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Modification of nickel micropatterns for sensor-active applications from deep eutectic solvents

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Abstract
In this work, we proposed a rapid single-stage laser-induced fabrication of bimetallic micropatterns on the oxide glass surface using deep eutectic solvents (DESs) consisting of choline chloride, citric acid along with nickel, copper and cobalt acetates as metallization solutions. The resulting bimetallic micropatterns were tested as working electrodes for non-enzymatic determination of dopamine. The linear range for dopamine detection was found to be 1–500 μM, with sensitivity of 340.4 μA mM^{-1} and 615.2 μA mM^{-1} and detection limit of 0.36 μM and 0.51 μM for Ni-Cu and Ni-Co sensor, respectively. For the first time, bimetallic Ni-Cu and Ni-Co structures have been obtained from DESs for high-performance dopamine detection with great potential for further application in non-enzymatic sensing and biosensing.

Keywords Deep eutectic solvents · Laser-induced deposition · Non-enzymatic sensors · Bimetallic materials

1 Introduction

An important objective for modern science is the development of new methods suitable for metallization of the dielectric surfaces (Huang et al. 2021; Zhang et al. 2019). In general, the methods of lithographic synthesis are used for this purpose (Windmiller et al. 2012). However, despite the undoubted advantages of this group of methods, lithography requires the use of masks, non-environmental reagents and multi-step experimental proce-

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dures (Yang et al. 2010). In this regard, additive methods of the electrode material fabrication, such as inkjet printing (Qin et al. 2016)·(Wang et al. 2022), a group of direct laser writing (DLW) methods, selective laser sintering (Binh Nam et al. 2021; Shin et al. 2020; Yoon et al. 2022), laser deposition (Butt et al. 2020; Mamonova et al. 2022) and others (Duobiene et al. 2022; Fiodorov et al. 2022), have attracted a lot of attention.

Single-stage direct laser printing processes are of particular interest in the context of this problem, which seems to be a promising alternative to lithography (Koritsoglou et al. 2019). Using these methods, the precursor metal source is irradiated with a laser (Mizoshiri et al. 2016). As a result, metallic micropatterns are formed within the laser spot (Binh Nam et al. 2021). It should be noted that no further sample processing is required after laser treatment, so the direct laser writing method provides a simple, waste-free and environmentally friendly approach for the electrode material fabrication (Mizoshiri et al. 2021; Tumkin et al. 2021). One of these methods is selective laser sintering (SLS), in which inks containing metal nanoparticles dispersed in a solvent are exposed by laser irradiation. The method of SLS allows to selectively create copper and nickel structures on the surface of polymers and other materials (Huang et al. 2021).

Another example of a single-step laser writing method is the laser-induced chemical liquid phase deposition (LCLD) of metals from solution (Khairullina et al. 2021b; Panov et al. 2020b; Smikhovskaia et al. 2019). This method involves a metal reduction reaction on the surface of a substrate within the focus of the laser beam with further formation of highly developed metal structures on its surface (Panov et al. 2020a). LCLD has many advantages: the method is simple, cheap and versatile that allowed to deposit a wide range of metals. However, the rate of metal deposition from aqueous and organic solutions is very low (~0.01 mm per second). In this regard, it has been proposed to use systems based on deep eutectic solvents instead of conventional aqueous or organic solutions. This replacement increases the speed of the process by more than hundred times. (Shishov et al. 2019). DESs are an eutectic mixture of proton donor and proton acceptor (Smith et al. 2014). Choline chloride, organic acids or sugars as donors and a salt (usually chloride or acetate (Shishov et al. 2019)) of the corresponding metal are used as a proton acceptor, donors and a metal source, respectively. All these reagents are water soluble and environmentally friendly, which makes it possible to classify the process of laser-induced reduction of metals from these solutions as “green chemistry” (Hansen et al. 2021). Also, an important advantage of using DES as a deposition medium is that the metal salt solutions are viscous enough to be applied as thin films on the substrate surface.

Previously, the physico-chemical factors affecting the formation of copper and nickel micropatterns have been optimized. In (Levshakova et al. 2022), it was shown that nickel micropatterns can be fabricated using systems based on choline chloride, nickel chloride or acetate and citric acid. It was demonstrated that the synthesized nickel micropatterns exhibit promising electrocatalytic characteristics for enzyme-free detection of dopamine (DA). DA is a vital catecholamine neurotransmitter that plays an important role in the proper functioning of the central nervous system, endocrine and cognitive development (Panov et al. 2020a). The presence of abnormal dopamine levels is a sign of neurological diseases such as Alzheimer’s and Parkinson’s (Wang et al. 2014).

In this work, bimetallic micropatterns based on nickel with copper and nickel with cobalt were obtained for the first time using the method described above. The co-deposition of nickel and the modifying metal onto pure substrates was carried out to obtain modified nickel

micropatterns instead of using previously obtained nickel micropatterns. In this approach, it was necessary to ensure a uniform distribution of metals over the sample surface. Materials of this type can exhibit properties substantially superior to the individual components. In addition, in many cases a synergistic enhancement of the electrocatalytic properties is observed when using polymetallic enzyme-free electrodes (Dindar et al. 2021; Han et al. 2020; Rajeev et al. 2021). It was found that hybrid bimetallic structures can take advantage of both metals to provide better catalytic activity (Khairullina et al. 2022; Khairullina et al. 2021a; Wu et al. 2017). We performed laser-induced deposition of bimetallic micropatterns from DES-based solution with dissolved nickel, copper and cobalt acetates as metal sources.

The applicability of the produced materials was demonstrated by the results of the electrochemical studies. In these experiments, the fabricated structures were used as working electrodes for non-enzymatic dopamine sensing. The overall results were also compared with those obtained for monometallic nickel micropatterns.

2 Experimental

2.1 Reagents, solutions and materials

Choline chloride, $Cu(CH_3COO)_2 \times 2H_2O$, $Ni(CH_3COO)_2 \times 4H_2O$, $Co(CH_3COO)_2 \times 4H_2O$ citric acid were purchased from Sigma Aldrich. Glass substrates were purchased from Levenhuk.

2.2 Preparation of DESs

For the preparation of deep eutectic solvents the necessary amounts of choline chloride, acid and metal salts were mixed. The ratio of acid, choline chloride and total dissolved salts was 1:1:1 mol. The vials with the mixture were placed in a desiccator at 110 °C. After the mixture was melted, it was placed on a magnetic heating stirrer and stirred at 120–140 °C until a viscous homogeneous liquid was obtained. After preparation, the obtained solutions were stored in the sealed vials. To place DES on glass, it was heated up to 80 °C in a desiccator, then applied to glass by direct transfer. The glass was placed on a hot plate and heated up to approximately 150 °C for a few minutes to allow the mixture to be spread evenly over the substrate with subsequent evaporation of any excess of water that might have infiltrated the DES during storage.

2.3 Procedure of laser-induced deposition

A detailed description of the experimental setup for direct laser writing and the schematic of the process were presented in our previous work (Fig. 1) (Shishov et al. 2021). A 532 nm diode-pumped continuous laser was used to carry out the laser deposition. The laser beam was focused on a vertically positioned substrate at the glass-solution interface. The substrate was placed on a computer-controlled XYZ stage, which was used to control the shape and size of the deposited micropatterns. A small amount of radiation was redirected to a webcam in order to monitor the deposition process. After the process, the removal of the unreacted DES was carried out using boiling water.

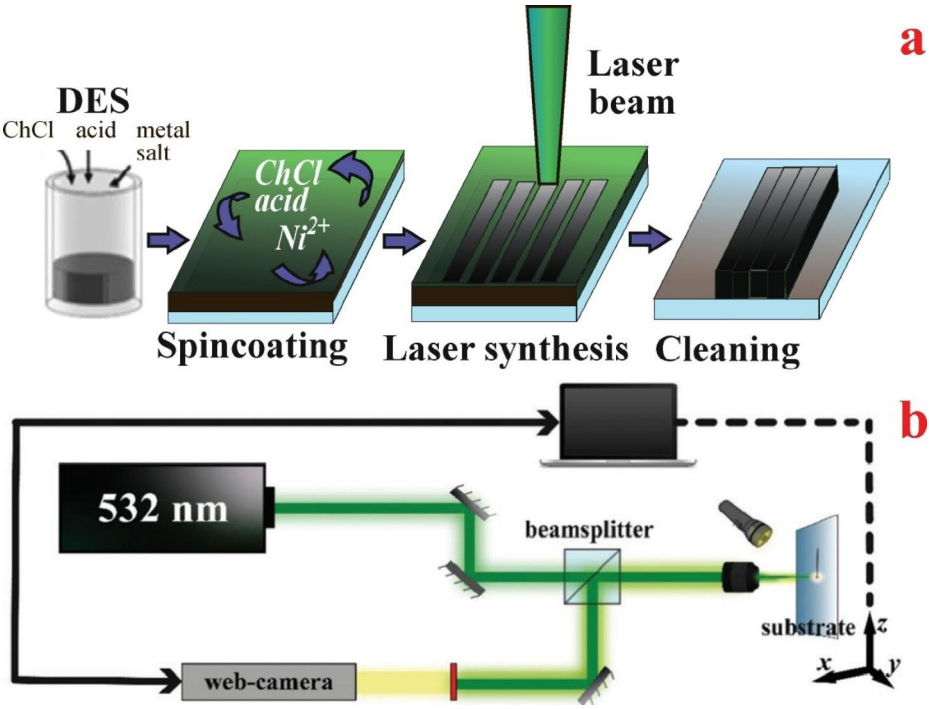

Fig. 1 The scheme of the procedure (a) and experimental set-up (b) for laser-assisted copper deposition using DESs

2.4 Characterization of the synthesized microstructures

The morphology of the fabricated structures was studied using scanning electron microscopy (SEM). The atomic composition of these structures was investigated using energy dispersive X-ray spectroscopy (EDX). The EDX-system was coupled with a Zeiss Supra 40 VP scanning electron microscope equipped with X-ray attachment (SEM, Zeiss Supra 40VP; EDX, INCA X-act, Oxford Instruments, UK).

The phase composition of copper deposits was evaluated using a Bruker D2 Phaser diffractometer equipped with a LynxEye detector (Bruker-AXS, Karlsruhe, Germany).

Electrocatalytic performance of the synthesized nickel and bimetallic micropatterns towards non-enzymatic sensing of dopamine (DA) was tested using voltammetric techniques at room temperature in a standard three-electrode cell. In this cell, the synthesized deposits were used as working electrodes, whereas platinum wire and Ag/AgCl electrode were used as counter and reference electrodes, respectively. Amperograms and cyclic (CV) voltammograms were recorded in 0.1 M PBS using Corrtest CS300 potentiostat (Wohan Corrtest Instruments Ltd., China). The scan rate of the potential was set at 50 mV s^{-1}. The solutions of DA of different concentrations were added to the background solution with simultaneous stirring.

Table 1 The compositions of DESs

№	Choline chloride (g)	citric acid (g)	$Ni(CH_3COO)_2 \times 4H_2O$ (g)	$Cu(CH_3COO)_2 \times 2H_2O$ (g)	$Co(CH_3COO)_2 \times 4H_2O$ (g)
1	1	1.38	1.74	-	-
2	1	1.38	0.87	0.76	-
3	1	1.38	0.87	-	0.87

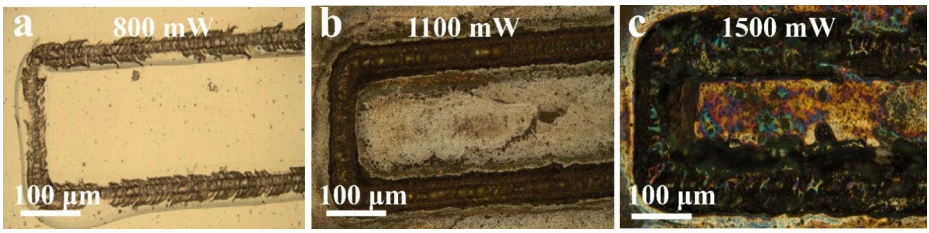

Fig. 2 Optical images of micropatterns deposited from DES containing Ni and Cu synthesized at 700 mV (a), 1100 mV (b), and 1500 mV (c)

3 Results and discussion

In order to determine the optimum DES compositions for the synthesis of micropatterns, we prepared DES solutions with different metal salt contents. As it has been shown previously (Shishov et al. 2021; Shishov et al. 2019), if the concentration of metal salt in the solution is low, the resulting deposits have discontinuous structures and have poor adhesion. On the other hand, if the concentration of metal salt is too high, DESs solutions have a tendency to delaminate. In view of the above, a molar ratio of 1:1:1 was chosen (choline chloride, citric acid, total metal acetates). Thus, we obtained the microstructures from the solutions, compositions of which are shown in Table 1.

The next stage of the experiment was focused on determination of the optimum parameters for laser synthesis. During the experiment, the laser power and scanning speed were varied between 500 and 2000 mW and between 0.025 and 2.5 mm s^{-1}, respectively. If the scanning speed is too high or the laser power is too low, the deposited structures would have ruptures and delaminate. If the power is too high or the scanning speed is too low, the components would burn off and the surface of the samples would be covered by residues of combustion products. The optimum deposition conditions were selected by evaluating the samples with an optical microscope (Fig. 2). It was shown that the samples with the fewest defects were obtained with a laser power of 1100 mW and a deposition rate of 0.25 mm s^{-1}.

Figure 3 shows optical and SEM images of the synthesized patterns deposited from DES solutions. In all three cases, it can be noted that the deposited patterns have a highly developed surface with no visible defects. According to XRD analysis, the deposits obtained from solution **1** mainly consists of metallic nickel and nickel(II) oxide. The deposits obtained from solution **2** consists of copper, nickel and there are also peaks of copper(I) oxide. In turn, the patterns obtained from solution **3** consist of metallic nickel and cobalt and NiO.

This observation corresponds to the results of EDX analysis (Fig. 4c, f). It is shown that the metallic structures are formed by a monolithic layer, the upper part of which is covered by micro- and nanostructured fragments consisting mainly of nickel and copper (solution **2**)

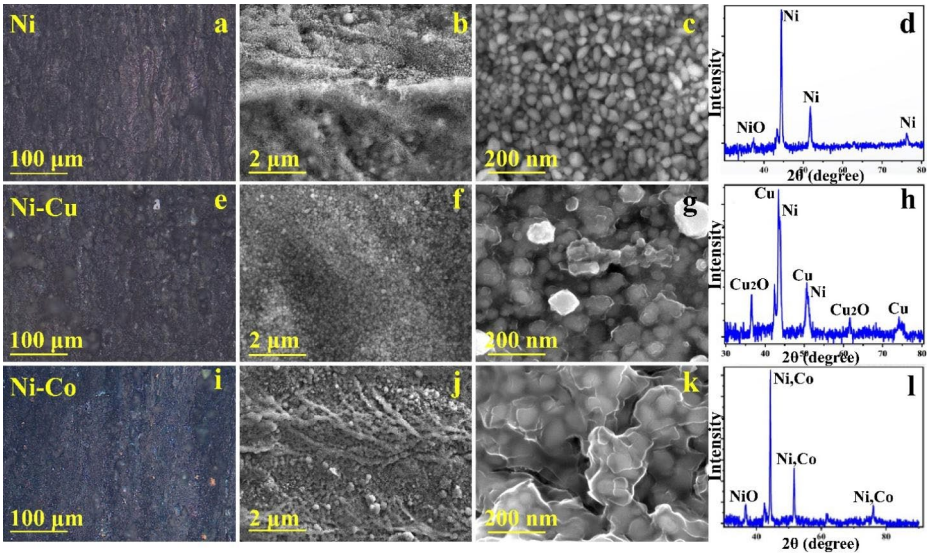

Fig. 3 Optical (a) and SEM (b and c) images, and X-ray analysis (d) micropatterns deposited from DES containing Ni; Optical (e) and SEM (f and g) images, and X-ray analysis (h) micropatterns deposited from DES containing Ni and Cu; Optical (i) and SEM (j and k) images, and X-ray analysis (l) micropatterns deposited from DES containing Ni and Co

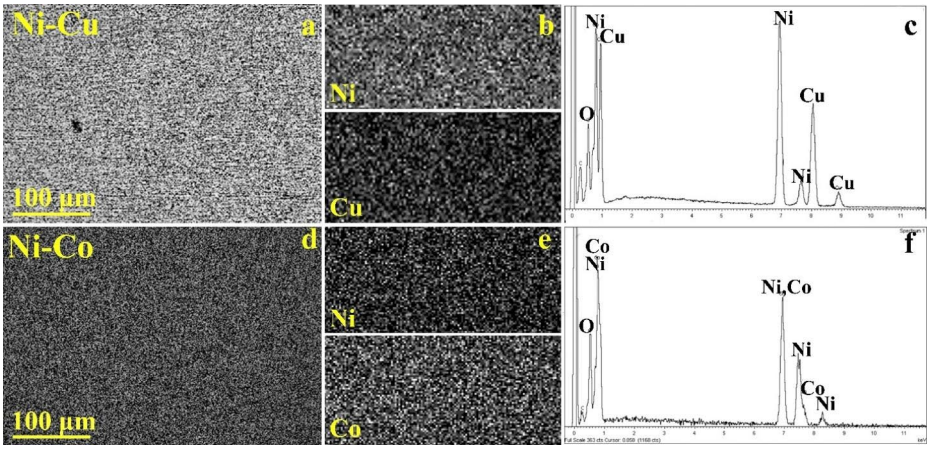

Fig. 4 EDX mapping and results of EDX analysis of Ni-Cu structures (a, b, c) and Ni-Cu structures (d, e, f)

as well as nickel and cobalt (solution **3**). The elemental mapping indicates that the metals in both cases are evenly distributed on the surface of the microelectrodes (Fig. 4a, b, d, e).

The deposited structures were used as working electrodes for the enzyme-free determination of dopamine concentrations. The sensory properties of the microelectrodes were investigated by recording cyclic voltamperograms in solutions containing different concentrations of dopamine (Fig. 5a-c). The CVs were recorded for different concentrations of ana-

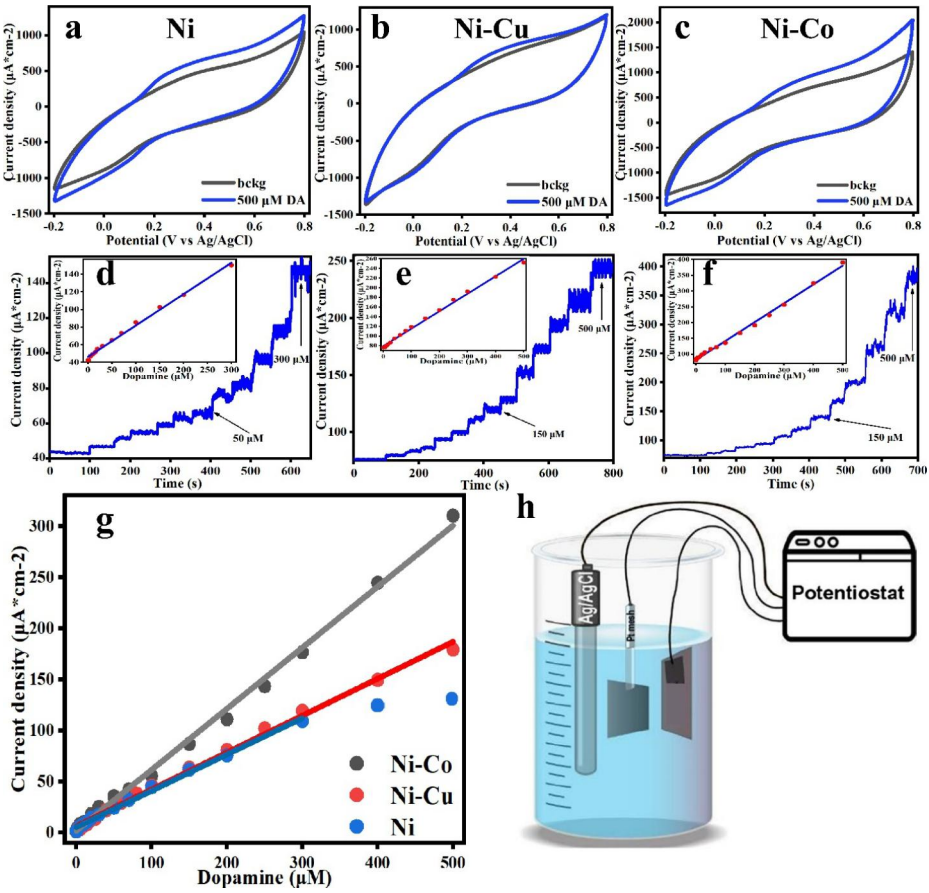

Fig. 5 Electrochemical studies of the synthesized electrodes: The CVs measured in 0.1 M PBS at different concentrations of dopamine (a- Ni, b- Ni-Cu, c- Ni-Co); the amperograms recorded in 0.1 M PBS with different concentrations of dopamine at 0.45 V potential (vs. Ag/AgCl); insets show the calibration curve obtained by plotting the measured Faraday current at 0.45 V (versus Ag/AgCl) as a function of dopamine concentration (d- Ni, e- Ni-Cu, f- Ni-Co); g - comparison of the calibration straight lines for all electrodes studied; h - three-electrode electrochemical cell

lytes for all electrodes to determine the operating potential for further chronoamperometric measurements. The amperometric responses of the synthesized electrodes were measured in a background solution of 0.1 M PBS with different concentrations of the target analyte (Fig. 5d-f). From these measurements, the calibration curves (Faraday current vs. analyte concentration) vs. voltammetric response were plotted. From the calibration curves, the main characteristics of the sensors such as sensitivity, detection limit and linear range were calculated (El Khatib and Abdel Hameed 2011). Table 2 shows the estimated electrochemical characteristics of the sensors presented in this work and their comparison with other sensor systems. It is obvious that the dopamine sensors synthesized in this study exhibit a wide linear range and high sensitivity.

From the results of the calculated electrochemical parameters, it can be seen that the modification of the nickel electrode allowed to extend the linear range (in the case of both

Table 2 Comparison of the electroanalytical performances of different modified electrodes for the detection of DA

Sensors	Analyte	Linear range, μM	LOD*, μM	Sensitivity, μA mM^{-1} cm^{-2}	References
Ni	Dopamine	1-300	0.74	343.5±15.2	This work
Ni-Cu	Dopamine	1-500	0.36	340.4±25.4	This work
Ni-Co	Dopamine	1-500	0.51	615.2±21.2	This work
Au@Pt/GO/GCE	Dopamine	0.5–177.5	0.11	329.0	(Yang et al. 2018)
UV LIG	Dopamine	0.5–3.0	0.5	93.0±2.8	(Santos et al. 2021)
CHI/VSG/PPY	Dopamine	0.1–200	0.019	632.1±23.5	(Liu et al. 2014)
PABSA-rMoS2	Dopamine	1–50	1.0	220.0±10.4	(Yang et al. 2017)
Au/GO/ITO	Dopamine	1–300	0.13	530.0±51.3	(Choo et al. 2017)

*LOD - limit of detection

bimetallic electrodes) and increase the sensitivity (in the case of Ni-Co electrode). The improved performance of bimetallic sensors compared to single metal based sensors can be explained by a synergistic effect (Wu et al. 2017). Therefore, it can be concluded that modifying nickel electrodes with copper and cobalt can significantly improve their electrochemical characteristics such as sensitivity and detection limits (LODs).

4 Conclusion

In this work, it was shown that the use of deep eutectic solvents in laser-induced deposition technique provides a simple and affordable approach for fabrication of bimetallic electrodes. A promising laser technology has been proposed to produce the high-performance sensor platforms for dopamine detection. Compared to many similar techniques, the proposed approach does not require the use of masks. Ni-Cu and Ni-Co electrodes have a highly developed surface area as well as excellent electrochemical characteristics. Compared to pure Ni electrodes, Ni-Co sensor showed a significant improvement in electrochemical performance. DA detection was achieved with high sensitivity of 615.2 μA/mM and low detection limit of 0.36 μM over a wide range of dopamine concentrations of 1-500 μM. In conclusion, the considered technique can be used for the synthesis and modification of the electrode materials with high electrocatalytic activity on the dielectric surfaces.

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Authors' contributions Conceptualization, I.I.T. and A.S.L.; methodology, I.I.T., E.M.K. and A.Yu.S.; formal analysis, E.M.K. and M.S.P.; investigation, A.S.L., E.M.K., R.N. and A.S.M.; data curation, E.M.K. and A.S.M.; writing—original draft preparation, A.S.L., R.N. and I.I.T.; writing—review and editing, I.I.T., E.M.K., A.Yu.S., and M.S.P.; visualization, E.M.K. and A.S.L.; supervision, I.I.T.; project administration, I.I.T.; funding acquisition, I.I.T. All authors have read and agreed to the published version of the manuscript.

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Data Availability The data presented in this study are available in the article.

Declarations

Ethical approval Not applicable.

Competing interests The authors declare no conflict of interest.

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