidants, the nature of the dopants, and the nature of bicontinuous thin layers at the interface will influence in controlling the structures of the conducting polymer materials.

The main rules of the dissertation submitted for defense:

1. The highest conductivity is 219 S/cm obtained for the nanosheet fabricated using a clean interface reactor system (DCM system) due to the absence of an interfacial barrier and easy transport of dopants to the polymer matrix.
2. The addition of p-toluenesulfonic acid (p-TS) to vanadium pentoxide (V_2O_5) and polypyrrole (PPY) made it possible to form an ordered structure of the composites and increase the mobility of charge carriers from 4.76 cm^2/Vs to 14 cm^2/Vs and due to this, the hydrogen gas response increased from 7.88% to 32.43%.
3. The method of obtaining various nanostructures of polyaniline derivatives (nanospheres, nanorods and nanobowls) using a bicontinuous microemulsion reactor system makes it possible to control their morphology and shape from rod to adhesive film structures.

Scientific results:

1. For the first time, a universal, easy, and scalable synthetic technique has been created for the design of 2D and 3D conducting polymers and their nanocomposites. This fabrication approach was founded on four distinct interface bicontinuous reactors: pure, nonionic, cationic, and anionic interfaces. The nature of the interfaces, the thickness of the thin layered interfaces, the monomer/oxidant ratios (and those between monomers, linkers, and oxidants), and the doping level were discovered to be important parameters in controlling the morphologies and electrical properties of conducting polymer materials. In the absence of a molecular layer, the pure interface provides substantially thicker 2D nanosheets than other interfaces such as cationic, nonionic, and anionic. The conductivity obtained for 2D nanosheets designed via pure interface bicontinuous systems was the highest of the four distinct systems, much above the values reported in the literature for 2D-sheet conducting polymers. The optimum electrical conductivity obtained for 2D PPY nanosheets is 219 S/cm, which is the highest literature value published so far. 3D PPY materials were successfully designed and produced using unique linkers in a bicontinuous reactor system. The nanocomposite was created by incorporating functional dispersed phase components into a combination of monomers and linkers.

2. A unique high-performance H_2 sensor has been successfully produced using p-TS doping on a hybrid VOH-PPY thin film. Microstructural investigations revealed that the presence of p-TS causes noticeable structural alteration and expansion of PPY chains with increasing lattice distance, increasing the surface area of the composite and improving its gas detection performance. At the same time, p-TS can operate as a dopant in VOH-PPY films, reducing charge movement resistance to enable greater conductivity and hole mobility. As the hydrogen content in a nitrogen environment ranges between 5-250 ppm, p-TS testing increased response time and sensitivity from 8% in 88s to 32% in 43s. The gas sensor can detect a lower concentration of hydrogen gas with a higher carrier concentration.

3. A simple synthesis method was established for the fabrication of various conducting polymer nanostructures, such as hollow spheres, nanobowls, 2D sheets with arrays of nanobowls, 3D and their composites. Changes in reaction conditions (pH, monomer and oxidant concentrations, and p-TS concentration) for the polymerization of aniline derivative monomer resulted in the nanostructures shown above. a bicontinuous microemulsion reactor was established as a foundation for producing diverse nanostructures of conducting polymers by the utilisation of interfacial polymerization and self-assembly methods. The process of self-assembly was manipulated to induce polymerization, resulting in the formation of nanorods. These nanorods were guided to assemble into nanobowl or hollow-spherical structures. The interface thin layer template procedure was optimised to generate hollow-spherical and 2D film nanostructures. This is the initial conducting polymer material that exhibits comparable adhesiveness (about 8 N/cm2) to that of gecko feet pads.

Novelty and importance of obtained results:

The first article named: “Strategic Synthesis of 2D and 3D Conducting Polymers and Derived Nanocomposites”, the use of bicontinuous microemulsion systems for producing conducting polymer nanostructures is an innovative and scalable technology that differs from interfacial polymerization. Manipulation of the structure by adjusting the ratio of oxidant to monomer provides opportunities for modifying the characteristics of conducting polymer nanostructures, presenting potential uses in the fields of electronics, sensors, and materials research.

The second article named: “p-Toluenesulfonic acid doped vanadium pentoxide/polypyrrole film for highly sensitive hydrogen sensor”, the results provide a new and simple method for

creating a highly responsive conductive polymer sensor that can detect small amounts of hydrogen gas. The addition of p-toluenesulfonic acid during the production of the hybrid thin films has resulted in enhanced sensing abilities with fast response and recovery times. This innovation is highly relevant in the area of gas sensing technology, especially when considering hydrogen as a potential energy source. The well-organized arrangement of the composites, together with the improved movement and abundance of charge carriers, provides to exceptional hydrogen gas detecting characteristics. This has significant potential for the advancement of efficient and accurate gas sensors for a range of applications.

The third article called: “Controlled Synthesis of Polyaniline-based Nanomaterials with Self-assembly and Interface-Manipulation” presents a new method for precisely creating polyaniline-based nanomaterials via self-assembly and interface modification techniques. This method provides a unique structure for producing diverse nanostructures composed of conductive polymers, such as nanorods, nanobowls, hollow spherical nanoparticles, nanosheets, and sticky nanofilms. The obtained varied nanostructures, ranging from hollow nanoparticles to 2D films, show exceptional control over morphology. The new nanostructures possess significant potential for many industrial applications, such as drug delivery, energy storage, and adhesive materials.

Theoretical and practical importance of the work. The research improves theoretical knowledge of conducting polymers and nanostructure design. These nanostructured materials could improve conductivity and enable flexible, lightweight, and efficient electronic devices as next-generation electronics. A single study showed that conducting polymer composites, particularly in hydrogen gas sensing, could help develop advanced and responsive sensor technologies for environmental monitoring and industrial safety. Nanostructured conducting polymers could be employed in supercapacitors and batteries. These materials could improve energy storage capacities, charge/discharge rates, and battery lifespans, enabling ecologically friendly and efficient energy materials.

Connection of the work with the plan of state scientific programs. This work received financial support from the Ministry of Education and Science of the Republic of Kazakhstan under project No. AP09258910, titled "Multifunctional Desulfurization Polymer Nanocomposites". Additionally, it was supported by a Faculty Development Competitive Research Grant from Nazarbayev University under Project ref. no. 021220FD4551, titled "Crosslinked 3D Nanoporous Conducting Polymer Materials via Bicontinuous Microemulsion-based Approach".

Publications and author's personal contribution to the research. Three scientific articles were published. The first article, titled "Strategic Synthesis of 2D and 3D Conducting Polymers and Derived Nanocomposites," was published in the journal Advanced Materials with an impact factor of 32 and Q1. The second article, titled "p-Toluenesulfonic acid doped Vanadium pentoxide/Polypyrrole film for highly sensitive hydrogen sensor," was published in the journal Advanced composites and hybrid materials with an impact factor of 20 and Q1. The third article, titled "Controlled Synthesis of Polyaniline-based Nanomaterials with Self-assembly and Interface-Manipulation," was published in the journal ACS Langmuir with an impact factor of 3.9 and Q1. Furthermore, in two out of three works, PhD student Dana Kanzhigitova has the position of the primary author.

1. M. Abutalip, G. Zhigerbayeva, **D. Kanzhigitova**, P. Askar, Y. Yeszhan, T. T. Pham, S. Adilov, R. Luque, N. Nuraje, Strategic Synthesis of 2D and 3D Conducting Polymers and Derived Nanocomposites. Adv. Mater. 2023, 35, 2208864. https://doi.org/10.1002/adma.202208864. Advanced Materials has an impact factor of 32, Q1 and highest percentile is 99%, which places it in the top 1% of journals in its field. She is a co-author of this work. She utilised an advanced

synthetic technique called surfactant-free microemulsion to synthesise conducting polymers. Additionally, she created a composite by including s-doped carbon dots.

2. Kanzhigitova, D., Askar, P., Tapkharov, A. et al. p-Toluenesulfonic acid doped vanadium pentoxide/polypyrrole film for highly sensitive hydrogen sensor. Adv Compos Hybrid Mater 6, 218 (2023). https://doi.org/10.1007/s42114-023-00796-0. Advanced composites and hybrid materials have an impact factor of 20, Q1 and with the highest percentile of 97%. She holds the position of first author in this work.

Dana Kanzhigitova developed the experimental framework and oversaw the synthesis of composite materials. Additionally, the researcher meticulously analyzed gathered data regarding material characteristics, interpreted and summarized findings, engaged in discussions surrounding the acquired experimental results, and uncovered correlations among different factors.

3. **Dana Kanzhigitova**, Munziya Abutalip, Faisal Nazir, Magzhan Amze, Perizat Askar, Yelriza Yeszhan, Tri Thanh Pham, Raikhan Rakhmetullayeva, Salimgerey Adilov, Nurxat Nuraje. Controlled Synthesis of Polyaniline-based Nanomaterials with Self-assembly and Interface-Manipulation. Langmuir, 2024 https://doi.org/10.1021/acs.langmuir.3c03167. The journal ACS Langmuir has an impact factor of 3.9, Q1 and with the highest percentile of 83%. She is first author. Dana Kanzhigitova made significant contributions to the idea and design of the experiments, the acquisition, analysis, and interpretation of data, as well as the drafting and revising of the manuscript for intellectual content. She also took responsibility for ensuring the accuracy and integrity of the work.