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# Thesis Changes Log

**Name of Candidate:** Timur Ermatov

**PhD Program:** Physics

**Title of Thesis:** Optical properties of hollow-core microstructured fibers modified by polymers and/or inorganic nano- and submicron particles

**Supervisor:** Prof. Dmitry Gorin

*The thesis document includes the following changes in answer to the external review process.*

Dear Reviewers,

I would like to say many thanks to you. I appreciate your time and efforts to provide very positive and in-depth comments on the draft of PhD thesis. I have revised the dissertation to address all issues raised by the Reviewers, and the changes are described in the point-by-point response below.

Sincerely yours,
Timur Ermatov

**Reviewer Nikolay Gippius:**

This thesis is devoted to the experimental investigation of functionalized optical fibers. Throughout the work, the author demonstrated the successful application of the layer-by-layer assembly technique for the modification of the fiber capillaries. The light guidance in the designed structures was characterized in the visible and Ir spectral ranges. The waveguiding losses were calculated using the cut back method. All the experimental findings were supported with the relevant theoretical calculations. Also, the author presents practical applications of the developed fiber-based sensors for the creation of an in-fiber multispectral refractometer. The topic is interesting to the community and attracts a lot of scientific interest. In this regard, the major achievements of this study are the following: the controlled shift of the transmission windows position of hollow-core fibers through the deposition of polymer nanofilms, the realization of real-time in-fiber refractometry measurements, the control of the roughness of the deposited films, in-situ monitoring of coating performance. The results were published at the peer review international level optics journals, such as "*Light: Science and Applications*", "*Optics Letters*" and "*Optics Express*".
Therefore, I recommend that the candidate should defend the thesis by means of a formal thesis defense.
Regardless of the general position evaluation of this thesis, I found few weak points to be addressed before the defense:

**Comment 1:**
The introduction section describing different types of microstructured optical fibers should be extended.

**Reply:**
An extra discussion about the fabrication of different types of microstructured optical fibers has been added to the section *2.5 Fabrication of hollow-core microstructured optical fibers*.

**Comment 2:**

More comparative data needs to be included, especially referring to the novel fiber-based sensors which were announced or published recently.

**Reply:**
The practical performance of the designed MOF-based sensor has been summarized and the references to recently published review articles describing fiber-based sensors have been included to the section *6.3.5 Refractive index sensitivity and figure of merit*. Novel references were added: A. A. Rifat, R. Ahmed, A. K. Yetisen, H. Butt, A. Sabouri, G. A. Mahdiraji, S. H. Yun, and F. R. M. Adikan, "Photonic crystal fiber based plasmonic sensors," Sensors and Actuators B: Chemical **243**, 311–325 (2017) and M. R. Hasan, S. Akter, A. A. Rifat, S. Rana, K. Ahmed, R. Ahmed, H. Subbaraman, and D. Abbott, "Spiral Photonic Crystal Fiber-Based Dual-Polarized Surface Plasmon Resonance Biosensor," IEEE Sensors Journal **18**(1), 133–140 (2018).

**Comment 3:**
The summary section can include more discussion about future research.

**Reply:**
An extra discussion about the future research and practical performance of the designed functionalized fibers have been added to the *Conclusions and future research* section.

**Reviewer Andre Skirtach:**

In his doctoral thesis, Mr. Timur Ermatov has conducted research work investigating different functionalization techniques applied for fabrication of advanced, in regard with sensing, coatings based on hollow-core fibers. Research area of optical fiber-based sensors is rapidly growing enabling development of novel and advanced devices with a broad range of potential and real applications. Thus, the study performed by the author is in the interest of the scientific community. The publications in the well-rated journals also justify the good quality of the research. Analyzing material of the thesis in more details, the title of the dissertation and the area of his specialization directly relate to the content of the thesis. And they are centered on the producing fiber-based optical sensors for biophotonic applications. The light guidance in optical fibers has been characterized both experimentally, employing scrupulous measurement, and theoretically, using advanced modeling and simulation. The measured optical transmittance is compared with the developed model and is applied for fibers of various geometries. The results are presented in a structured way with detailed description of experimental methods.
Overall assessment: the thesis represents in-depth characterization of LbL coated optical fibers. After correcting some minor points mentioned above, I recommend that Timur Ermatov should defend the thesis by means of a formal thesis defense.
The material is solid and is presented in a cohesive and organized way. However, I found few points that need to be addressed in the final version of the thesis:

**Comment 1:**
The author discussed only very limited materials used for the creation of advanced coating for the fibers. Can the reported approach be expanded for the other materials? Are there any limitations coming from the specific fiber structure which is different from planar surfaces?

**Reply:**
An overview of the existing materials which were successfully applied for the creation of LbL assembled coatings and the relevant studies were included into the section *3.3.3 Multilayered deposition process*.

**Comment 2:**
Page 48: Figure 2-16 presents sketches for the section discussing 1D materials: I would suggest here to clarify a reader how 1D geometry is implemented. It can be done either by adding a new schematic or explaining this in the text.

**Reply:**
The following discussion was included after the Figure 2-16 describing the appearance if sharp resonance.
"Since the dielectric permittivity of the prism is greater than that of the analyte under test, there is a critical angle at which total internal reflection occurs [126]. At some angle greater than the angle of total internal reflection, a sharp minimum is observed in the reflection coefficient, due to losses in the metal [126]." The novel reference was added: A. P. Vinogradov, A. V Dorofeenko, A. A. Pukhov, and A. A. Lisyansky, "Exciting

surface plasmon polaritons in the Kretschmann configuration by a light beam," Physical Review B 97(23), 235407 (2018).

**Comment 3:**
Page 63: it should be clear from description of figure caption if the thickness is measured in air or water.

**Reply:**
The following statement clarifying this issue was added to the figure caption: "The thickness of polymer coating was extracted by SEM analysis of dried samples".

**Comment 4:**
Page 66: please reformulate for clarity the following statement: "However, due to its small thickness (in the range of 3 nm), a smaller number of silica particles are adsorbed".

**Reply:**
This phrase has been rewritten as "However, due to the small thickness of a single PDDA layer (in the range of 3 nm), the deposition of intermediate PDDA layer between the silica particles does not create the necessary substrate layer contributing to the following adsorption of silica particles".

**Comment 5:**
Can the author say few words about the stability of the deposited coating?

**Reply:**
An additional discussion regarding to the stability of the polymer coating was included to the section *"3.4.1 Morphology of PAH-PSS multilayers".* The long-term stability and the stability to various environmental conditions such as temperature, pH levels, and ionic strength were investigated. These findings were related with the article T. Ermatov, R. E. Noskov, A. A. Machnev, I. Gnusov, V. Atkin, E. N. Lazareva, S. V German, S. S. Kosolobov, T. S. Zatsepin, O. V Sergeeva, J. S. Skibina, P. Ginzburg, V. V Tuchin, P. G. Lagoudakis, and D. A. Gorin, "Multispectral sensing of biological liquids with hollow-core microstructured optical fibres," Light: Science & Applications 9(1), 173 (2020).

**Comment 6:**
What about the practical applications of the proposed fiber sensors?

**Reply:**
The discussion of the possible practical application fields of the designed structures was included to the *Conclusions and future research* section: "From a practical point of view, the anticipated applications of functionalized fibers are fiber-based sensors, endoscopic probes, and drug delivery tools".

**Comment 7:**
Could the author add more comparative data between the designed sensors and the existing fiber-based solutions?

**Reply:**
The practical performance of the designed MOF-based sensor has been summarized and the references to recently published review articles describing fiber-based sensors have been included to the section *6.3.5 Refractive index sensitivity and figure of merit*. Novel references were added: A. A. Rifat, R. Ahmed, A. K. Yetisen, H. Butt, A. Sabouri, G. A. Mahdiraji, S. H. Yun, and F. R. M. Adikan, "Photonic crystal fiber based plasmonic sensors," Sensors and Actuators B: Chemical **243**, 311–325 (2017) and M. R. Hasan, S. Akter, A. A. Rifat, S. Rana, K. Ahmed, R. Ahmed, H. Subbaraman, and D. Abbott, "Spiral Photonic Crystal Fiber-Based Dual-Polarized Surface Plasmon Resonance Biosensor," IEEE Sensors Journal **18**(1), 133–140 (2018).

**Comment 8:**
Please add description on what are the losses upon coupling into fibers.

**Reply:**
The negligible coupling losses using free-space setup were highlighted in the section *3.3.4 Optical transmission of functionalized MOFs* as "Thus, the dimensions of fiber hollow-core in the range of ~240 μm allow the easy focusing of the incoming light by 10X objective minimizing the coupling losses".

**Comment 9:**

Page 85: Figure 4-4: is this a schematic or microscopic image? This should be clear from Figure caption.

**Reply:**
It has been specified in the figure caption that this figure is a schematic.

**Comment 10:**
Page 119: it should be clear from Figure caption to Figure 7-1 from where experimental and theoretical data are taken.

**Reply:**
The origin of theoretical and experimental transmission spectra has been specified in the caption to the Figure 7-1.

**Minor:**
- Page 52: ".. the angle dependent diffraction or color .." -> "wavelength" would be better here than "color", although it is clear what is meant.
- Page 61: "10X states for the 10X Olympus objective.." -> ".. 10X denotes a 10X Olympus objective..".
- Page 66: "..at their adsorption.." -> ".. is deposited to improve adsorption of silica particles".
- Page 74: "further growth of silica nanoparticle size leads to": I guess it is meant that adsorbing of nanoparticles of different (or larger) size, because particles do not seem to be growing on fibers.

**Reply:**
All the minor points were fixed in the main text of the thesis.

**Reviewer Kirill I. Zaytsev:**

In this thesis by Timur Ermatov, entitled "Optical properties of hollow-core microstructured fibers modified by polymers and/or inorganic nano- and submicron particles", several approaches to functionalize the microstructured optical fibers by different biocompatible and removable nanocoatings were developed, studied experimentally and, then, applied for sensing of liquid analytes. For this aim, the author proposed a fiber-based refractive-index sensor of liquids. It relies on measurements of the spectral shift of the Fabri-Perot resonances at the fiber output end, while a liquid analyte is streamed through the fiber capillaries via a judiciously-designed liquid chamber. The developed functionalized fibers possess high sensitivity to changes in the refractive index of a liquid analyte, along with a high energy efficiency. These forms advantages of the developed functionalized fibers over the existing ones in sensing applications. Microstructured optical fibers and fiber-based sensors attract considerable attentions in modern optics and photonics. This is justified by a comprehensive overview of this topic by the Author, as well as by increasing number of research papers in these demanding areas according to the Scopus, Web of Science, and other databases. This work is quite interdisciplinary in nature. In order to solve the problem posed in this thesis, the Author applied experimental methods of fiber optics, colloidal chemistry, biophysics, and other disciplines. In my opinion, properly selected methods of the experimental study ensure correctness of all Author's estimates. This thesis is clearly written and well organized. It presents novel scientific results in the areas of physics, optics and material sciences. It was shown that the obtained results are of practical importance and can be applied in different branches of fiber optics and optical sensing technologies, including sensing the refractive index of biological liquids aimed at medical diagnosis. The abovementioned minor issues and comments do not reduce the overall positive opinion about the PhD thesis by Timur Ermatov. The author has published his finding in top-rank journal in the areas of optics and photonics, fiber optics and optical materials technologies, including the Light: Science & Applications (Q1, Impact Factor: 17.782), Optics Letters (Q1, IF: 3.776), and Optics Express (Q1, IF: 3.894). He also presented his research results at several leading scientific events. Such a high publication level emphasizes novelty and importance of the obtained results.
Thus, I recommend that Timur Ermatov should defend the thesis by means of a formal thesis defense

**Comment 1:**
I have few minor comments to be addressed to the author. Nowadays, a number of hollow-core fibers exist, which exploit different fiber cross-section geometries and which rely on antiresonant (anti-resonant reflecting optical waveguide – ARROW), Fabri-Perot, photonic crystal (Bragg), or even mixed guiding mechanisms. All these hollow-core fiber designs have a potential in sensing applications. In my opinion, the work lacks some classification of the existing hollow-core fibers and description of the related guiding mechanisms, before selection of the particular hollow-core fiber geometry, that was considered in this study.

**Reply:**
The extended discussion about the light guiding principles in the existed solid-core and hollow-core fibers was included on page 27: "Solid-core MOFs exploiting the principle of total internal reflection for light guidance in a high refractive index core, represent the major group of these fibers, however, they can also guide light in a low refractive index core based on the photonic bandgap guidance [10]" and "In addition to all the other advantages and features of optical fibers, MOFs with their capability to guide light in the HC region and the strong interaction with an injected medium open new perspectives for their practical applications, which are not possible with all-solid fibers [10]". Also in the section *2.7 Light guidance in hollow-core microstructured optical fibers* extra discussion about the types of hollow fibers was added: "Hollow-core microstructured optical fibers formed by a microstructured array of cladding capillaries running along the entire fiber length that prevent light escaping from the central hollow-core core due to a photonic bandgap (bandgap fibers), topological effect (kagome fibers), negative curvature phenomenon (antiresonant fibers) or coherent Bragg scattering from the air-glass interface (Bragg fibers) [40]".

**Comment 2:**
Why did the author select this particular geometry of the hollow-core microstructured optical fiber for his experiments? Was the fiber cross-section geometry optimized somehow for the further functionalization and sensing of liquids? Please, comment.

**Reply:**
The following statements describing the relevance of the selected fiber structure to the coupling into the hollow-core region and the facilitation of in-fiber solution flow were included to the sections *3.3.4 Optical transmission of functionalized MOFs* and *6.3.7 IMOS in real-time. "Thus, the size of fiber hollow-core in the range of ~240 µm allows the easy focusing of the incoming light by 10X objective minimizing the coupling losses"* and *"The geometrical structure and the relatively large sizes of the hollow-core and the surrounding cladding capillaries allow the controllable and persistent stream of solutions inside the hollow channels at various flow rates (from 50 to 1000 µL min$^{-1}$)".*

**Comment 3:**
I guess the considered fiber operates in a multimode regime due to considerable dimensions of a fiber core. Please, comment, whether the large core diameter and, thus, the multimode operation regime are necessary for the considered sensing application.

**Reply:**
The light-guiding mechanism in the considered HC-MOF is well described by Fabry-Perot resonances in the wall of the central fiber capillary, and other capillary layers are needed to provide mechanical stability of the fiber, not affecting the light guidance. The main goal of our research is to present a simple technique for all-optical characterization of both liquid filling of HC-MOF and the coating performance in real time. To this end, the dips in the fiber transmission for the fundamental fiber mode only were used for the analysis since higher order modes demonstrate much stronger losses resulting in much lower sensitivity. Thus, higher-order modes and the modal effective indexes did not consider in this thesis. The following statement highlighting that the dips in the fiber transmission for the fundamental fiber mode only were used for the analysis was added to the main text on page 116: "Real-time tracking of the transmission spectra minima for the fundamental fiber mode only was achieved by means of LabVIEW software (Figure 6.11)".

**Comment 4:**
Please, comment, whether it is possible to supplement your analytical and experimental estimates of the Fabri-Perot resonances positions by some numerical analysis of the fiber guiding properties? Can such a large-cross-section fiber be modeled using, for example, eigenmode expansion technique in Lumerical MODE Solutions or COMSOL Multiphysics?

**Reply:**
The novel references describing the numerical analysis of the guiding properties at the similar structures were added to the main text into the section *3.3.1 HC-MOF samples*: A. Stefani, M. Stecher, G. E. Town, and O. Bang, "Direct Writing of Fiber Bragg Grating in Microstructured Polymer Optical Fiber," IEEE Photonics Technology Letters 24(13), 1148–1150 (2012) and L. Ding, Z. Li, Q. Ding, X. Shen, Y. Yuan, and J. Huang, "Microstructured optical fiber based chloride ion sensing method for concrete health monitoring," Sensors and Actuators B: Chemical 260, 763–769 and C. Wu, B. Guan, Z. Wang, and X. Feng, "Characterization of

Pressure Response of Bragg Gratings in Grapefruit Microstructured Fibers," Journal of Lightwave Technology 28(9), 1392–1397 (2010).

**Comment 5:**
Coupling and banding losses, mode coupling, and decoupling of core-guided modes into lossy cladding modes are quite interesting topics of fundamental and applied research topics. Are you planning to consider them for your functionalized fibers in future work?

**Reply:**
The following statements regarding to the direction of future work were added to the *8. Conclusions and future research section:* "Thus, considering the induced optical losses introduced by functional coatings, the post-processing techniques directing to the smoothing of the initial rough coatings would be an asset to the field of hybrid optical fibers.
The overall idea of functionalized optical fibers is the integration of materials, which are traditionally not used in fiber optics, directly into fiber capillaries, for a controllable tuning of the fiber optical properties and to bring novel functionalities expanding the fields of applications to novel critical areas such as biophotonics, environmental science or chemical and biochemical sensing [9]. The functionalized hollow-core fibers investigated in this thesis represent the structures with unique properties, that generally highlight the potential of this research field from a device and applications perspective. This research direction has been triggered by improvements in fiber fabrication technology and by the emergence of post-processing techniques, accompanied by the investigation of new material combinations. From a practical point of view, the anticipated applications of functionalized fibers are fiber-based sensors, endoscopic probes, and drug delivery tools".

**Reviewer Andrei V. Zvyagin:**

I examined PhD thesis "Optical properties of hollow-core microstructured fibers modified by polymers and/or inorganic nano- and submicron particles" by the candidate Mr Timur Ermatov. This thesis addresses an important problem of the application of microstructured fibres and photonic crystals for determination of refractive indices of liquids, including biological fluids. This research topic is hot because it responds to the need of rapid in-line sensing relying on accurate determination of the refractive index of analytes. The reported approach is proven superior to conventional Abbe refractometers in terms of versatility and application scope. The top result in my opinion is presented in Chapter 7 describing in-fibre multispectral optical sensing. This result has been reported in a premier journal in optics, Light: Science and Applications, and I believe this result is truly impressive. The candidate and co-authors have demonstrated determination of the refractive index of albumin, which was elusive due to its high sensitivity to solvents and physiological conditions. The introduced microstructured optical fibre (MOF) technique enabled these measurements alongside with the determination of the refractive index dispersion across the broad visible and near-infrared spectral range. This top result was prepared step-by-step, first, by careful characterisation of MOF devices modified by polyelectrolyte coating of their inner surfaces and testing their accuracy and reproducibility. The reported experimental techniques and methods for the functionalisation of MOFs with submicron and nanoscale particles to endow extra sensitivity to liquids and gases is worthwhile.
This thesis is well structured and written in clear concise language with appropriate number of schematic diagrams and graphical result presentations. The thesis introductory part contains comprehensive account of the state-of-the-art of the field, including optical fibres, MOFs and hollow fibers functionalisation approaches. The results are competitive at the international level, published in credible optics journals, such as "Light: Science and Applications", "Optics Letters" and "Optics Express".
I have no doubts that the candidate Mr Timur Ermatov deserves a PhD degree based on my examination of his PhD work. I suggest the following changes to the existing version of his thesis, which are optional and up to the candidate to implement:

**Comment 1:**
Could the author provide more examples of the existing point-of-care devices based on optical fibres and discuss their pro-s and con-s.

**Reply:**
Following the Reviewer's suggestion, the novel references describing the existed fiber-based point-of-care devices were added into the section *6.1 Introduction*: 191 - A. Ricciardi, A. Crescitelli, P. Vaiano, G. Quero, M. Consales, M. Pisco, E. Esposito, and A. Cusano, "Lab-on-fiber technology: a new vision for chemical and biological sensing," Analyst 140(24), 8068–8079 (2015), 192 - H. Zhu, S. O. Isikman, O. Mudanyali, A.

Greenbaum, and A. Ozcan, "Optical imaging techniques for point-of-care diagnostics," Lab on a Chip 13(1), 51–67 (2013), 193 - S. Tabassum and R. Kumar, "Advances in Fiber-Optic Technology for Point-of-Care Diagnosis and In Vivo Biosensing," Advanced Materials Technologies 5(5), 1900792 (2020), 194 - M. Soler, C. S. Huertas, and L. M. Lechuga, "Label-free plasmonic biosensors for point-of-care diagnostics: a review," Expert Review of Molecular Diagnostics 19(1), 71–81 (2019).

**Comment 2:**
Referring to Fig. 4-8, where the key results of the humidity measurements are presented, discussion of these results is largely missing. I suggest the candidate to provide a brief summary of the main findings, as well as the key merits and liminations of the reported technique for high-sensitivity sensing.

**Reply:**
The key advantageous of the proposed method for the humidity measurements were summarized in the section *4.2.4 Optical characteristics of water condensation on the sensor surface* and the following discussion was added: "The main advantage of the proposed sensor structures is the potential for the realization of multiple-zones sensitive surfaces based on hydrophilic and hydrophobic particles. Also, the designed coating allows the relative humidity detection in a wide range starting from ~5% and up to 95%. Moreover, the stability of the signal on the hydrophobic part makes it possible to simultaneously detect different gasses with no interference to the outside humidity level. Moreover, the psychical adsorption of water vapor allows its evaporation at the end of experiments and therefore a single sensor can be used multiple times".

**Comment 3:**
Does the reported approach allow decoupling the refractive index and thickness of the deposited layer?

**Reply:**
The reported approach for the extraction of both the refractive indices of the filling media inside the hollow-fibers and the thickness of the deposited coating based on the direct relation between these two parameters. Therefore, for the theoretical calculation of one of these parameters the preliminary knowledge of anouther parameter is necessary.

**Comment 4:**
How was the surface concentration of silica particles measured? Figs. 3.8-3.11.

**Reply:**
The following information about the concentration of silica particles and the method used for its measuring was added into the section *3.4.2 The structure of silica particle-based fiber coating*: "The final concentration for all samples of the silica particles was equal to 12.8 mg/mL and was measured by the dry residue method".

**Comment 5:**
Fig. 3-20 quality is poor, please replace.

**Reply:**
Figure 3.20 was removed.

**Comment 6:**
Fig. 3.8. The surface is ostensibly rough when coated with silica sub-micron particles, although the candidate infers best surface quality from these images. Is it based on SEM images or other observations?

**Reply:**
In the section *3.4.2 The structure of silica particle-based fiber coating*, there are the following sentence: "Silica nanoparticles at the diameters of 300 nm and 420 nm homogeneously cover the almost full surface of the core capillary after the single layer is deposited (Figure 3.8)". However, the term *homogeneously* implies to the closely packing silica particles which form a porous layer onto the fiber capillaries. The spherical shape of the particles defines the rough structure of the silica coating which is getting even more observable while the deposition of silica multilayers.

**Comment 7:**
I am curious what the speed of water through the smallest capillaries was to cause the deposition of 900-nm beads on the rear surface of the capillaries?

**Reply:**
The detailed explanation of this effect and the comparion of the flow speed at the central hollow-core and cladding capillaries is given in the section *5.3 Experimental section*. Below is a brief explanation.
This effect is attributed to the enormous difference in the hydraulic resistance of the central and side capillaries. In the framework of the Hagen–Poiseuille model, the capillary hydraulic resistance is inversely proportional to its radius to the fourth power that means that a flow rate in the side channels is at least 1000 times slower than in the core channel. The capillary hydraulic resistance can be expressed as:

$$R = \frac{8\mu L}{\pi r^4} \quad (5.1)$$

where $\mu$ is dynamic viscosity, $L$ is capillary length, $r$ is the capillary radius.

**Comment 8:**
All the studies were performed based on 6-cm long fibres; can the functionalisation techniques reported in the thesis be also used to modify longer sections?

**Reply:**
Since the experimental setup for the functionalization of fiber capillaries is based on automotive peristaltic pump which creates the controllable and persistent flow of applied solutions through the whole fiber length, this technique can be successfully used for the functionalization of longer sections. This statement was included to the main text in the section *3.3.3 Multilayered deposition process.*

**Comment 9:**
The transmission peaks and troughs are mostly periodic versus e.g. layer thickness. Does it cause problems with unwrapping?

**Reply:**
The critical problem that limits the performance of functionalization is the associated waveguiding losses originated from rough deposited surface. Regardless of the material combinations used for the layer-by-layer assembly, the optical losses increases proportionally to the number of deposited layers or coating thickness. This can be seen in Figures 3.15, 3.20 and 5.5. Therefore, the coatings at higher roughness lead to stronger light scattering that result in significant deformation of the spectral curves (transmission minima and maxima) (Figure 3.17).

**Comment 10:**
The conclusion and future work can be more elaborated.

**Reply:**
The section 8. Conclusions and future research was written. The novel statements regarding to the practical application areas for the proposed structures and the future work were included.

**Reviewer Sakellaris Mailis:**

The thesis authored by Timur Ermatov is investigating the topic of modifying microstructured optical fibres (MOFs) to tune their optical properties and to functionalize them for sensing applications. The candidate has successfully deposited various organic and inorganic substances onto the inner wall of hollow core MOFs and demonstrated the changes in the spectral transmission along with sensing performance.
The thesis represents a substantial amount of, mainly experimental, work that yielded excellent results, as demonstrated by the rich research output in terms of publications and conference contributions. The candidate has published six papers in four of which is the first author, including a review article, and is a co inventor in three patent applications. Furthermore, the majority of papers are published in high quality/impact photonic journals, which is evidence for the quality and novelty of the results.
The thesis represents a substantial contribution in the area of fibre sensing with notable results i.e. the multispectral optical sensing used to derive the refractive index of pure substances from measurements in solvents thus providing reference data for materials as well as real time concentration measurements.
The content of the thesis is in line with the intended work and the methods that have been used are appropriate for this research work.
The work is extremely relevant to applications in the area of bio medical sensing using microstructured optical fibres. This is evident from the number of patents that stem from this work.

The draft of the thesis that was available to me for review was not however free from imperfections and can be definitely improved. I have therefore chose the second option in the provisional recommendation that calls for revisions. These revisions are outlined below and are listed in an annotated version of the thesis.
A summary of general remarks for the improvement of the thesis by Mr Ermatov is given here.
A detailed list of the required revisions are included in the annotated version of the thesis that I am submitting along with this document.

**Comment 1:**
The introductory part to the thesis, and to some of the chapters requires reorganization as well as additional components.

**Reply:**
The introduction part was rewritten. In the second chapter the sentences which link the content of the sections were appeared.
"Sections 2.2 – 2.4 will introduce Maxwell equations, complex refractive index formula and the theory of effective medium approximation used for the extraction of refractive indices of single compounds out of complex mixtures".
"Section 2.5 is devoted to the description of the light guidance of the conventional optical fibers. Sections 2.6 – 2.8 introduce the other type of optical fibers which is HC-MOFs and give information about their fabrication technique along with the description of the main optical properties".
"The next section is devoted to the functionalized optical fibers and contains information about the materials, methods and applications of produced structures".
"Sections 2.13 – 2.15 introduce the concept for the creation of sensors based on photonic crystals modified by porous layers".

**Comment 2:**
The section on the outlook of the research is actually missing. The conclusion and outlook part must be rewritten to reflect the prospects of the research outcomes.

**Reply:**
The chapter *8. Conclusions and future research* was rewritten. The part of future work was added.

**Comment 3:**
There are several presentational deficiencies that have been identified

**Reply:**
All the suggested by Reviewer corrections were applied. The numerous English correction were made as well.

**Reviewer Andrei Sapelkin:**

In his thesis the author describes fabrication and experimental testing of functionalized hollow-core microstructured optical fibers (HC-MOFs). I found that the overall quality of the doctoral thesis as well as its structure are very good, with the latter requiring some changes (see below). The thesis topic is relevant to its actual content, while methodology used by the author is commensurate with the challenges being addressed in this work.
My view is that the subject of the thesis, its content and significance of the findings are certainly at the current state of the art in the field internationally. This is further supported by a number of high quality articles already published as a result of this work. Both the description of the work carried out under this project and the results so far clearly suggest high potential for a wide variety of bio-medical applications as well as in the field of fluid analysis in general.
Particularly notable is the amount of experimental work carried out by the author as well as the detailed account of all experimental activities, techniques and methodologies, which makes this thesis especially valuable to further the research in the field of development of HC-MOFs tailored for applications. I found that author provides adequate motivation for the work carried out as a part of the project with clear objectives for each of the research streams. The methodology selected to address the project challenges – detection of changes in a variety of biologically relevant fluids – is well justified, while the results obtained by the author are adequately discussed in the context of the project aims and objectives. Finally, conclusions are commensurate with and are well supported by the main findings of this work.

At the same time there are a number of corrections that I feel need to be completed before proceeding to the formal thesis defense. I outline some of these below and will also provide my handwritten notes in the thesis document to the author.

**Comment 1:**
As far as the scientific content and methodology is concerned, my main comment is that I found no information anywhere how the many theoretical calculations presented in the thesis have been carried out (e.g. who wrote the code or what software tools have been used etc.). It would benefit the subject delivery and thesis assessment to have this information in the thesis.

**Reply:**
The relevant references were included into the main text while the discussion of calculated data. These included the referring to both the appropriate equations within the thesis and relevant articles.
"Using the general transfer matrix method and taking into account the model of the Fabry-Perot resonator [41], the resonance positions of the investigated HC-MOFs have been calculated *(Equation 2.13) using MATLAB software* referring to the minima of transmission spectra" – section 3.4.5 Demonstration of mid-IR guidance in designed HC-MOFs.
"Figure **Error! No text of specified style in document.**-1: Polymer coating thickness versus the number of PE bilayers. The thickness is fitted to obtain the coincidence of the minima positions for both the experimental and calculated transmission spectra *using MATLAB software (Equation 2.13)*. The thickness of polymer coating was extracted by SEM analysis of dried samples" – section 3.4.1 Morphology of PAH-PSS multilayers.

In addition, the software tools used for the calculations and the information about the creators of the codes were indicated in the text.

**Comment 2:**
The abstract is currently a mixture of background and some of the results – this has to be adjusted to contain a brief description of the purpose/rationale for the work, methodology applied in course of the project and the key results/outcome.

**Reply:**
The abstract section was rewritten to make in more concise and clear. Also the sections of Chapter 2 were rewritten and the sentences that link the content were added.

**Comment 3:**
A number of sections (e.g. 2.10-2.12) are introduced without motivation/rationale, which results in interrupted logical flow. In general, I suggest to have an introductory and a concluding sentence to each of the section to maintain logical flow in the overall document. For example, something along the lines "In the next section we will introduce THIS and THAT to address/explain/resolve THIS and THAT", and/or something like "In this section we will look into THIS and THAT in order to address THIS and THAT". There should also be some concluding remarks at the end of Chapter 2.

**Reply:**
The motivation for every section of the second chapter was included making the reading of the thesis easier. Each section of the second chapter close with a link-sentence describing the importance of the next section.

**Comment 4:**
I also found that Chapter 4 in the current thesis structure significantly interrupts the overall logic of the work carried out in the project and the overall thesis structure whereby each chapter builds on the results of the previous one. As such, I would suggest it should be moved to the end of the thesis.

**Reply:**
The Chapter 2 was rewritten. In particular, the sentences that explain the overall logic of the thesis structure were included. This makes the appearance of the Chapter 4 in such an order more logical.

**Comment 5:**
I note that not all of the abbreviations used in the thesis are currently listed in the List of Symbols, Abbreviations. Besides, abbreviations need to be rearranged in alphabetical order.

**Reply:**

The missing abbreviations were included to the abbreviation list. All the abbreviations were rearranged in alphabetical order.
AFM – atomic force microscopy
FOM – figure of merit
FWHW – full width at half maximum
LC – liquid cell
LMR – lossy mode resonance
LPG – long period grating
LSPR – localized surface plasmon resonance
MRI – magneto resonance imaging
OFS – optical fiber sensor
PBS – phosphate buffer saline
PC – photonic crystal
RIS – refractive index sensetivity
RIU – refractive index unit
QCM – quartz crystal microbalance
SFM – surface force microscopy
SPR – surface plasmon resonance
TFBG – tilted fiber Bragg grating

**Comment 6:**
There are a few issues with the document formatting with figure captions split between pages. This can be addressed by relatively simple text rearrangements. The same can be said about some of the sections that are finished with equations, figures or tables: this should be avoided– a sections (and a chapter too) should finish with a concluding sentence or two, preferably logically linking it with the subsequent section (or chapter).

**Reply:**
The thesis was structured properly, all the figure captions became without breaks and the new chapters start form the new pages.

**Comment 7:**
Finally, there are number of English language corrections that I have made – these should be implemented to improve the clarity of the delivery.

**Reply:**
All the suggested English corrections were accepted within the thesis.