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Transition from BODIPY Solutions to Solid-State Sensors: Cellulose and Textile Matrices for Hydrogen Sulfide Detection

Alexander Bobrov,[@] Evgeniy Molchanov, Natalya Moleva, Evgenii Ivanov, and Daniil Gryaznov

Ivanovo State University of Chemistry and Technology, 153000 Ivanovo, Russia
[@]Corresponding author E-mail: bobrovalexanderv@gmail.com

Boron-dipyrromethene (BODIPY) fluorophores are well-known for their high fluorescence quantum yields, chemical stability, and tunable optical properties, which make them excellent candidates for sensing applications. This work focuses on the transition from BODIPY-based fluorescent solutions to solid-state materials, specifically cellulose and fabric matrices, designed for hydrogen sulfide (H_2S) detection. The study demonstrates how immobilization of BODIPY dyes into cellulose-derived or textile substrates preserves, or even enhances, their photophysical characteristics while providing mechanical robustness and practical usability. Spectroscopic analysis revealed that the microenvironment within the matrix affects fluorescence intensity and spectral shifts, influencing the dye's sensitivity to gaseous H_2S. The prepared hybrid materials show rapid, visible, and reversible fluorescence responses under ambient conditions, highlighting their potential for environmental and industrial gas sensing. These results establish a foundation for developing cost-effective, flexible, and reusable optical sensors based on BODIPY-doped natural matrices.

Keywords: BODIPY, materials, sensor, fluorescence, hydrogen sulfide.

Переход от растворов BODIPY к твердотельным сенсорам: целлюлозные и текстильные матрицы для обнаружения сероводорода

А. Бобров,[@] Е. Молчанов, Н. Молева, Е. Иванов, Д. Грязнов

ФГБОУ ВО Ивановский государственный химико-технологический университет, 153000 Иваново, Россия
[@]E-mail: bobrovalexanderv@gmail.com

Флуорофоры на основе бор-дипиррометена (BODIPY) хорошо известны своим высоким квантовым выходом флуоресценции, химической стабильностью и настраиваемыми оптическими свойствами, что делает их отличными кандидатами для применения в сенсорных устройствах. В данной работе основное внимание уделяется переходу от флуоресцентных растворов с BODIPY к твердотельным материалам, в частности к целлюлозным и тканевым матрицам, предназначенным для обнаружения сероводорода (H_2S). Исследование демонстрирует, как иммобилизация красителей BODIPY в матрицах на основе целлюлозы или текстиля сохраняет, или даже улучшает их фотофизические характеристики, обеспечивая при этом механическую прочность и практическую применимость. Спектроскопический анализ показал, что микросреда внутри матрицы влияет на интенсивность флуоресценции и спектральные сдвиги, влияя на чувствительность красителя к газообразному H_2S. Подготовленные гибридные материалы демонстрируют быструю, видимую и обратимую флуоресцентную реакцию в условиях окружающей среды, что подчеркивает их потенциал для экологического и промышленного газового анализа. Эти результаты создают основу для разработки экономичных, гибких и многоразовых оптических датчиков на основе природных матриц, легированных BODIPY.

Ключевые слова: BODIPY, материалы, сенсоры, флуоресценция, сероводород.

Introduction

Fluorescent boron–dipyrromethene (BODIPY) derivatives have become a cornerstone of modern optical sensing because of their exceptional photophysical properties such as high fluorescence quantum yields, sharp absorption/emission bands, and structural modularity that enables targeted tuning of spectral position, sensitivity and reaction mechanisms.[1–3] These features have driven a rapid expansion of BODIPY-based probes and devices across chemical, environmental and biological sensing over the last decade.[4-6]

In the study,[7] Paul *et al.* synthesized and characterized a new chemosensor based on the BODIPY dye with a 4-azidophenyl substituent for the detection of hydrogen sulfide (H_2S). The sensing mechanism is based on a specific reduction reaction of the azide group to the amino group under the action of the hydrosulfide anion (HS^-), which leads to a change in the color of the solution from pale yellow to orange and a sharp quenching of fluorescence. The probe demonstrated high selectivity for H_2S over other competing analytes (F^-, Cl^-, Br^-, I^-, NO_2^-, NO_3^-, $S_2O_3^{2-}$, SO_3^{2-}, SO_4^{2-}, SCN^-) and achieved an exceptionally low detection limit of 0.17 μM.

Although solution studies of BODIPY dyes provide fundamental insights into photophysical mechanisms – such as photoinduced electron transfer (PET), intramolecular charge transfer (ICT), and heavy-atom effects – the practical implementation of these systems in sensing requires the development of solid-state materials.[8,9] Immobilization of BODIPY fluorophores into polymeric or natural supports converts soluble probes into robust and reusable materials, offering advantages such as enhanced mechanical stability, reusability, and compatibility with optical readout devices.[10–12]

Among available matrices, cellulose derivatives and woven or non-woven fabrics are especially promising due to their abundance, porosity, biocompatibility, and ability to provide uniform dye distribution.[13,14] Embedding BODIPY molecules into cellulose or textile materials not only preserves fluorescence but also enhances analyte accessibility and sensitivity through favorable micro-environmental interactions.[15,16]

Hydrogen sulfide is a highly toxic yet biologically relevant gas produced endogenously in mammals and encountered in many industrial processes. Its dual role as both a hazardous pollutant and a physiological signaling molecule has motivated the development of numerous optical probes for its detection.[17–19] Fluorescent sensors, particularly those based on BODIPY derivatives, provide a fast, selective, and visually distinguishable response under ambient conditions.[20] The tunable chemistry of BODIPY allows introduction of H_2S-reactive substituents such as azides, nitro groups, or selenium derivatives that convert chemical reactivity into fluorescence modulation.[21]

When transitioning from solution to materials, several factors control sensor performance: dye aggregation, pore accessibility, matrix polarity, and the balance between photostability and reversibility.[22] Recent studies demonstrate that cellulose- and fabric-based supports yield materials with stable luminescence, fast diffusion of gaseous analytes, and the possibility of tailoring response kinetics by matrix composition and dye concentration.[3,10,13,16]

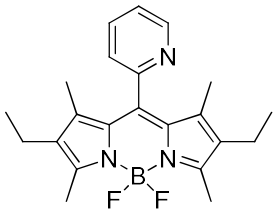

Figure 1. Structure of *meso*-pyridine substituted BODIPY.

BODIPY-based H_2S probes represent a prominent class of sensors due to their high quantum yield, photostability, and tunable emission. Typical designs employ dinitrobenzene sulfonyl (DNBS) or dinitrophenyl (DNP) groups that are selectively cleaved by H_2S,[23] ratiometric BODIPY scaffolds that undergo H_2S-triggered structural transformation,[24] or BODIPY-metal complexes in which HS^- restores fluorescence by ligand displacement.[25] The essential characteristics of such sensors are outlined below: high selectivity over biothiols (glutathione, GSH; cysteine, Cys), low detection limits (μM-nM), rapid response, aqueous stability, low toxicity, and – when used for imaging – suitably red-shifted emission.

In this work, we explore the transition from BODIPY solutions to solid-state sensory materials based on cellulose and textile matrices. Using *meso*-substituted BODIPY (Figure 1) as a model system, we investigate how matrix composition and dye loading affect spectral properties and fluorescence response to hydrogen sulfide vapours. The obtained results contribute to understanding structure-property relationships in hybrid fluorescent materials and demonstrate the practical potential of BODIPY-modified cellulose and fabric substrates for optical H_2S detection.

Experimental

The BODIPY compound was obtained earlier.[26]

Ethyl cellulose of 33 cps viscosity (Acros Organics) was used as a bearing matrix for solid-state sensory materials. All organic solvents were of analytical grade and obtained from ChemMed, Russia and utilized without further purification.

The fluorescent signal of samples was recorded in the air-tight box filled with vapor of a pure solvent or cyclohexane-solvent mixture of various composition. Spectra were recorded using an optical fiber probe with excitation wavelength λ_{ex} = 480 nm (Figure 2) with Varian Cary Eclipse fluorometer (Agilent technologies, USA).

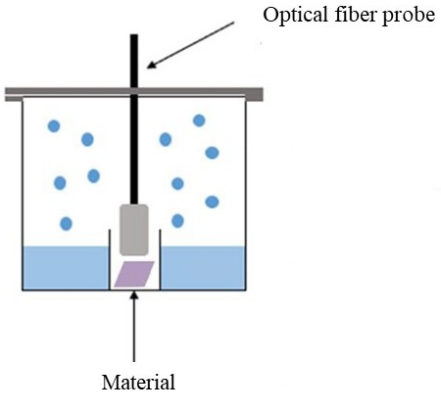

Figure 2. Schematic representation of the experimental installation.

Cylindrical cellulose tablets (height 1.0 ± 0.15 mm, diameter 7 mm, mass ≈ 30 mg) were formed with PGR-10 hydraulic press under a 150 bar pressure. Ethyl cellulose cylinders were soaked for 60 s in 1 mL of BODIPY solution in cyclohexane with different dye concentrations ($2.5 \cdot 10^{-5}$ M, 10^{-4} M, $4 \cdot 10^{-4}$ M, $2 \cdot 10^{-3}$ M, 10^{-3} M). Afterwards, tablets were dried at 100°C to constant weight (for about 30 min).

The materials were manufactured from woven fabrics, including cotton-polyester (35:65%), pure linen and pure cotton, as well as non-woven polypropylene (see Figure 3), by soaking them in a 10^{-4} M BODIPY-acetonitrile solution for 5 min. The resulting material was then dried to a constant weight.

The generation of H_2S within the cell was achieved through a chemical reaction involving the Na_2S solution and HCl. The reaction was initiated following the recording of the spectrum at 0 minutes by the addition of 1 mL of acid to the same volume of Na_2S solution at the bottom of a large glass. Thereafter, the system was promptly closed and the kinetic experiment commenced. This allowed us to create a hydrogen sulfide concentration in the cell ~ 300 mg/m^3. This concentration was used in all experiments.

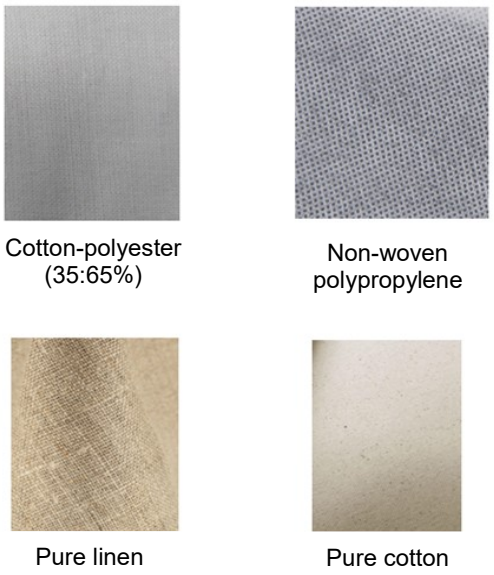

Figure 3. Studied fabrics.

Results and Discussion

Cellulose-based materials

The effect of hydrogen sulphide vapours on the spectral characteristics of a meso-pyridine-substituted BODIPY fluorophore in an ethylcellulose-based matrix was evaluated. Measurements were taken over a period of 15 minutes. The fluorophore's molar concentration in the matrix varied from $2.5 \cdot 10^{-5}$ M to 10^{-3} M.

As shown in Figure 4, the graph indicates that the sensory response intensifies as the concentration of BODIPY increases. However, when the concentration reaches $4 \cdot 10^{-4}$ M, the changes plateau. This is most likely because concentrations that are too low do not completely fill the pores of the matrix. Once a concentration of $4 \cdot 10^{-4}$ M is reached, the pores are completely filled and increasing the concentration of the impregnating solution does not lead to an increase in the sensory response. Therefore, a BODIPY concentration of $4 \cdot 10^{-4}$ M is preferable for this matrix.

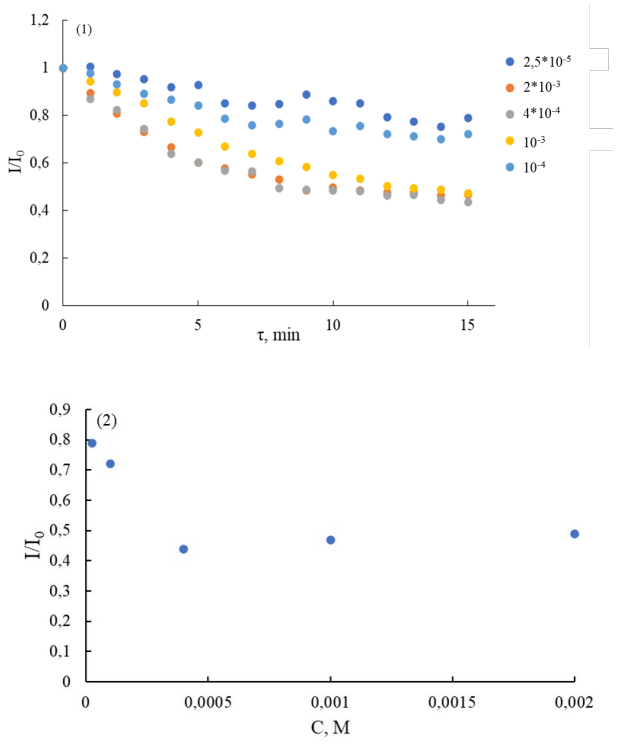

Figure 4. Dependence of the relative fluorescence intensity of BODIPY@EtCel on the duration of treatment with hydrogen sulphide vapour (1). Dependence of the sensor response on the concentration of BODIPY (2).

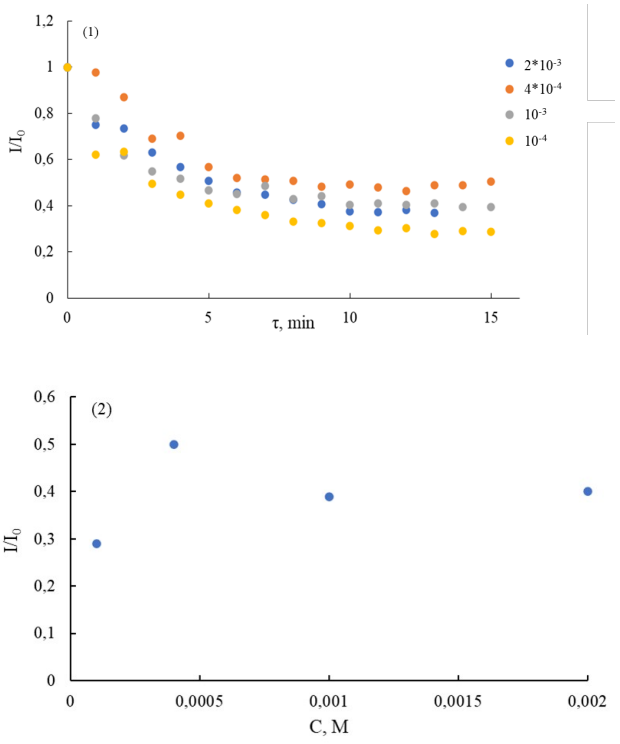

Figure 5. Relative fluorescence intensity of BODIPY@EtCel as a function of hydrogen sulphide vapour treatment duration (1). (2) Dependence of the sensor response on the concentration of BODIPY.

Similar experiments to detect hydrogen sulfide were conducted using cellulose materials (filter paper), with the molar concentration of the fluorophore varying from 10^{-4} to $2 \cdot 10^{-3}$ M.

It should also be noted that the greatest fluorescence quenching occurred in materials with a BODIPY concentration of 10^{-4} M (see Figure 5). In this case, using the lowest of the selected concentrations is most appropriate. Additionally, the sensor response in the cellulose (filter paper) matrix is ~15% higher than in the ethylcellulose matrix. This effect is most likely due to the dye being more readily available for interaction with the analyte.

Fabrics based materials

For the study of fabric materials, an impregnation solution with a concentration of 10^{-4} M was used. The fabric-based materials were treated with H_2S vapours for 15 min, during which time their fluorescence spectra were recorded (see Figures 6–9).

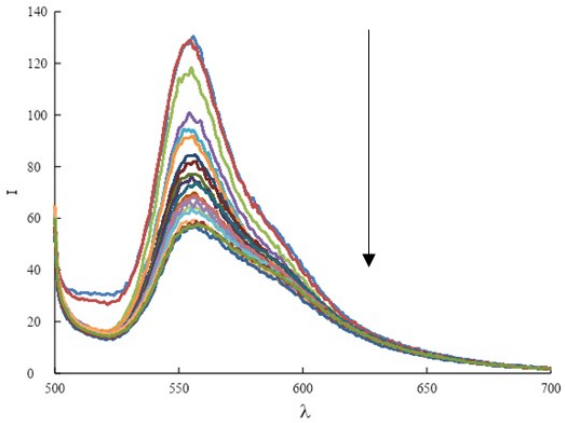

Figure 6. Change in BODIPY@Cotton fluorescence during H_2S treatment. The direction of the spectrum change is indicated by the arrow.

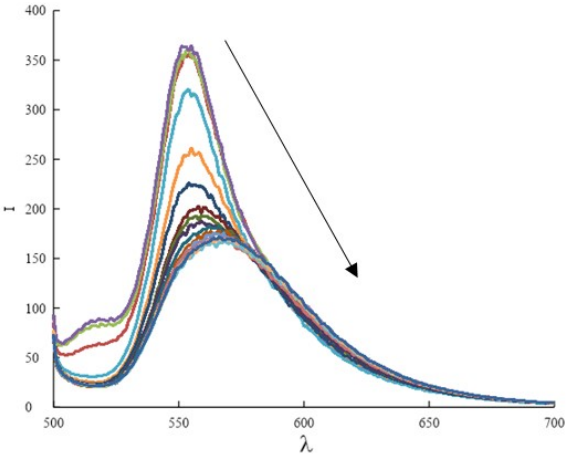

Figure 7. Change in fluorescence of BODIPY@ Semi-synthetic during H_2S treatment. The direction of the spectrum change is indicated by the arrow.

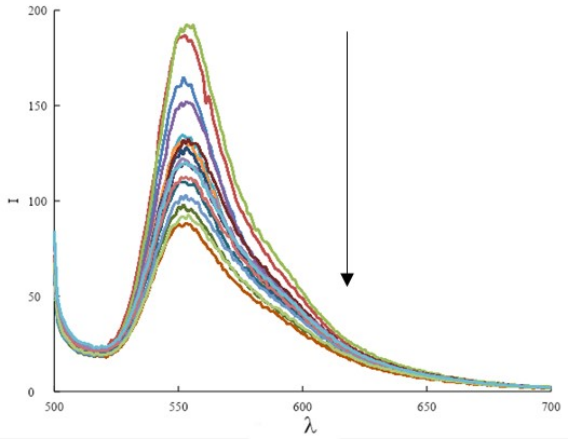

Figure 8. Change in BODIPY@Linen fluorescence during H_2S treatment. The direction of the spectrum change is indicated by the arrow.

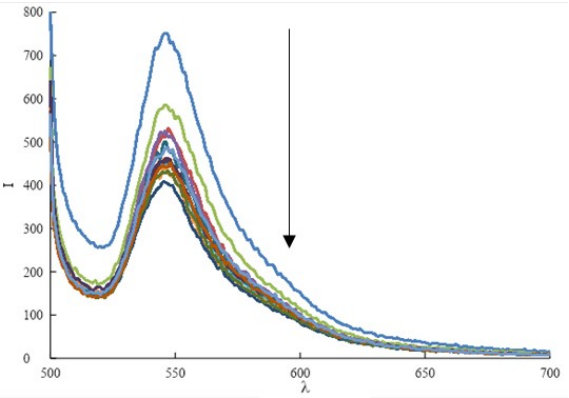

Figure 9. Change in BODIPY@Polypropylene fluorescence during H_2S treatment. The direction of the spectrum change is indicated by the arrow.

Studies have shown that the nature of the carrier material significantly affects the sensory response. Cotton-based and cotton-polyester blend materials (with an extinguishing rate of ~60%) are the most sensitive to relative changes in response, while flax-based and polypropylene materials (with an extinguishing rate of ~40%) are less sensitive. The time taken to reach the final value varies greatly (8 min for cotton-polyester blends versus 20 min for linen). In one case, the nature of the changes differs: quenching on a cotton-polyester blend is accompanied by a bathochromic shift of the fluorescence maximum by 25 nm.

To better understand these effects, we examined the morphology of woven materials (see Figure 11). Photographs were taken under a microscope at 10× magnification. These photographs demonstrate that the sorption surface of cotton and semi-synthetic materials is larger than that of linen and polypropylene. This enables a greater quantity of dye to be absorbed during impregnation, resulting in a stronger sensory response.

This and previously mentioned nature of fiber makes materials on a woven base the undisputed leaders in terms of practical application, as the changes are clearly visible to the naked eye.

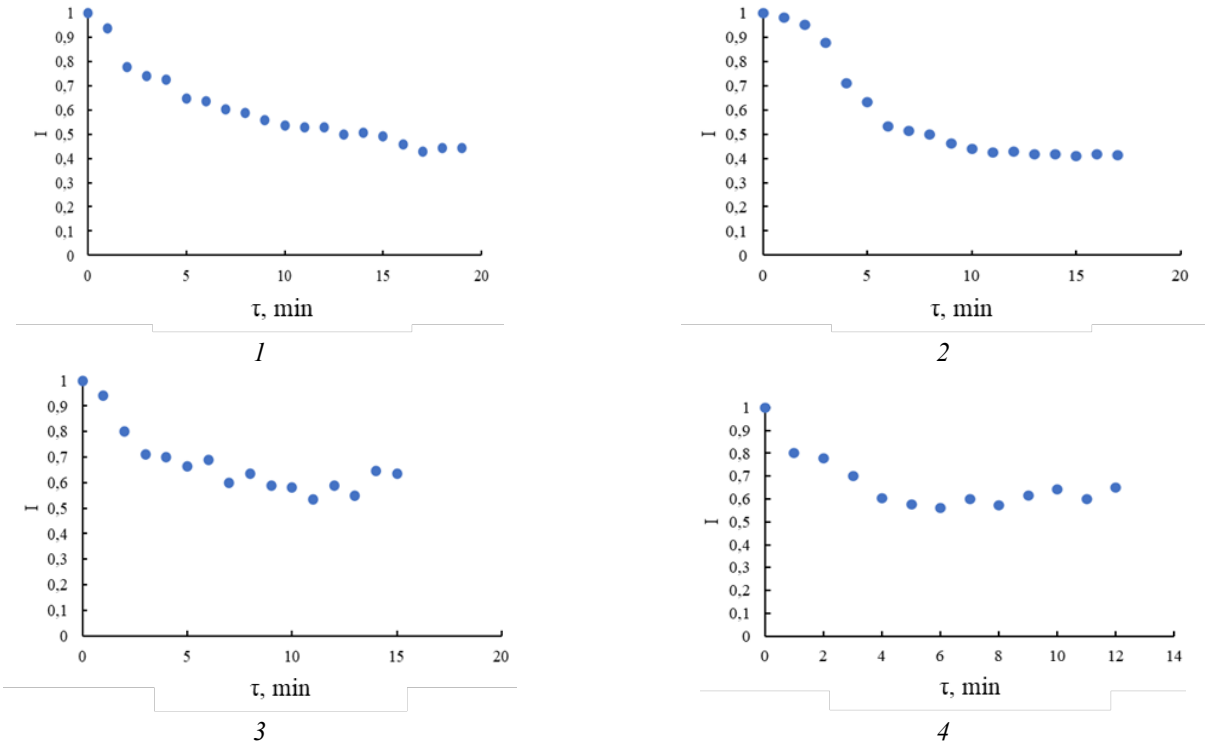

Figure 10. Change in fluorescence maxima with H_2S treatment time: 1 – BODIPY@Cotton; 2 – BODIPY@Semi-synthetic; 3 – BODIPY@Linen; 4 – BODIPY@Polypropylene.

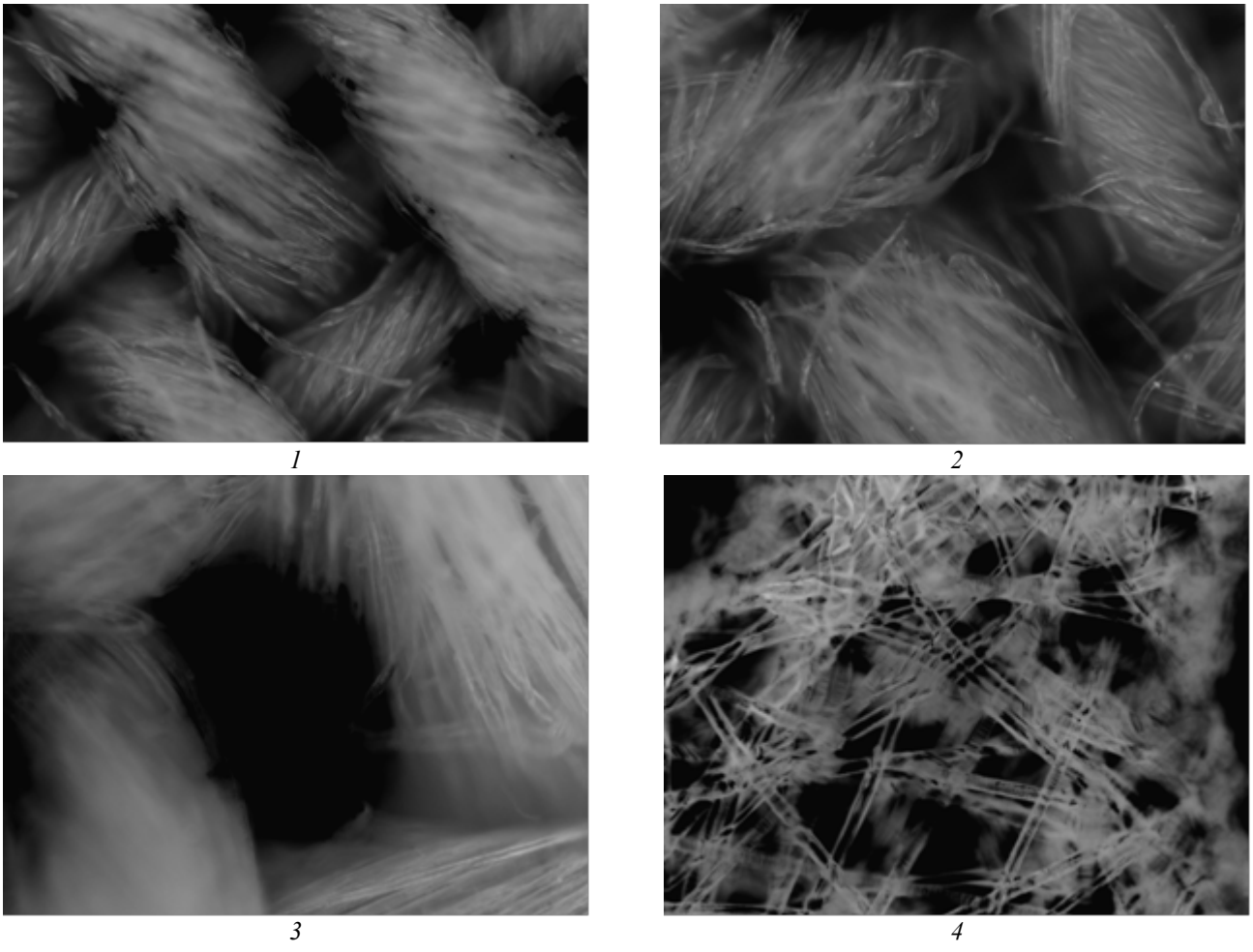

Figure 11. Photographs of woven materials taken under a microscope (10× magnification): 1 – BODIPY@Cotton; 2 – BODIPY@Semi-synthetic; 3 – BODIPY@Linen; 4 – BODIPY@Polypropylene.

Conclusions

In this study, we successfully demonstrated the transition from liquid-phase BODIPY fluorophore systems to solid-state sensory materials incorporated into cellulose and textile matrices. The immobilization of BODIPY dyes preserved their luminescent characteristics and enabled stable, reproducible optical responses to hydrogen sulfide vapors. The influence of the matrix composition, dye concentration, and morphology on the sensing performance was analyzed, revealing that the porous structure and surface chemistry of the support play crucial roles in analyte accessibility and signal stability. The obtained materials combine high fluorescence efficiency with environmental resistance and ease of fabrication, making them promising candidates for practical optical H_2S sensors. Future studies will focus on improving selectivity and exploring the use of other natural polymer matrices for multifunctional sensing applications.

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