Use of liquid-core waveguides as photochemical reactors and/or for chemical analysis – An overview

Groeneveld, I.; Jaspars, A.; Akca, I.B.; Somsen, G.W.; Ariese, F.; van Bommel, M.R.

DOI
10.1016/j.jpap.2023.100168

Publication date
2023

Document Version
Final published version

Published in
Journal of Photochemistry and Photobiology

License
CC BY

Citation for published version (APA):
Use of liquid-core waveguides as photochemical reactors and/or for chemical analysis – An overview

Iris Groeneveld a,*, Amber Jaspars a, Imran B. Akca b, Govert W. Somsen a, Freek Ariese b, Maarten R. van Bommel c, d

a Division of Bioanalytical Chemistry, Amsterdam Institute for Molecular and Life Sciences, Vrije Universiteit Amsterdam, De Boelelaan 1108, Amsterdam, 1081 HZ, The Netherlands
b LaserLab, Department of Physics and Astronomy, Vrije Universiteit Amsterdam, The Netherlands
c Analytical Chemistry Group, van ’t Hoff Institute of Molecular Sciences, University of Amsterdam, Science Park 904, Amsterdam, 1098 XH, The Netherlands
d Conservation and Restoration of Cultural Heritage, Amsterdam School for Heritage, Memory and Material Culture, University of Amsterdam, P.O. Box 94552, Amsterdam, 1091 GN, The Netherlands

ARTICLE INFO

Keywords:
Photoreactor
Photochemistry
Liquid-core waveguide
In-situ analysis
Spectroscopy

ABSTRACT

The study of photochemical reactions is of great importance in many fields including the pharmaceutical, food, and paint industry. Most of these photochemical processes are being studied to better understand how to apply them for a specific purpose or how unwanted effects can be prevented. Advances are still being made in photoreactor design, where in-situ detection of the involved reagents and products is an important development. Liquid-core waveguides (LCWs) allow simultaneous illumination and optical assessment of liquid samples and, therefore, constitute one way of combining photoreactor design with on-line or in-situ analytical detection methods. LCWs possess several interesting characteristics, such as low light loss, increased optical path length, and possibilities for coupling with spectroscopic techniques. The current review discusses the state-of-the-art of LCWs applied as photoreactors, for analytical detection, and their combinations. We discuss the differences between several total internal reflection (TIR)-based LCWs, including polymer and polymer-coated capillaries, and silica aerogels, and interference-based waveguides, including Bragg fibers, holey fibers, Kagomé fibers and anti-resonance reflecting optical waveguides (ARROWs). Assessed characteristics include the (freedom of) design, the degree of light attenuation, the range of transmittable wavelengths, gas permeability, compatibility with analytical techniques, current challenges, and applications.

1. Introduction

Photochemistry in this review includes any chemical reaction or modification of a molecule initiated by visible (Vis) or UV light. Such processes generally start with the excitation of a molecule either directly upon absorption of a photon or indirectly upon energy transfer via a photoexcited photosensitizer or photocatalyst. There is an interest in studying and applying photochemistry for many areas, including medicine [1–4], water purification [5–7], food quality conservation [8–10], and cultural heritage [11–13], among many others. A photochemical reaction can be initiated on purpose, for instance in photochemotherapy where light is used to ‘activate’ a drug in combination with an oral or topical photosensitizer for the treatment of diseases [4], or for the purification process of drinking water, where high-intensity UV lamps are used to degrade potentially harmful chemicals [7]. If such a reaction leads to molecular fragmentation or loss of functional chemical properties, we usually speak of light-induced degradation or photodegradation. Photodegradation may also be an unwanted process. Examples are change of quality of taste and color of food products, appearance of harmful byproducts during irradiation of waste water, or color fading of paints [14,15].

1.1. Studying light-induced degradation – conventional approaches

Suitable analytical techniques allowing the detection of changes in the molecular structure must be available in order to probe and understand photochemical processes. Ideally, monitoring photochemistry is done in situ (i.e., in the reaction mixture) so that the chemical process...
can be studied in real-time and in a non-invasive manner, requiring as few analytical steps as possible. However, in practice, these conditions are difficult to meet. Traditionally, photochemical reactions are performed in relatively large batch reactors that can be difficult to homogenize and hard to irradiate in a homogeneous way. Distributing the available light over a large area implies a relatively low irradiance and therefore relatively long reaction times. Moreover, these approaches typically require sampling at specific time points in order to monitor the reaction off-line, making it labor-intensive. One way to resolve some of the above-mentioned challenges is by decreasing the volume of the cells (photoreactors) to enhance irradiation efficiencies and to increase the reaction kinetics. On-line monitoring of the extent of degradation would have several practical advantages and circumvent some sources of error.

1.2. Optofluidics

A solution for in-situ monitoring of photochemistry has often been found in optofluidics, which is the field where fluids and optics are combined to (i) guide the direction of light by means of a fluid, or (ii) analyze fluids or compounds/particles in fluids by means of light. Microfluidic optofluidics or lab-on-a-chip devices result in faster mixing of reagents and more efficient irradiation of the whole sample due to their small volumes. Monitoring of light-induced reactions can be achieved by coupling microfluidic photoreactors with analytical techniques, such as mass spectrometry (MS) [16], nuclear magnetic resonance (NMR) [17], liquid chromatography (LC) [18,19], and UV/Vis absorption [20,21], fluorescence [22] and Raman spectroscopy [23,24]. Sun et al. [2] presented a droplet microfluidic platform for continuous flow-based photochemical reactions with on-line analysis by electrospray ionization (ESI) MS. The generated droplets (5-10 nL) were irradiated in a continuous flow using a blue LED array that was placed above the microfluidic device. This enabled the simultaneous irradiation of up to 100 nL-sized reaction droplets at the picomolar level and a high analysis throughput of 0.3 samples s\(^{-1}\). Azzouz et al. [7] developed a microfluidic flow reactor with zinc oxide nanowires as a photocalytic nanomaterial for water purification. The samples were irradiated with a UV lamp (365 nm) for only 5 s at a distance of 10 cm from the 3-cm\(^2\) microfluidic device, which resulted in degradation of up to 95%. The reduction of sample volumes in combination with microfluidic channels also comes with challenges. Irradiation of a sample in a flat, chip-based microreactor is generally performed by illumination perpendicular to the flow cell through some optical window, which could be inefficient due to scattering losses at the surface and focusing of the beam to match the size of the microreactor channel. In addition, higher limits of detection (LOD) may be the result when spectroscopic analysis is performed in a perpendicular fashion as a result of the short optical path lengths. Irradiation from within or along the inner volume of the photoreactor is a way to increase the irradiation efficiency and the light intensity received by the sample, enhancing the photochemical reaction rates and, therefore, shortening analysis times [25,26]. This way of irradiating also increases the optical path length for spectroscopic methods when the detector is positioned at the other, distal end of the photochemical cell, which results in higher sensitivity.

1.3. Liquid-core waveguides as photoreactors

The principle of waveguiding can be used to increase irradiation efficiencies in photochemical reaction cells [20,27]. Hollow waveguides are capillaries that can guide light along their axial direction, thereby completely irradiating a liquid sample if loaded inside the capillary core, making it a liquid-core waveguide (LCW). Waveguiding can be achieved by different principles [27]. A frequently used approach is the application of total internal reflection (TIR), where incoming light is guided along the length of the LCW due to differences in refractive index between the cladding material and the sample solution inside the core [28]. A second approach is based on the use of wave interferences to localize the electromagnetic wave, where multiple layers of materials are used as cladding. This creates a refractive index profile in the cross-section of the waveguide, which initiates multiple reflections of the electric field, which can interfere constructively or destructively [29].

1.4. Waveguides and chemical analysis

Waveguides have been used to increase the detection sensitivity in absorbance-based methods [30]. The large optical path lengths (\(L\)) offers increased absorbance (\(A\)) as follows from Lambert-Beer’s law (Eq. (1)), where \(I_0\) is the molar absorption coefficient, \(C\) the concentration, and \(I_0\) and \(I\) the intensity of the transmitted light in the absence and presence of the analyte, respectively [31,32].

\[ A = \log \left( \frac{I_0}{I} \right) = \varepsilon LC \]  

(Eq. 1)

The use of LCWs in combination with on- or in-line detection for studying photochemistry provides an interesting solution to the irradiation and detection limitations that are faced with microfluidic chips. With LCWs both irradiation and detection are along the axis of the waveguide, yielding improved illumination efficiency and detection sensitivity. Furthermore, in spite of the increased optical path length, the inner volume can remain low by using small diameter cores.

Several reviews have been published about specific types of waveguides for in-situ detection or sensing purposes, such as photonic crystal fibers [33-36], Bragg fibers [37], and anti-resonance reflecting optical waveguide (ARROW) fibers [38], and leaky waveguides [39]. Other authors discussed specific applications, e.g., fluorescence-based fiber optics or biosensors [40,41]. In 2008, Schmidt et al. [29] presented a review article on developments and the current status of LCWs in optofluidics. Four years later, Pasco et al. [42] described applications of LCWs in flow-based analysis techniques. In 2018, Pidenko et al. [43] published a review on the current state-of-the-art of biosensors based on various types of optical fibers loaded with a solution inside the hollow core. However, a comprehensive review on waveguides with in-situ or in-line spectroscopic techniques to study and monitor photochemical processes is currently lacking. Most recently (in 2019), Rehm et al. [44] provided an extensive overview on the developments of continuous flow photoreactors and their applications to photochemical synthesis. Waveguides were also mentioned as potential candidates, but coupling with analytical techniques was addressed only briefly.

Several reviews aim to point out the benefit of a certain type of waveguide in the field of photochemistry or analytical sciences. The purpose of this review is to report on the developments in both fields, with a focus on where photochemistry and spectroscopic analysis are performed simultaneously. Here, we describe different types of waveguides that have been applied as microreactors in photochemistry and/or for analysis, with emphasis on the differences between several TIR-based (i.e., polymer and polymer-coated capillaries, and silica aerogels) and interference-based LCWs, including Bragg fibers, holey fibers, Kagome fibers, and ARROWs. The waveguides were assessed based on their design and flexibility of their design, optical loss, applicable wavelengths, compatibility with analytical techniques, applications, and current challenges.

2. Total internal-reflection liquid-core optical waveguides

In the second half of the 20th century, advances were made on LCW spectrophotometric cells with a longer path length for enhanced absorbance and sensitivity while maintaining small sample volumes. First, LCWs were often tubes made of quartz or glass coated with highly reflective metals containing a liquid core, based on the principle of reflection or TIR exploiting Snell’s law (Eq. (2)). This law describes the refraction (\(\theta_2\)) of a light beam with an angle of incidence (\(\theta_1\)) hitting the
interface of two transparent media of different refractive indices \((n_1, n_2)\) [45]:

\[
\frac{\sin(\theta_1)}{\sin(\theta_2)} = \frac{n_1}{n_2}
\]  

(Eq. 2)

TIR occurs when \(n_2 > n_1\) and the angle of incidence is equal to or larger than the critical angle \((\theta_c)\), which is determined by Eq. (3). To successfully exploit this effect, the core of the LCW (e.g., the solvent or sample solution) should have a higher refractive index (RI) than that of the cladding material [28],

\[
\sin\theta_c = \frac{n_2}{n_1}
\]  

(Eq. 3)

The conventional way of coupling light into an LCW is by focusing a collimated light beam into the core. Light entering the core at an angle larger than \(\theta_c\) will be totally reflected at the core/cladding interface and transmitted along the liquid core, providing an efficient way of irradiating the whole sample inside the LCW [46].

Despite the fact that quartz and metal-coated tubes provided long-path LCWs, their high attenuation along the axis of these cells contrated any benefit of the increased optical path length [47,48]. Since metal-coated tubes were designed to reflect light through any transparent core over large angles, they were independent of the RI of solvents. However, they were mostly suitable in the Vis, microwave, and infrared regions. Glass or quartz tubes worked on the principle of TIR, but in order for TIR to take place very high RI solvents (e.g., bromobenzene [49], \(n = 1.56\)) had to be used. Suitable materials with an RI lower than most solvents were not available at the time. This changed in 1989 when DuPont introduced the polymers Teflon AF 1600 and 2400, which have a lower RI (\(n = 1.29\)) than that of water (\(n = 1.33\)) [50]. Teflon AF is an amorphous copolymer of 2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxol (PDD) and tetrafluoroethylene (TFE) and is transparent for light above a wavelength of 200 nm [50,51]. Teflon AF tubes could be used for TIR-based waveguiding of light between 200 and 1600 nm using solvents such as methanol \((n = 1.329)\), acetonitrile \((n = 1.344)\) or hexane \((n = 1.375)\) [51]. This resulted in a significant leap forward for LCWs, as Teflon AF was moldable into tubing, films or coatings, resulting in chemically inert waveguides with low attenuation [52].

### 2.1. Polymer-coated capillaries

The first step of applying the new low-RI Teflon for LCWs was to coat fused silica capillaries externally with Teflon AF, producing the so-called type II LCWs that are compatible with a large range of solvents. In 1997, Altkorn et al. showed how a type II LCW could effectively replace fused silica-only LCWs [53].

A disadvantage of type II LCWs, however, is that TIR does not occur at the core/silica interface, but rather at the Teflon AF/silica and the Teflon AF/air interfaces (Fig. 1B). This resulted in light being trapped inside the cladding material and, therefore, leading to inefficient irradiation of the core solution. This could also lead to decreased analytical sensitivity when it is used for detection purposes, due to a high background signal originating from the stray light from the cladding [28].

Dasgupta et al. [54] described how the background signal can be rejected by applying an opaque coating to the tip of the capillary or by using a light collection fiber that is equal to or smaller than the core diameter of the LCW, such that it only collects light transmitted through the liquid core.

Type II LCWs are commercially available as long optical path length detector-cells for UV–Vis absorbance spectroscopy. These optical flow cells have been used by Melchert et al. [55] for the determination of carbaryl pesticides in natural waters at concentrations as low as 200 \(\mu g L^{-1}\) using a 100-cm long flow cell. The same flow cell was studied by Rocha et al. [56] for the analysis of phosphates in fresh waters, which was achieved after on-line photochemical conversion of organic phosphorus into orthophosphate. They used molybdenum blue as a color indicator for the total amount of orthophosphate in the fresh water samples reaching detection limits down to 2 \(\mu g L^{-1}\), i.e., much lower than reported by Melchert et al. [55]. The detection is directly related to the absorption coefficient of the analyte. Therefore, more strongly absorbing compounds will result in lower detection limits. This also means that the concentration of the solution should be taken into consideration for photochemical reactions, as a too-high concentration will result in total absorption of the light in the first few centimeters of the LCW, resulting in heterogeneous and slower reaction rates along the length of the waveguide.

### 2.2. Polymer capillaries

In an attempt to prevent the background interferences that occur with type II LCWs, type I LCWs were produced, which consist of capillaries made entirely of Teflon AF, so that TIR will occur at the liquid/Teflon AF interface (Fig. 1A). The LCWs made of Teflon AF tubing show relatively high losses (dB m\(^{-1}\)) compared to other waveguides discussed in this review, e.g., holey and Kagome fibers. The difference between the type I and type II Teflon AF waveguides is small with regards to optical loss, however, type I waveguides have the added benefit of gas permeability because there are no obstructing silica wall, which makes them interesting for studying (photo)reactions under oxic vs anoxic conditions. For photochemistry, the type I waveguides show more efficient irradiation of the core compared to type II waveguides, due to the differences in the TIR interface.

Teflon AF LCWs have been used frequently for trace analysis, for example in water and marine chemistry [28,57,58]. Other applications have been described, for example by Cheng et al. [32], who used a 9-cm long Teflon AF tube for the determination of organophosphorus pesticides in vegetables and fruits by absorbance spectroscopy, improving the LOD by a factor of 1000 compared to classical spectrophotometry. The large inner diameter (2.56 mm), leading to enhanced optical paths, as well as reduction of noise both contributed to the LOD enhancement. Another example of long optical path length UV–Vis absorbance spectroscopy was provided by Rubles et al. [52], who developed and characterized the type I LCW for the use in a commercial spectrophotometer for measuring low light absorbance values of dilute aqueous solutions, reaching LODs as low as 3 mAU (equivalent to an optical density of 36
µAU cm$^{-1}$). Type I LCWs have also been used for fluorescence spectroscopy [59–61]. Liu et al. [61] developed a setup for capillary isoelectric focusing of naturally fluorescent or fluorescently labelled proteins with a fluorescence whole-column imaging detection system based on a type I LCW (Fig. 2). For excitation, the authors focused an argon-ion laser axially into the LCW capillary. The fluorescence signal that was transmitted through the Teflon AF walls was read across the whole LCW length (5.5 cm) by a CCD camera positioned at a 90° angle with respect to the LCW. When compared to a commercially available instrument with UV absorbance detection, the separation efficiency was similar, whereas the detection sensitivity was enhanced by 3–5 orders of magnitude. The enhanced detection was mainly attributed to the high quantum yields of the fluorescent proteins in combination with the highly advantageous signal-to-noise ratio obtained for fluorescence detection.

Raman spectroscopy has also shown to be an interesting application for these specific LCWs [62–70]. Upon irradiation of an analyte, approximately 1 in a million photons are scattered inelastically, i.e., as Raman photons. Therefore, measuring a Raman signal of low analyte concentrations can be challenging. The length of the LCW significantly improves the Raman signal by the propagation of excitation light along the length of the waveguide, increasing the number of molecules that may emit Raman signals. In the case of fluorescence and Raman spectroscopy, interfering irradiation could be reduced by illuminating transversely, where the light source is placed at a 90° angle relative to the LCW tube (Fig. 3) [54,70–74]. Excitation light passes through the tubing walls and interacts with molecules inside the tube, resulting in fluorescence or Raman scattered photons in every direction. A part of these photons is guided along the length of the LCW towards the detector, while most of the excitation light exits through the tubing walls. In reality, some of the excitation light is also guided along the length of the LCW and a part of the emitted fluorescence/Raman will exit the LCW through the walls. Using this irradiation method, Holtz et al. [70] were able to collect Raman shifts close to 200 cm$^{-1}$ without the use of a holographic notch filter.

Type I LCWs have also been used as photoreactors, mostly in combination with a reactor gas, exploiting their gas permeability which allows for gas-liquid reactions. This is not possible with any other optical waveguides discussed in this review. Many have studied the use and performance of Teflon AF capillaries for gas-liquid reactions [75–81]. For example, Polyzos et al. [82] developed a tube-in-tube reactor for continuous-flow synthesis of carbonylic acids using CO$_2$ and a combination of several Grignard reagents. The Teflon AF tube was placed inside a PTFE tubing, through which the CO$_2$ gas was delivered at a flow of 400 µL min$^{-1}$. They found that these experimental settings resulted in high conversions with a short residence time (42 s), meaning that diffusion through the Teflon AF wall occurred rapidly. However, none of the above-mentioned works used light to initiate photochemical reactions. Ponce and colleagues demonstrated an optical micro photo-reactor of Teflon AF combining fast gas-liquid mass transfer in combination with in-situ absorbance spectroscopy [83]. The light was coupled into the Teflon AF LCW using a standard optical fiber. With a tube-in-tube configuration, such as the one described by Polyzos et al., oxygen was introduced for the methylene blue catalyzed oxidation of
I. Groeneveld et al.

2.3. Silica aerogels

A third, more recent approach to the construction of TIR-based LCW photoreactors is based on silica aerogels. Silica aerogels are nanostructured materials forming a solid structure with a large number of air-filled pores. The resulting high porosity leads to an RI close to that of air \((n = 1.00)\). Hollow channels can be made through the aerogels, which can be filled with a higher RI liquid so that light is guided along the length of this channel \((\text{Fig. 4})\). Light that can be used for waveguiding along the length of such a channel is limited to wavelengths higher than 300 nm, due to the absorbance of light of shorter wavelengths by the silica.

In recent studies, aerogels have been used quite successfully for waveguiding, although they may show significant losses of 150–1000 dB m\(^{-1}\), which appears to be mostly caused by the faults made in the channel formation \([85–91]\). This is also why the lengths used for aerogel waveguides is limited to a few centimeters at most.

Xiao et al. \([89]\) were the first to report on LCWs consisting of water-filled microchannels in aerogels, which allowed the transmittance of laser light of 635 nm with relatively low intensity losses. Eris et al. \([85]\) were able to produce both straight and U-shaped waveguides inside aerogels, opening up possibilities for the creation of complex three-dimensional networks. Later, Yalizay et al. \([92]\) applied femtosecond-laser ablation as a more accurate alternative for the milling and cutting procedures for the creation of microchannels, which reduced light losses. Ozbakir et al. showed that the aerogel LCWs could be used for applications including the detection or identification and quantification of particular chemical compounds by placing a power meter at the exit of the channel \([86]\). The aerogel LCW was used as a micro photoreactor for studying the photodegradation of methylene blue \((\text{MB})\) with an initial concentration of 37 \(\mu\text{M}\) using a laser with a wavelength of 388 nm. The sample was analyzed off-line by absorption spectroscopy after collection from the waveguide at different time intervals. Within 60 min, the concentration of MB decreased by 83% when exposed to an incident light power of 250 mW. They also found that the degradation rate was proportional to the light power \([87]\). Later, the same group embedded titanium particles in the walls of the aerogel microchannels to establish rapid photocatalytic transformation of MB; however, the readout was still performed off-line \([88]\). Most recently, the same authors showed an application of the titanium embedded aerogel waveguide for the photocatalytic degradation of an aqueous phenol mixture into \(\text{CO}_2\) and water \([93]\).

These results show that aerogel LCWs can be suitable as photoreactors, and provide flexibility for adapting the surface for catalytic reactions. Disadvantages of silica aerogels are their low transmittance of light below 300 nm, their high optical losses, and the high adsorptive behavior for organic molecules, although modifying the gels may be a solution to this problem.

3. Interference-based optical waveguides

Interference-based waveguiding presents an alternative for TIR-based LCWs. In interference-based waveguides, multiple layers of dielectric materials are used as a cladding material, as shown in \(\text{Fig. 5}\). These layers create multiple reflections at each interface of the structured cladding material that can interfere constructively or destructively \([29]\). The key idea in the present context is that near-perfect reflections into the liquid medium can be achieved even if that medium has a lower RI than all of the cladding layer materials.

Based on the light guiding properties, the interference-based optical waveguides can be divided in two categories: (i) photonic crystal fibers (PCFs) and (ii) ARROWs \([29,91,94]\).

3.1. Photonic crystal fibers (PCFs)

PCFs are optical fibers with a variety of cross-sectional structures as shown in \(\text{Fig. 5}\). PCFs are generally produced by the so-called stack-and-draw method, where glass capillaries are stacked into a macroscopic version of the geometry desired in the fiber. This preform is then heated and drawn into a fiber with a final diameter of, e.g., 125 \(\mu\text{m}\). The cladding layer, therefore, consists of microscopic hollow capillaries along the length of the entire fiber \([33]\). The waveguiding principle is determined by the design of this cladding and the dimensions of the core. The light guiding of the discussed PCFs is based on TIR, but their efficiencies depend on the specific geometry and structural parameters of the PCF \([95]\). TIR will still occur when the RI of the core is higher than...
that of the cladding, which is generally the case for PCFs with a solid core or fluid-filled hollow core. Due to the tight light confinement and reduced sample volume that PCFs offer, they have been widely used as LCWs for chemical sensing, using absorbance [96, 97], fluorescence [98, 99], and Raman spectroscopy [100–103], but also for studying photochemistry.

Based on the design and the mode of light propagation of the PCFs, the following three subcategories can be discerned: (i) Bragg fibers, (ii) holey fibers, and (iii) Kagomé fibers (Fig. 5).

3.1.1. Bragg fibers

The Bragg fiber (Fig. 5A) is an interference-based waveguide, and is also known as the one-dimensional PCF. Bragg fibers contain multiple dielectric layers of low (n₁) and high (n₂) RI around a hollow core that are repeated periodically. An incident photon is guided along the length of the Bragg fiber when a) the Bragg frame is highly reflective, and b) the transverse component of the wave vector fulfills the same phase resonance condition as in the case of TIR. The partial reflections are equivalent to the Bragg reflections that are known from X-ray analysis of crystalline materials [94].

Temelkuran et al. [104] showed that these hollow-core fibers were perfectly suited for the efficient transmission of the light of a carbon dioxide laser, with transmission losses of less than 1 dB m⁻¹. Kuriki et al. [105] reported comparable transmission losses for the guiding of light in the mid-IR range measured with a Fourier-transform infrared (FTIR) spectrometer, using a lens to couple light into the fiber and an external detector. These examples, however, do not make use of a liquid-filled core.

A hollow-core Bragg fiber can be filled with a liquid or a gas, which changes the properties of the guided light and paves the way for new applications. This will result in shifts in the detected band gaps peaks, which makes it an interesting tool to study the RI of solutions [95, 106–109]. The fiber sensor operates using a resonant sensing principle, meaning that the fiber transmission spectrum changes in response to the RI of the core solution. Milenko et al. [95] used Bragg fibers for bio-sensing applications, where the core was filled with aqueous solutions to detect changes in their RI. In 2011, Qu et al. [109] similarly demonstrated a Bragg fiber with a liquid core as a sensor for liquid analyte RI detection. The Bragg fiber was 40 cm long and had a core diameter of 0.8 mm surrounded by alternating layers of polymethyl methacrylate and polystyrene. The core was filled with NaCl solutions with different weight concentrations, resulting in RIs ranging from n = 1.33 to 1.38. They were able to analyze the transmission spectra of these solutions with a spectrometer coupled on-line (Fig. 6).

Despite the many publications that mention Bragg fibers as LCWs for the purpose of detection, as far as we are aware they have not been reported as photochemical microreactors yet. Most papers focus on the fabrication of Bragg fibers and its use as an air-filled, light-guiding tool. The limitation of Bragg fibers lies in the complex fabrication process, which involves multiple material deposition steps. This may result in imperfections that ultimately limit the transmission as well as the level of light confinement that can be achieved. Another reason why hollow Bragg fibers may not have been used for photochemical monitoring yet is due to the fact that these fibers offer a very narrow range for light transmission [110], which means that only a small part of the light spectrum can be used. Despite or due to this reason, Bragg fibers have shown to be especially well suited for RI sensing, with low-refractive-index-contrast Bragg fibers in particular. High-refractive-index-contrast Bragg fibers have shown to be most suitable for gas-core sensors. Although no reports were found on photochemical reactors based on Bragg fibers, if the very specific wavelength that is transmitted is applicable for photochemistry and translatable to a change in molecular structure, then this could also be detected using a Bragg fiber.

3.1.2. Holey fibers

Contrary to Bragg fibers, holey fibers have a solid core (glass or flexible polymer) surrounded by a cladding that consists of many closely spaced air holes (Fig. 5B). Normally, the hollow channels are filled with air to reduce the effective RI of the cladding below that of the solid core, which causes the guidance of light through the solid core by TIR [33]. The holey fibers offer a large degree of freedom in the microstructure design, which allows for large mode areas, high nonlinearity, and remarkable control of dispersion. Advances in fabrication techniques have reduced transmission losses down to 18×10⁻⁵ dB m⁻¹ at 1550 nm [111] and guiding of ultrabroad wavelength ranges of 400–2400 nm has been reported as well, which makes them suitable for broadband applications [112].

The hollow channels may be filled with a fluid or liquid sample with a RI lower than that of the solid core to benefit from the same TIR effect. When doing so, the light is again guided through the solid core and now interacts with the edge of the liquid sample via an evanescent wave that penetrates the liquid filled channels. The penetration depth of the evanescent field into the channels, however, is limited, and the light, therefore, does not affect the whole sample. Fortunately, this can be optimized by changing the core size, hole diameter and the distance between the hollow channels [113].

Examples where holey fibers were used for absorption, Raman and fluorescence spectroscopy include the detection of dyes [95,114], biomolecules [115–117], solvents [118] and gasses [119–121]. In the case of Raman or fluorescence, the emitted photons are also transported through the core. The microchannels, however, may result in large flow resistance, which is a limitation in optofluidics. To circumvent the issue of high flow resistance, a holey fiber with different geometry was designed where the solid core is held together by three relatively large nanowebs (Fig. 5C). Due to the size of the three cladding holes, the sample is easily pumped into the holey fiber and overlaps of 30% of the evanescent field with the liquid cores could be reached for relatively small cores [33]. Webb et al. [122] made several of these nanoweb holey fibers by drilling holes into a silica preform and drawing them into narrow fibers. The solid core size varied between 0.8 – 1.8 μm and the webs were around 8 μm in diameter. They concluded that the relatively high losses (0.29 dB m⁻¹ at 1550 nm) were mainly due to scattering losses because of the rough surfaces followed by drilling. They found that these fibers have a lower flow resistance and the evanescent wave

![Fig. 5. The four PCFs discussed in Section 3.1: (A) Bragg fiber, (B, C) holey fibers, (D) Kagomé fiber.](image-url)
will have stronger interaction with the analytes inside the channels due to the penetration depth, but losses are higher compared to regular holey fibers.

Due to the evanescent wave mechanism, these fibers are ideal for the detection of surface-bound analytes [115, 123]. In order to increase photochemical reaction rates, catalysts could be bound to the surface of a hollow channel and the photocatalytic reactions could be studied in situ. However, applications of holey fibers have not yet been reported for such studies. The reason may be the shallow penetration depth of the evanescent wave, which does not offer sufficient interaction with the solutes, resulting in long reaction times. In addition, we suspect that the evanescent wave is not as strong at the outer edges of the fiber as it is close to the core, meaning that in the design of Fig. 5B the channels may be irradiated heterogeneously. However, many improvements can be made in the design of the holey fibers, which may lead to the application for photochemical studies in the future.

### 3.1.3. Kagomé fibers

Another type of hollow core PCF that is quite popular for photochemistry and chemical sensing is the Kagomé PCF, named after its particular lattice arrangement in the cladding structure (Fig. 5D) [33]. Kagomé fibers are generally made by the stack-and-draw method using silica or polymers such as PMMA. This type of PCF does not follow the guiding principles regularly observed for hollow core fibers, but through inhibited coupling (IC), resulting in losses up to 0.1 dB m\(^{-1}\). IC is established by minimizing the spatial overlap between the fields of the core and cladding modes and by creating a strong mismatch between their spatial phases [124], which is why losses of Kagomé fibers are highly dependent on their structure. An advantage of Kagomé fibers is their large transmission window over a very broad wavelength range from UV to the NIR region, which is caused by the particular cladding structure.

Kagomé fibers have been widely applied as LCWs for broadband spectral detection and photochemical studies in solution. Cox et al. were the first to perform SERRS measurements inside a 20-cm long Kagomé fiber (ID=30 µm) filled with an aqueous solution of 0.21 µM Rhodamine B adsorbed to colloidal silver [125]. An Argon-ion laser was directed into the core of the fiber through a 20x microscope objective, which was also used to collect the back-scattered Raman signal. The researchers found that both the incoming Argon-ion laser beam and the scattered Raman signals originating from the analyte were guided along the fiber, which led to an enhanced signal compared to conventional Raman analysis. However, they also noticed that besides the core, the fiber cladding also displayed weak Raman peaks, which indicated that the enhanced signal is partly a result of resonance reflection.

Williams et al. [99] performed long pathlength fluorescence measurements in solution and compared the results obtained with a Kagomé fiber with those of a holey fiber. The detection limit of the Kagomé fiber was at the attomolar level, whereas that of the holey fiber was at the nanomolar level. They also found that in the Kagomé fiber the excitation of the analyte is confined to the bulk solution, whereas in holey fibers exclusively molecules at the solution-cladding interface were excited. This is no surprise as the evanescent wave will penetrate the sample only close to the surface of the cladding. The use of Kagomé fibers for reaction chemistry is therefore preferred over holey fibers.

Williams et al. [126] used a Kagomé fiber for the photoisomerization of azobenzene. In 10 s the reaction process was completed, whereas using a cuvette, almost three orders of magnitude more power was needed to achieve the same result in a comparable reaction time. Cubillas et al. [127–129] used a Kagomé fiber to study complex multicompartment homogeneous and heterogeneous photocatalytic reactions. In one of their reports [129], they present the photolysis of (HBPz)\(_2\)Rh(CO)\(_2\) in toluene in a 35-cm long Kagomé fiber with a total volume of less than 175 nL. They irradiated the core solution with a 405 nm diode laser with excitation powers ranging between 5 and 30 µW, and the reaction was monitored by measuring the absorbance of the solution. At an excitation power of 15 µW, photolysis was complete within 60 min, whereas the same reaction studied in a cuvette took more than 8 h. The optimized light–matter interaction in the fiber strongly enhanced the reaction rate.

Chen et al. [97] used a Kagomé LCW to study the photo-aquation of vitamin B12 (cyanocobalamin), and Unterkofler et al. [130] studied the same reaction in continuous flow in a 25 cm long Kagomé fiber and were able to measure the reaction products by on-line high-resolution MS. A total volume of 85 nL at 5 µM vitamin B12 was irradiated with a laser of 488 nm. Due to the continuous flowrate of 27.7 µL s\(^{-1}\) the irradiation time inside the fiber was only 20 s. A stunning 30% decrease in transmittance at 488 nm was observed at only 0.71 s, which indicated the photodissociation of vitamin B12. Later, the same set-up was coupled to ESI-MS to demonstrate its applicability for the efficient activation and analysis of photoactivatable drugs. A di-nuclear ruthenium complex was used as a model drug and was compared to standard irradiation techniques using the same 488 nm irradiation source [30]. They studied the reactions in the presence of small biomolecules, which were found to bind faster to the ruthenium complex when irradiated. The Kagomé fiber setup drastically reduced the sample volumes and irradiation times from hours to seconds and findings were in line with studies using cuvettes. Unfortunately, the reduced sample volume also resulted in a reduced MS signal intensity.

Overall, the Kagomé fiber shows good performance for chemical sensing and proves to be an efficient photoreactor due to its low attenuation and broad spectral transmittance. A limitation of Kagomé fibers is...
their small internal volumes, which could complicate measuring at low concentrations. In order to increase the volume, longer fibers should be used since their inner diameters are typically below 50 µm. However, an increased optical path length also means more absorption across the length of the fiber, meaning that the last few centimeters receive less light compared to the first centimeters: an effect undesirable in photochemistry.

3.2. Anti-resonant reflecting optical waveguides (ARROWS)

In ARROW fibers, the principle of thin-film interference is applied to guide light with low-intensity losses. Here, light waves are reflected by the upper and lower boundaries of a thin film, either enhancing or reducing the reflection of light (Fig. 7). The thickness of the film (\(t_i\)) is essential as it determines which effect will occur. When the thickness of the film is an odd quarter-wavelength (\(1/4 \lambda\), \(3/4 \lambda\), \(5/4 \lambda\)), the reflected waves interfere and cancel each other out. However, when the thickness of the film is half a wavelength different from that of the incident light \((1/2 \lambda, \lambda, 3/2 \lambda\)), the reflected waves reinforce each other and increase the reflection \([131]\). In contrast to PCFs, the high- and low-index alternating layers \((n_1\) and \(n_2\)) in ARROW waveguides do not require high periodicity in the structure, which simplifies the manufacturing process.

With roughly 1000 dB m\(^{-1}\), ARROWS result in the highest optical losses among the interference-based optical waveguides. Similar to Bragg fibers, ARROWS are complex to fabricate. The small inner diameters and short lengths result in very small volumes of the core. This may be an issue for analytical techniques that require larger volumes than a few nano- or picolitres in order to analyze the sample. However, White et al. \([132]\) demonstrated how they could actually make use of these high transmission losses. They used an ARROW to couple light into a liquid core optical ring resonator (LCORR) via evanescent interaction at the points of contact. The LCORR contained immobilized analytes on the inner surface, which could interact with the evanescent field, resulting in a sensing signal.

Liquid-core (LC-)ARROWS have been used for several other detection applications, such as UV–Vis absorbance spectroscopy \([133]\), transmission measurements \([134]\), fluorescence spectroscopy \([135–137]\) and Raman spectroscopy \([29,138]\). The work of Yin et al. \([136]\) and Rahman et al. \([139]\) describes how LC-ARROW can be used for single-molecule detection due to the pico- and nanoliter volumes.

Due to their small size, ARROWS are highly applicable for use in microfluidics or on-chip applications. Various optical elements have been added onto LC-ARROW chips in such a way \([140–143]\). For example, multimode interference (MMI) waveguides based on ARROWS have been used in on-chip optofluidic interferometers \([144–148]\). Several of such integrated optofluidic interferometric devices have been demonstrated in optofluidic ring resonators \([149]\) and Mach–Zehnder interferometers \([150,151]\) and other optofluidic devices \([152,153]\). Stambaugh et al. \([154]\) presented an MMI-ARROW device with a fluorescence probe for the detection of single SARSCoV-2 and influenza A antigens.

Bernini et al. \([155]\) fabricated a liquid-core/liquid-cladding integrated ARROW device, which reduced optical losses in ARROWS. The design is different from the above-mentioned applications, where thin films are used, but makes use of the same guiding principle.

To our knowledge, until now no researchers have made an effort in using LC-ARROWS for the design of photo microreactors, despite their success in sensing applications. This may be because of the relatively high transmission losses, meaning that the waveguide must be made quite short and volumes may be too low to initiate and study photochemical reactions.

4. Conclusions

There are many different ways to use LCW based photoreactors for in-situ detection. The low light losses and possibilities for coupling with analytical techniques are great assets for the design of a photoreactor. Due to the direct irradiation within the core, optimum illumination of the whole sample can be reached, which can be difficult with other types of reactor cells. However, compared to microfluidic devices, the fabrication of interference-based optical waveguides can be quite tricky due to the thin-layered materials that are used and design flexibility is lacking, which may be considered as a disadvantage.

The waveguides discussed in this review each possess several unique advantages, but also disadvantages. The PCFs show low losses and small volumes compared to the polymer and aerogel LCWs, which may result in a higher reaction rate. Especially Kagome fibers show very promising results for coupling to advanced analytical techniques. However, the small volumes of PCFs may also be a limitation for the detection of analytes at very low concentrations, which is likely to occur when photodegradation products are formed in low quantities. A unique advantage of the Teflon AF LCWs is their gas permeability, so photochemical processes can be studied under oxic vs anoxic conditions.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in this article.

Acknowledgements

This work is part of the TooCOLD project (Toolbox for studying the Chemistry Of Light-induced Degradation; project number 15506) carried out in the TTW Open Technology Programme and is (partly) financed by the Dutch Research Council (NWO).

References
