

Microstructured fiber refractometer with scalable performance for *in situ* detection of dissolved gases in aquatic environmental monitoring

Keywords: microstructured fibers, photonic crystal fibers, capillary fibers, plastic fibers, *in situ* measurements, refractometry, dissolved gas sensors, mode loss, evanescent fields, synchronous detection

Description of PhD research project

Context: A major societal challenge facing the world today is climate change (CC) caused by global warming (GW) attributed to the increasing concentration of greenhouse gases (GHGs) in the atmosphere [1]. Methane (CH₄) is recognized as the second contributor to GW [2] after carbon dioxide (CO₂) due to its higher global warming potential (GWP) of ~86 relative to CO₂ over a 25-yr period. While 20% of the temperature increase observed during the last two decades are attributed to CH₄ emissions, both CH₄ and CO₂ make up more than 90% of the total GHG contributions to GW. Unlike anthropogenic sources that are now well characterized and quantified, natural sources are still poorly constrained in terms of dynamics, processes, reservoir and stability [3]. The main difficulty lies, therefore, in estimating natural CH₄ and CO₂ emissions from aquatic environments which contain unknown quantities of emitting sources [3] that are controlled by various biological, geological and physical processes [4].

In the long term, CC has the potential to increase CH₄ and/or CO₂ emissions by impacting the global temperature, hydrology of the wetlands, global sea level and chemical composition of the oceans, the most obvious consequences being ocean acidification and coral bleaching. Robust high precision *in situ* sensors capable of detecting and monitoring long-term emissions of these aquatic gases with high spatial and temporal resolutions are thus critical for more accurate estimation of their global budget and biogeochemical cycles. This can, in turn, facilitate the implementation of more efficient environmental strategies to mitigate global warming over a realistic timescale [2].

To address the above challenge, this PhD project will develop a next-generation fiber refractometric sensor for high resolution, high sensitivity *in situ* detection of dissolved CH₄ and CO₂ over an ultra-wide concentration range in the aquatic environment [5-7].

Objectives: This PhD research will build on previous refractometer development through several research projects (ANR FRAME, ANR-DFG PROMETHEUS, etc) to design a robust high-precision fiber refractometer prototype dedicated to long-term *in situ* detection of dissolved CH₄ and CO₂ gases in the aqueous environment, by harnessing the combined capabilities of different fiber technologies, such as multimode and microstructured fibers.

This research will focus on microstructured optical fibers, including photonic crystal fibers (PCFs), capillary fibers (CFs) as well as micro-patterned plastic fibers (PFs) that will be investigated as the sensing element as they offer propagation characteristics that are not achievable in conventional optical fibers. PCFs, although initially designed for optical telecommunications, are increasingly exploited in nonlinear optics, optical continuum generation, and, more recently, metrology, particularly in biochemical sensing applications, where the air-holes render these fibers particularly advantageous for *in situ* refractive index (RI) measurements. Nevertheless, filling the air-holes with analytes is not an optimal solution as renewing the sensing volume in these air-holes is a complex issue. CFs are a recent class of fibers that, to date, have been widely used for high optical power transmission as well as in continuum light source generation. Here, their highly configurable geometry will be investigated using fusion splicing to obtain an optimum microstructure for mode propagation in the outer capillary of the fiber. Patterned “plastic” fibers or PFs, fabricated from polymers or plastics and exhibiting generally higher RIs than conventional silica optical fibers, will be investigated for their potential to probe very high gas concentration.

We target better than 10⁻⁶ RI unit (RIU) resolution across a dynamic range extending from 1.3 RIU to beyond 1.65 RIU (for example, 5.5 x 10⁻⁶ RIU corresponds to ~1 nmol/L CH₄ [8]) for probing a very wide range of concentrations of dissolved CH₄ and CO₂. The design strategy will be built on our current MSF models to extend their capacity for fast, accurate sensor simulation enhanced by data-backed inputs (including sensing fiber geometry, optical characteristics, fabrication and fusion-splicing properties, etc) to enable rapid sensor prototyping via iterative data-processed or parametric scalable engineering. Finally, probe interchangeability will also be implemented in the refractometric sensor to facilitate laboratory tests and, more significantly, for preventive maintenance purposes.

Proposed Approach and Scientific Innovation: Principal work will concentrate on analyzing the evanescent wave penetration into the transverse structure of the selected MSFs in order to propose a suitable sensing fiber geometry that can enable massive dispersion of propagating modes from the core to the fiber periphery [9,10]. Studies will next be carried out to enhance their sensitivity to RI variation in the external medium (sensing environment) that will modify the propagation characteristics of the excited optical modes. RI variation will, in turn, lead to variation of the optical power propagated in the fiber element that can then be accurately measured by a synchronous photodetection system.

The approach proposed here is to enhance evanescent wave interaction with the analyte in an out-of-fiber configuration. Effort will thus focus on investigating different fiber geometries and microstructures necessary to enhance their sensitivity to minute RI variation induced by the change in concentration of the measurand gases while reducing or even eliminating other external perturbations to eliminate cross-sensitivity to other parameters. To achieve this, the microstructures of both

PCF and CF will be engineered to propagate the excited modes in the effective cladding instead of in the core region to potentially enable orders of magnitude improvement in interaction with the external medium. This will be carried out by developing a physics-based model able to predict and empower intense mode rejection of the propagating core modes toward the outer cladding region that is exposed to the external environment. For higher RI measurement range, polymer/plastic fibers will also be studied. These new MSF designs will then be fabricated in collaboration with XLIM research institute, followed by their characterization and validation in the laboratory for RI measurements.

To sensitize the dissimilar fiber refractometer for specific gas detection, the exposed fiber sensing element will be functionalized by a thin layer of sensitized polymeric film incorporating either molecular traps [8] or metal-organic frameworks with customized cavities. Additionally, the refractometer prototype will be designed to incorporate probe interchangeability that will allow the fiber-based sensing element to be replaced with ease. This capability will not only enable various dissimilar-fiber probes to be validated rapidly by simply switching probe elements on the refractometer mainframe during laboratory tests, but, more importantly, also facilitate any worn or damaged probes to be rapidly replaced with minimal loss in performance characteristics in the context of preventive maintenance. The next phase will then implement these microstructured fibers as high-performance CH₄ and CO₂ gas sensors that will be validated by a characterization campaign on a dedicated laboratory test bench. A low-energy anti-biofouling system will also be implemented to reduce or suppress the build-up of organic matter on the surface of the sensing element during submersion in water. The sensor prototype will finally be qualified for continuous dissolved gas detection in collaboration with GET-OMP under simulated laboratory conditions before deployment to a selected test site for preliminary *in situ* trials in the aquatic environment.

Working environment: This PhD will be conducted at LAAS-CNRS, within the Optical Sensors and Intelligent Integrated Systems team located at the ENSEEIHT site. The candidate will be enrolled in the GEETS (Electrical Engineering, Electronics, Telecommunications and Health) Doctoral School, and is expected to travel to XLIM in Limoges for novelty fiber design and manufacturing (3/4 weeks per year). Other travel arrangements will be decided later.

Collaborations: XLIM (novelty fibers) and GET-OMP (environmental sensing)

PhD supervision:

Dr Han Cheng SEAT and Dr Olivier BERNAL (co-supervisor)

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Complementary information:

Applicants are expected to have the following **skills**:

- good knowledge in one or several of the following domains: optics, fiber optics, sensors and instrumentation, refractometry, modeling (COMSOL, Lumerical, Matlab); some notions of chemistry, basic signal processing
- ability to work in a research team
- autonomy and a keen sense of problem solving
- critical thinking and analytical skills
- good writing skills for preparing scientific articles
- English proficiency is compulsory, knowledge of French will be an advantage

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