

SENSOR PROBE FOR USE IN IN-SITU FO-LIBS SYSTEM

RELATED APPLICATION

[0001] This application claims the benefit of priority to the Singapore patent application no. 10202403033U filed on September 30, 2024, the entire contents of which are hereby incorporated by reference for all purposes.

TECHNICAL FIELD

[0002] The present disclosure relates to fiber optic laser induced breakdown spectroscopy (FO-LIBS) detection and more particularly to apparatus for FO-LIBS.

BACKGROUND

[0003] The detection of environmental pollutants conventionally requires samples to be collected from a site and then transported to the laboratory where the samples can be analyzed. The transportation of potentially hazardous samples materials is a matter of serious concern and special arrangements need to be made to ensure that the transportation can be carried out without spreading health and safety. In situations where environmental pollution is monitored over time, such repeated transportation of potentially hazardous samples can lead to an increased risk of pollutants being leaked along the transportation chain.

SUMMARY

[0004] The present application discloses various embodiments of a sensor probe for use with a fiber-optic laser induced breakdown spectroscopy (FO-LIBS) system. The sensor probe includes an elongate member and a sensor head. The sensor head is detachably couplable with a distal end of the elongate member to define a continuous interior in which one or more optical fibers are disposed, in which proximal ends of the one or more optical fibers are couplable to a laser source of the FO-LIBS system and a spectrometer of the FO-LIBS system, respectively. The sensor head includes: a casing, a sensing window, and a collimation-and-focusing sub-system. The casing has a wall defining a probe interior. The sensing

window is disposed at the wall of the casing. The collimation-and-focusing sub-system being disposed in the casing and configured to define one or more optical paths between distal ends of the one or more optical fibers and the sensing window.

[0005] The sensor head of the sensor probe may further include or provide a cavity defined at least partially by the wall of the casing. The cavity may be defined about the sensing window on one side of the sensing window, with the probe interior being on another side of the sensing window.

[0006] The sensor head may further include a cover. The cover may be spaced apart from the sensing window to define the cavity between the sensing window and the cover.

[0007] The cover may be configured to be actuatable and/or deformable to change a state of the cavity between a closed state and an open state. The cavity is configured to have a default state in which the cavity is the closed cavity.

[0008] The sensing window may include a sapphire lens.

[0009] An in-situ fiber-optic laser-induced breakdown spectroscopy (FO-LIBS) system includes a laser source; a spectrometer; one or more optical fibers; and the sensor probe, in which a plasma plume formed by laser irradiation of an in-situ sample is at least partially receivable in the cavity and detectable via the sensing window.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] To aid understanding, various embodiments of the present disclosure will be described with reference to the following figures:

[0011] **FIG. 1** is a schematic diagram of a fiber optic laser-induced breakdown spectroscopy (FO-LIBS) system according to embodiments of the present disclosure.

[0012] **FIG. 2** shows schematic diagrams of the internal structure of the sensor probe 200 according to various embodiments of the present disclosure.

[0013] **FIG. 3A to FIG. 3C** are images of a prototype according to an "L"-shaped configuration.

[0014] **FIG. 4A to FIG. 4C** are images of another prototype according to an "I"-shaped configuration.

[0015] **FIG. 5A** is a schematic cross-sectional view of a casing of the sensor head of **FIG. 4C**.

[0016] **FIG. 5B** is a schematic perspective view of the casing of **FIG. 5A**.

[0017] **FIG. 6A** is a schematic side of a framework that may be provided in the interior of the sensor head of **FIG. 3C**.

[0018] **FIG. 6B** is a schematic perspective view of the framework of **FIG. 6A**.

[0019] **FIG. 7A** is a schematic diagram of another embodiment of the present disclosure in which the sensor probe includes a space limiting device.

[0020] **FIG. 7B** is a schematic diagram of yet another embodiment of the present disclosure in which the sensor probe includes another space limiting device.

[0021] **FIG. 8A to FIG. 8C** show 3D (three dimensional) models of different examples of the space limiting device according to embodiments of the present disclosure.

[0022] **FIG. 9** is a schematic diagram of laser ablation and plasma formation processes.

[0023] **FIG. 10** is a schematic diagram of plasma evolution with and without spatial constraints.

[0024] **FIG. 11A** and **FIG. 11B** are schematic diagrams illustrating further embodiments of the proposed sensor probe with space limiting devices.

[0025] **FIG. 12 to FIG. 17** show exemplary results obtainable from the proposed FO-LIBS system.

DETAILED DESCRIPTION

[0026] The following detailed description is made with reference to the accompanying drawings, showing details and embodiments of the present disclosure for the purposes of illustration. Features that are described in the context of an embodiment may correspondingly be applicable to the same or similar features in the other embodiments, even if not explicitly described in these other embodiments. Additions and/or combinations and/or alternatives as described for a

feature in the context of an embodiment may correspondingly be applicable to the same or similar feature in the other embodiments.

[0027] The word “exemplary” is used herein to mean “serving as an example, instance, or illustration.” Any embodiment described herein as “exemplary” is not necessarily to be construed as preferred or advantageous over other embodiments. As used herein, the singular ‘a’ and ‘an’ may be construed as including the plural “one or more” unless apparent from the context to be otherwise. In the context of various embodiments, the articles “a”, “an” and “the” as used with regard to a feature or element include a reference to one or more of the features or elements.

[0028] As used herein, the term “and/or” includes any and all combinations of one or more of the associated listed items.

[0029] In the context of various embodiments, the term “about” or “approximately” as applied to a numeric value encompasses the exact value and a reasonable variance as generally understood in the relevant technical field, e.g., within 10% of the specified value.

[0030] Terms such as “first”, “second”, “third”, “fourth”, etc., are used in the description and claims only for the sake of brevity and clarity, and do not necessarily imply a priority or order, unless required by the context.

[0031] Some methods may be described in terms of steps, stages, phases, or the like, merely to aid understanding and/or for convenient reference. The delineation between one step and another step may be merely for convenient reference in the present disclosure. It will be understood that in actual implementation there may not be a clear division or transition from one step to another subsequent step. There may be a certain amount of overlap among the steps and/or more than one step may occur or be performed concurrently in time, etc., unless the context dictates otherwise.

[0032] In the present disclosure, terms such as “3D printing” and “additive manufacturing” may be used interchangeably.

[0033] **FIG. 1** schematically illustrates a fiber optic laser-induced breakdown spectroscopy (FO-LIBS) system 100 according to embodiments of the present disclosure. The FO-LIBS system 100 proposed herein is also referred to as an in-

situ FO-LIBS system as it is suitable for use on site to measure in-situ samples, e.g., the in-situ samples are measured where they are found and not removed to the laboratory. This minimizes the risk of spreading contamination or manages the risk of exposure, especially when the samples potentially contain hazardous materials.

[0034] The FO-LIBS system 100 may include a portable power supply 110 to power a laser head 130 and a spectrometer 140. The laser head 130 (also known as a laser source) is configured to provide or transmit laser pulses to a coupling system 150. For example, the laser head 130 may be a pulsed infrared laser operable at 1064 nanometers (nm) with a Q-switched output, adjustable in a range of 0 hertz (Hz) to 20 Hz, available from CNI Optoelectronics.

[0035] The FO-LIBS system 100 includes one or more optical fibers 160 to deliver or transmit the laser pulses from the coupling system 150 to a distal end 162 of the one or more optical fibers 160.

[0036] The high-energy laser pulses or laser sparks at the distal end 162 of the optical fiber 160 are delivered via one or more optical paths defined by a collimation-and-focusing sub-system, via a sensing window, to irradiate in-situ samples and break down the materials at the surface of an in-situ sample (also referred to as "localized breakdown"), generating one or more plasma plumes. The resulting plasma plume is characterized by atomic and/or molecular emissions or spectral lines as excited atoms and ions return to their ground state. The emission lines correspond to each element present in the sample. Another optical fiber 170 collects the light emitted by the plasma plume and transmits the light (via the coupling system 150) to the spectrometer 140. The collected atomic and/or molecular emission spectra are then analyzed to identify and/or to quantify the elements present in the in-situ sample via the sensing window and directed along an optical path to the distal end 162 of the optical fiber 160.

[0037] The FO-LIBS system 100 includes a sensor probe 200. The sensor probe 200 includes an elongate member 202 and a sensor head 204. The sensor head 204 is detachably couplable with a distal end of the elongate member 202. The elongate member 202 and the sensor head 204 together define a continuous

interior. For example, when coupled together, the interior of the elongate member 202 and the interior of the sensor head 204 are in fluid communication with one another, providing a space in which the one or more optical fibers 160 may be disposed. Optical fibers 160 may be extended through a probe interior 211 of the sensor probe 200 such that the respective distal ends 162 of the optical fibers 160 can be positioned at the sensor head 204, e.g., to bring the laser sparks into proximity with the in-situ samples, or to collect light emitted from the plasma plumes (spectrometer input). In the present disclosure, for the sake of brevity and convenient reference, a longitudinal direction or longitudinal axis 109 may be defined by the elongate member 202.

[0038] The sensor probe 200 enables the laser output to be delivered or collected at a relatively great distance away from the laser head 130 or the spectrometer 140. The probe interior 211 of the sensor probe 200 includes one or more fiber flanges 220 to couple with the two or more optical fibers 160. Fiber flanges 220 are preferably integrally formed with a wall of the casing 210 of the sensor probe 200. The wall of the casing 210 defines the space referred to herein as the probe interior 211. Each optical fiber 160 may be coupled to one or more fiber flanges 220 so that the optical fiber 160 extends longitudinally straight through the elongate member 202 to dispose a distal end of the optical fiber in the interior of the sensor head 204.

[0039] **FIG. 2** shows schematic diagrams showing the internal structure of the sensor probe 200, and more particularly the structure of the sensor head 204, according to various embodiment of the present disclosure. The casing 210 of the sensor probe 200 includes a side wall 212 and a terminal wall 214. In some embodiments, e.g., as shown in part (A) of **FIG. 2**, the side wall 212 defines an opening 216. A sensing lens is mounted at the opening 216 to form a sensing window 270. In some examples, the sensing lens is a sapphire lens. In some examples, the sensing lens may be made of a mineral or a polymer, the mineral or the polymer being selected from transparent or substantially transparent materials. In some examples, the material selected for use at the sensing window includes a single crystal of silicon oxide or aluminum oxide. In some examples, the sensing

lens is made of a synthetic (or man-made) crystal having a light transmission range comparable with that of a sapphire lens.

[0040] The sensor head 204 includes lenses 240 disposed therein. For example, a double-cemented lens 242 may be fixed in the interior of the sensor head 204 to receive light from the distal end of the optical fiber 160. In the present disclosure, the term "collimator" refers to a device configured to increase alignment of light rays in a specific direction or to form parallel light rays. Embodiments of the collimator include and are not limited to, for example, a double-cemented lens module, an aspheric lens module, a graded-index (GRIN) module with one or more GRIN lenses, a ball lens module with one or more ball lenses, a doublet lens module, other fiber-end focusing elements (such as but not limited to ball lenses), etc. For example, the collimator 241 may include double-cemented lens 242 formed by two glass lenses of different refractive indices and dispersion properties. The double-cemented lens 242 is configured to convert the divergent light output from the optical fiber 160 into a parallel beam, and to reduce chromatic aberration as well as other optical aberrations that may be present. In the prototypes tested, the double-cemented lens formed by a combination of two individual glass lenses of different refractive indices could yield better image quality compared to a single lens.

[0041] The sensor head 204 may include a collimating-and-focusing sub-system that includes a collimator 241. In some embodiments, the collimator 241 includes an aspheric lens 244 (also referred to as a non-spherical lens) disposed in proximity to the sensing window 270. The aspheric lens 244 is configured to focus the parallel beam formed by the double-cemented lens 242, increasing the power density of the laser beam as it is directed through the sensing window 270. In the prototypes tested, it was observed that the aspheric lens 244 enabled correction of spherical aberrations brought about by the spherical lens used in the collimation-and-focusing sub-system presented herein. Spherical aberrations could be eliminated or at least reduced to a negligible level. It was verified that the stability of the FO-LIBS system 100 could be significantly improved without having to increase the size or the footprint of the FO-LIBS system 100.

[0042] In some embodiments, e.g., as shown in part (A) of **FIG. 2**, the collimation-and-focusing sub-system of the sensor head 204 includes a collimator 241 that in turn may optionally include a right-angled prism lens 246 to defect the light rays from a longitudinally oriented parallel beam (e.g., from the double-cemented lens 242) to the aspheric lens 244 proximal to the sensing window 270. Right-angled prism lens enables a more robust structure in terms of stability and strength against mechanical stress. For the sake of brevity and convenient reference, the configuration of part (A) of **FIG. 2** may be referred to herein as a "L"-shaped configuration.

[0043] In some other embodiments of the sensor probe 200, as shown schematically in part (B) of **FIG. 2**, the opening 216 of the FO-LIBS system 100 may be defined at the terminal wall 214 of the casing 210 (or, generally, wall of the sensor head). In the example illustrated, the sensing window 270 provided at the opening 216 also serves as a substantial portion (or almost the whole) of the terminal wall 214.

[0044] The sensor head 204 includes a collimation-and-focusing sub-system that includes lenses 240 disposed therein. For example, the collimation-and-focusing sub-system preferably includes a double-cemented lens 242 and an aspheric lens 244, aligned along the longitudinal axis and in respective fixed positions relative to the sensor probe 200. Light from the distal end of the optical fiber 160 is collimated by the double-cemented lens 242 and focused by the aspheric lens 244. As mentioned above, the double-cemented lens 242 is configured to convert the divergent light output from the optical fiber 160 into a parallel beam, and to reduce chromatic aberration as well as other optical aberrations that may be present. The aspheric lens 244 is configured to focus the parallel beam formed by the double-cemented lens 242, increasing the power density of the laser beam as it is directed through the sensing window 270. For the sake of brevity and convenient reference, the configuration of part (B) of **FIG. 2** may be referred to herein as an "I"-shaped configuration.

[0045] Prototypes of the "L"-shaped configuration and the "I"-shaped configuration were fabricated, and laboratory simulations of long-distance sample

element monitoring were carried out. **FIG. 3A** is an image of a prototype of the sensor head of the "L"-shaped configuration, made by 3D printing, with the casing omitted to avoid obfuscation of the interior structure. **FIG. 3B** is an image of the "L"-shaped configuration with a partial casing (e.g., with part of the casing removed). **FIG. 3C** are images of the sensor head with a casing that provides full encapsulation of the collimating and focusing sub-system. The longitudinally aligned optical fiber can have its output rotated and directed at sensing window disposed at the side wall of the casing.

[0046] **FIG. 4A** is an image of a prototype of the sensor head of the "I"-shaped configuration, made by 3D printing, with the casing omitted to avoid obfuscation of the interior structure. **FIG. 4B** is an image of the "I"-shaped configuration with a partial casing (e.g., with part of the casing removed), showing the sensing window disposed in longitudinal alignment with the various lenses. **FIG. 4C** are images of the sensor head with a casing that provides full encapsulation of the collimating and focusing sub-system, ready for use. The fully enclosed casing enables the sensor head to be used in extreme or harsh environments, including underground and underwater. The various optical components were secured to a 3D-printed framework (e.g., supporting structure integrally 3D printed with the casing or the wall of the casing). In this example, the various optical components shown includes the optical fiber (also referred to as fiber optic), the doublet lens, and the non-spherical lens.

[0047] Different embodiments of the sensor probe 200 may be selected for use, e.g., based on the relative location of the sample. Both the "L"-shaped configuration and the "I"-shaped configuration can provide 360 degrees omnidirectional detection. The "I"-shaped configuration may be preferred in situations where the in-situ sample is below the sensor head.

[0048] The casing 210 may be variously dimensioned to suit the lenses and/or optical fibers used. **FIG. 5A** is a cross-sectional view of one embodiment of the casing 210. The casing 210 includes an optical fiber port 218. The optical fiber port 218 may be a through hole dimensioned to receive an optical fiber therethrough into the interior of the casing 210 of the sensor head. The interior of the casing 210

may include structural elements 230 integrated with the wall of the casing 210 or assembled therewith. The structural elements 230 may provide structural and/or alignment functions. As an example of the "I"-configuration, a sensing window 270 is provided in alignment with the optical fiber port 218. In the example illustrated, a sensing axis 271 (defined to be normal to the sensing window 270) is longitudinally disposed and parallel with a longitudinal axis 101 extending through the casing 210.

[0049] **FIG. 5B** is a schematic perspective view of another embodiment in which a sensing window 270 is provided out of alignment relative to the optical fiber port 218 as an example of the "L"-configuration. In this example, the casing 210 includes an optical fiber port 218 defining the longitudinal axis 101 extending through the casing 210. A sensing window 270 is transversely disposed relative to the longitudinal axis 101. A sensing axis 271 (defined to be normal to the sensing window 270) is perpendicular or substantially perpendicular to a longitudinal axis 101 extending through the optical fiber port 218. In this example, the sensing window 270 is curved and transversely disposed at a radial distance from the longitudinal axis 101. The sensing window may be transversely disposed in the sense that the sensing window axis 271 may extend radially from the longitudinal axis 101. The optical fiber port 218 may be a through hole dimensioned to receive an optical fiber therethrough into the interior of the casing 210 of the sensor head. The interior of the casing 210 includes structural elements 230 integrated with the wall or the casing 210. The structural elements 230 may serve as structural framework or structural support to locate and/or fix the optical fibers and/or the lenses in place, relative to the casing 210.

[0050] **FIG. 6A** and **FIG. 6B** illustrate another embodiment of the framework or structural element that may be disposed in the interior of the sensor head. The casing is not shown in **FIG. 6A** and **FIG. 6B** to reveal the structural element 230. The structural element 230 may be 3D printed to be integrally formed with the casing 210. The structural element 230 also serves to locate and/or fix the various optical components (e.g., double-cemented lens, prism lens, aspheric lens, etc., in place, relative to the casing 210. An optical fiber port 218 may be disposed at a first end of the casing (or structural element 230) to receive a longitudinally oriented

optical fiber. A sensing window 270 may be disposed at a second end of the casing (or structural element 230), the second end of the casing being longitudinally spaced apart from the first end, with the sensing window transversely oriented relative to the longitudinally oriented optical fiber port 218.

[0051] In some situations, it may be preferred to study the in-situ samples at different depths as the sensor head is lowered down a deep hole. In such cases, the "L"-shaped configuration would enable a more efficient sample collection process. The "L"-shaped configuration as proposed herein offers another advantage of a smaller size or footprint, enabling the sensor head to be delivered to small or tight spaces previously not possible using just a conventional optical fiber. This is because the energy density required to excite a sample and form a plasma plume is relatively high, e.g., in a range of gigawatts per square centimeters (GW/cm^2). Conventionally, the optical fiber has to be minimally of a certain thickness to handle the require energy density. However, such optical fibers have larger end face diameters and larger static bending radii, i.e., they are more difficult to bend.

[0052] With the sensor head proposed herein, it is possible to reduce or minimize aberration of the lenses, such that it is possible to achieve a smaller focal point area and a higher energy density without the need for thicker optical fibers and without the need to bend the thicker optical fibers. As illustrated, in embodiments of the present disclosure, the optical fibers are kept relatively straight, e.g., extending longitudinally along the elongate member and into the sensor head. Within the sensor head, any bending of the light rays is made by using lenses 240, without bending the optical fiber 160 itself.

[0053] Even in the "L"-shaped configuration of the sensor head 204, for example, a prism lens is used to bend the light rays. Decoupling the bending and the transmission of light in the optical fibers advantageously mean that thicker optical fibers (optical fibers with larger end-face diameters and higher energy tolerance) can be used. The prototypes made were as small as 2 cm x 2 cm x 2 cm in overall dimensions.

[0054] The sensor head proposed herein can advantageously be made by 3D printing. The method of fabrication may include preparing the digital 3D drawings, 3D printing the casing integrated with the structural support, and assembly the casing with the lenses. The sensor head (except for the lens and the optical fiber) may be entirely made by 3D printing. The material for 3D printing the sensor head may be any one or more selected from the group consisting of polymer, metal powder, ceramic, gypsum, etc. The polymer may be any one of PLA plastic, ABS, nylon, thermoplastic polyesters, etc. The metal powder may include aluminum. Other possible materials, depending on the actual use scenario, may include synthetic rubber or casting wax, etc. As demonstrated by the prototypes, it is possible to provide a sensor probe that is flexible for use in various composite application scenarios while at the same time achieve the stability of a conventional fixture made of metal. Advantageously, the proposed sensor probe can be made using biocompatible printing materials for scenarios with high safety requirements while enabling sample collection and analysis on-site, obviating the need to transport potentially hazardous materials.

[0055] Further Embodiments

[0056] **FIG. 7A** and **FIG. 7B** schematically illustrate different embodiments in which the casing 210 of the sensor head further defines a cavity 300 about the sensing window 270. The cavity 300 may be embodied in any one of the following, including but not limited to, a recess, a concave section or a spatially constrainable space (e.g., a constrained space) defined by a spatial constraint 310 about or proximity to sensing window 270. The cavity 300 and the probe interior 211 may be on different sides of the sensing window 270. In some embodiments, the cavity 300 may be described as being external to or outside of the probe interior 211. The cavity 300 is open to (or in fluid communication with) the external environment. The cavity 300 may be described as an open cavity. In some examples, the cavity 300 is hemispherical in shape, with the sensing window 270 disposed in the center of the cavity 300.

[0057] **FIG. 8A** to **FIG. 8C** shows variations of a part of the casing 210 and the cavity 300 in the form of a concave spatial constraint 310. The spatial constraint

310 may define cavities of various shapes and dimensions, including but are not limited to, hemispherical shape cavities, V-shaped cavities which are also referred to as triangular prism shaped cavities (e.g., **FIG. 8A**), cylindrical shape cavities (e.g., **FIG. 8B**), frustoconical shape cavities (e.g., **FIG. 8C**), etc.

[0058] The spatial constraint 310 enables a spatial confinement-based approach to enhance the accuracy of the FO-LIBS system. That is, the sensing window 270 is disposed in a cavity 300 that is shaped to provide a specific confined space condition.

[0059] **FIG. 9** schematically illustrate a process of laser ablation and plasma formation that forms the basis of LIBS. Irradiation of a laser 410 (also referred to as a laser beam, etc.) on a sample 400 may result in laser ablation without formation of plasma plumes. For LIBS, the laser 410 provided is preferably of a certain energy density, such that plasma plumes corresponding to the materials present are formed. There is mutual interaction among different plasmas, and their complex interactions involve laser parameters, sample properties, and plasma chemistry.

[0060] When the plasma's lifetime is extended, the effective spectral acquisition time also increases. As the laser ablation mass increases, the particle collision probability increases, the plasma lifetime prolongs, and the plasma temperature rises, the number of emitted photons increases accordingly, resulting in stronger LIBS signal intensity. Therefore, laser ablation mass, particle collision probability, plasma lifetime, and plasma temperature are four factors directly affecting the signal intensity of LIBS.

[0061] **FIG. 10** show schematic diagrams of plasma evolution with and without confinement or spatial constraints 310. According to embodiments of the present disclosure, one or more spatial constraints 310 are provided to reflect the shockwaves during the expansion process of the LIBS plasma. The spatial constraint 310 are provided to hinder the outward expansion of the plasma located at the center of the constraint, compressing the plasma volume (**FIG. 10**) and thereby increase the electron temperature, electron density, and particle collision probability within the plasma. Additionally, reflecting shockwaves can prolong the lifetime of the plasma to some extent, resulting in stronger emission signals.

[0062] Spatial constraints defining cavities such as hemispherical cavities, V-shaped plates, cylindrical cavities, etc., may be used to restrict the expansion of the LIBS plasma and to increase the signal intensity of LIBS. Compared to other methods, spatial constraint methods are advantageous because the spatial constraints proposed herein are physical structural components that can be cost-effectively fabricated and do not consume power to provide the desired technical effect.

[0063] Using a hemispherical cavity to confine the LIBS plasma for detecting manganese (Mn) in steel, under laboratory "optimal" conditions, the electron temperature of the LIBS plasma increased by 3,600 K (Kelvin), and the signal emission intensity of Mn increased by 12 times. It is thus verified that adding a "cavity" to the part where the FO-LIBS sensor probe contacts or is proximal to the sample can achieve spatial confinement in a practical, feasible and effective manner.

[0064] **FIG. 11A** and **FIG. 11B** are schematic diagrams illustrating further embodiments of the proposed sensor probe to address measurements of in-situ samples under complex conditions such as underground or underwater environments. More specifically, **FIG. 11A** shows an example in which the spatial constraint 310 is not deformable while a cover 320 is deformable and includes a part 340 made of an elastic material. **FIG. 11B** shows another example in which the cover 320 is partially opened with a hole 350 in the cover 320.

[0065] Various embodiments of the spatial constraint 310 may be possible. In some examples, with the provision of the spatial constraint 310, the lens at the sensing window may be optional. In some examples, the elastic material portion may be partially replaced with the same 3D printing material as that used for 3D printing other parts of the sensor head. In some examples, an electromagnet 330 is coupled to the cover 320 and configured to operate the cover 320 and to change a state of the cavity between a closed state and an open state. The cavity in a default state is a closed cavity or in a closed state. The position of the electromagnet 330 may be varied. Combined with 3D printing technology, various shapes can be

produced, including spatial constraints that are not easily achievable using conventional methods, e.g., to provide irregularly shaped cavities.

[0066] The opening and closing mechanism of the FO-LIBS sensor probe can be activated by the integration of a deformable component (e.g., component made of deformable materials) and an electromagnetic unit.

[0067] According to some embodiments, the sensor probe includes an electromagnetic control unit that is configured to controllably operate the cover. For example, the cover may function as a default-closed (enabling the cavity to be in a default closed state) and optionally a fail-safe mechanism (or a fallback mechanism). The cover may include a thin elastic membrane coupled with a magnetically responsive insert (e.g., magnetic component). In a default state, e.g., when the electromagnetic control unit is not powered on (or in a non-operating state), the membrane of the cover seals the cavity. When the electromagnet control unit is energized, the insert (e.g., magnetic component) is attracted by the electromagnetic force(s) generated. In response thereto, the membrane deforms to form an aperture. The aperture may be aligned with the optical axis of the sensing window. A hard stop ring may be provided proximal to membrane to limit displacement and/or deformation of the membrane, and to stabilize plume dynamics. In response to the electromagnetic control unit being de-energized, the membrane may undergo elastic recovery to return the cavity to the default closed state. Optionally, the elastic recovery of the membrane may be assisted by a return spring. The closed state of the cavity or the sealed configuration of the cover provides ingress protection and safeguards the sensing window. Actuation of the electromagnetic control unit may be configured in a series of short pulses synchronized with laser firing of the pulsed laser. Advantageously, this configuration can reduce power consumption and avoid overheating, while the default-closed state of the cavity enables safe operation, even when there is a fault in the system (fault conditions). Experiments using a prototype of the proposed system used a membrane formed from TPU or silicone, with a thickness in a range from 0.3 millimeters (mm) to 0.8 mm. The magnetic component may be a discrete article embedded in an elastomer or the a plurality of magnetic articles in an elastomer. In

some embodiment, the membrane includes an elastomer matrix with stainless steel or iron particles disposed in the elastomer matrix. The electromagnetic control unit includes a coil that may be encapsulated in an epoxy with an O-ring or a lip seal to achieve IP68/69K protection.

[0068] In some embodiments, the deformable component is made from flexible synthetic materials, such as thermoplastic elastomers or soft 3D-printed polymers, which can change shape when exposed to mechanical or magnetic stimuli. Coupled to the deformable component is an electromagnetic unit that includes a magnet designed to interact with ferromagnetic or magneto-responsive elements embedded within or attached to the deformable component (e.g., elastic membrane).

[0069] In a default state, the deformable cavity stays closed (e.g., closed state), shielding the optical components (in the casing) from environmental exposure. When the FO-LIBS system is activated, an electromagnetic field is created by the internal coil of the electromagnet unit. The electromagnetic field applies a force to the responsive elements in the membrane, causing the elastic structure to deform. As a result, the cover opens and LIBS measurement. After the measurement is taken, the electromagnetic field may be switched off, in response thereto, the elastic material would return to its original shape, effectively resealing the cavity and restoring its protective function.

[0070] The FO-LIBS system is highly adaptable to field conditions because the contactless electromagnetic actuation removes the need for mechanical parts, making it suitable for remote or underwater use. Second, the system is easy to customize; both the deformable membrane and magnetic control elements can be 3D printed and arranged into various shapes based on specific environmental needs. Lastly, the normally closed setup provides ongoing protection for delicate components like lenses and fiber-optic interfaces, shielding them from physical damage, corrosion, or contamination.

[0071] The operation of the components may be described as follows:

- The deformable component, e.g., the deformable elastic membrane, expands or contracts when activated by electromagnetic signals, acting as a dynamic gate that seals or uncovers the sensing cavity.
- When the electromagnet is activated, it causes movement in the membrane to open the cavity.
- When the electromagnet is turned off, the membrane passively returns to its original closed position, ensuring the system's integrity and readiness for the next operation cycle.

[0072] In some other embodiments, the proposed sensor probe includes a spatial constraint 310 with a cover 320 that is operable by mechanical actuation. The spatial constraint 310 and the probe interior 211 are separated by the sensing window 270. For example, the cover 320 may be coupled with a spring-loaded mechanical valve in place of the electromagnet. The valve may be closed in a default state. The valve may be manually operable or manually adjustable with the aid of servo motors or piezoelectric actuators.

[0073] In some embodiments, the proposed sensor probe is preferably provided with a deformable or openable cavity or spatial constraint in which the cavity can be an open cavity enabling the plasma plumes to come into direct contact with the sensing window. At the same time, the cavity can be closed to reduce contamination at the sensing window, e.g., when the sensor head has yet to reach the intended location or before measurements are taken. The signal strength and signal clarity are better, and the sensor head would require less frequent maintenance or replacement, despite being used under harsh field conditions.

[0074] In some alternative embodiments, the cover 320 may be a permanent barrier, e.g., the spatial constraint 310 may define a closed cavity. For example, the cover may be a thin and transparent film, e.g., made of Mylar or sapphire. Anti-fouling or hydrophobic coatings may be applied to the cover to reduce contamination of the cover by the environment.

[0075] In some embodiments, a coating may be provided on a surface of the deformable component of the cover, with the coating being configured to be hydrophobic and/or anti-fouling.

[0076] **FIG. 12 to FIG. 17** are examples of results obtainable from the proposed FO-LIBS system of the present disclosure, used on-site to detect possible contaminants of in-situ samples, for example, silver (Ag), gold (Au) and copper (Cu), nickel (Ni), titanium (Ti), and zinc (Zn), etc., including various heavy metals and other substances. The term "in-situ samples" refers to samples that are measured where they are found, without the samples being removed off-site to a laboratory. The results confirm that the proposed FO-LIBS system works.

[0077] Industrial Applications

[0078] The FO-LIBS system finds applications across various domains, including environmental monitoring, industrial quality control, geological analysis, and even on-site analysis of hazardous or remote samples. Its remote sensing capability makes it particularly valuable in scenarios where direct contact with potentially dangerous materials is challenging.

[0079] The FO-LIBS system and sensor probe thereof can be used for remote sensing. For example, the FO-LIBS system can be used to enable analysis of samples at a distance, reducing the need for direct contact with potentially hazardous materials. Advantageously, minimal sample preparation is required, compared to other techniques like wet chemical analysis. The FO-LIBS system enables real-time analysis, e.g., providing real-time results suitable for rapid analysis and decision-making. In many cases, the method of detection using the FO-LIBS system is non-destructive, allowing repeated measurements to be made on the same sample. Another practical application of the FO-LIBS system is elemental mapping, e.g., to create elemental distribution maps of sample surfaces.

[0080] The proposed sensor probe provides a more accurate and feasible method for in-situ monitoring and detection, either as a standalone test or as an improvement to existing detection devices. The proposed FO-LIBS system can facilitate in-situ feasibility testing of complex environments, such as waste, soil, air, and wastewater, including, e.g., marine, and underground exploration applications.

[0081] Advantageously, the sensor probe proposed herein can be modular. For example, the environmental scientist or investigator may carry a kit including an elongate member and a variety of interchangeable sensor heads configured to be

releasably engageable with the elongate member. Different sensor heads may be selected according to the environment, the expected location of the in-situ samples, etc. The sensor head may be replaced when it becomes contaminated or dirty. In other words, the proposed FO-LIBS system is a field-ready, modular, and yet integrated system enabling a more practical solution for various and remote environmental monitoring scenarios.

[0082] Various embodiments of the present disclosure may be described as a sensor probe for use with a fiber-optic laser induced breakdown spectroscopy (FO-LIBS) system. The sensor probe includes an elongate member and a sensor head. The sensor head is detachably couplable with a distal end of the elongate member to define a continuous interior in which one or more optical fibers are disposed, in which proximal ends of the one or more optical fibers are couplable to a laser source of the FO-LIBS system and a spectrometer of the FO-LIBS system, respectively. The sensor head includes: a casing, a sensing window, and a collimation-and-focusing sub-system. The casing has a wall defining a probe interior. The sensing window is disposed at the wall of the casing. The collimation-and-focusing sub-system being disposed in the casing and configured to define one or more optical paths between distal ends of the one or more optical fibers and the sensing window.

[0083] The sensor head of the sensor probe may further include or provide a cavity defined at least partially by the wall of the casing. The cavity may be defined about the sensing window on one side of the sensing window, with the probe interior being on another side of the sensing window.

[0084] The sensor head may further include a cover. The cover may be spaced apart from the sensing window to define the cavity between the sensing window and the cover.

[0085] The cover may be configured to be actuatable and/or deformable to change a state of the cavity between a closed state and an open state. The cavity is configured to have a default state in which the cavity is the closed cavity.

[0086] The cover may include a deformable component. The deformable component may be configured to be deformable to enable the state of the cavity to

be change between the close state and the open state. The deformable component may be elastically deformable.

[0087] The cover may include a coating on a surface of the deformable component. The coating may be configured to be hydrophobic and/or anti-fouling.

[0088] The cover may include an electromagnetic control unit. the electromagnetic control unit being configured to change the state of the cavity between the closed state and the open state.

[0089] The sensor probe may further include an electromagnetic control unit and a membrane. The electromagnetic control unit may include a coil and a magnetic component, in which the magnetic component is displaceable under an electromagnetic force generated by the electromagnetic control unit. The magnetic component may be coupled to the membrane. The membrane may be elastically deformable in response to the magnetic component being displaced.

[0090] The collimation-and-focusing sub-system may include a double-cemented lens and an aspheric lens. The double-cemented lens may include two lenses of different refractive indices arranged to form a parallel beam of light. The aspheric lens is configured to define a fixed distance between the collimation-and-focusing sub-system and the sensing window.

[0091] The collimation-and-focusing sub-system may further include a prism lens, in which the prism lens is disposed to deflect the parallel beam between the double-cemented lens and the aspheric lens.

[0092] The sensing window may be disposed at any one of a side wall of the casing and a terminal wall of the casing.

[0093] The one or more optical fibers may extend longitudinally straight through the elongate member to the sensor head.

[0094] The cavity may be any one of a hemispherical shape, a frustoconical shape, a cylindrical shape, and a triangular prism shape.

[0095] The sensing window may include a sapphire lens.

[0096] An in-situ fiber-optic laser-induced breakdown spectroscopy (FO-LIBS) system includes a laser source; a spectrometer; one or more optical fibers; and the sensor probe, in which a plasma plume formed by laser irradiation of an in-situ

sample is at least partially receivable in the cavity and detectable via the sensing window.

[0097] The sensor probe provides a sensing window at a side wall of the casing or at a terminal wall of the casing. The sensor probe may further define a cavity in which a plasma plume formed by laser irradiation of an in-situ sample can be at least partially received and detectable via a sensing window of the sensor probe. The cavity may be defined about the sensing window on one side of the sensing window, with a probe interior being on another side of the sensing window. A cover may be configured to be actuatable and/or deformable to open or close the cavity. The cavity is configured to have a default state in which the cavity is the closed cavity.

[0098] It can be understood from the foregoing description of various embodiments that the proposed sensor probe enables sensing of the plasma plume in-situ as sufficiently strong emissions for elemental analysis can be obtained real-time and/or on-site / in-situ. With the proposed sensor probe and FO-LIBS system, risks associated with the transport of potentially hazardous samples from the site to the laboratory can be averted.

[0099] All examples described herein, whether of apparatus, methods, materials, or products, are presented for the purpose of illustration and to aid understanding and are not intended to be limiting or exhaustive. Modifications may be made by one of ordinary skill in the art without departing from the scope of the claimed invention.

CLAIMS

1. A sensor probe for use with a fiber-optic laser induced breakdown spectroscopy (FO-LIBS) system, the sensor probe comprising:

an elongate member; and

a sensor head, the sensor head being detachably couplable with a distal end of the elongate member to define a continuous interior in which one or more optical fibers are disposed, wherein proximal ends of the one or more optical fibers are couplable to a laser source of the FO-LIBS system and a spectrometer of the FO-LIBS system, respectively,

and wherein the sensor head includes:

a casing, the casing having a wall defining a probe interior;

a sensing window, the sensing window being disposed at the wall of the casing; and

a collimation-and-focusing sub-system, the collimation-and-focusing sub-system being disposed in the casing and configured to define one or more optical paths between distal ends of the one or more optical fibers and the sensing window.

2. The sensor probe as recited in claim 1, wherein the sensor head further comprises a cavity defined at least partially by the wall of the casing, the cavity being defined about the sensing window on one side of the sensing window, the probe interior being on another side of the sensing window.

3. The sensor probe as recited in claim 2, wherein the sensor head further comprises a cover, the cover being spaced apart from the sensing window to define the cavity between the sensing window and the cover.

4. The sensor probe as recited in claim 3, wherein the cover is configured to be actuatable and/or deformable to change a state of the cavity between a closed state and an open state, and wherein the cavity in a default state is the closed cavity.

5. The sensor probe as recited in claim 4, wherein the cover comprises a deformable component, the deformable component being deformable to enable the state of the cavity to be change between the close state and the open state, the deformable component being elastically deformable.

6. The sensor probe as recited in claim 5, wherein the cover comprises a coating on a surface of the deformable component, the coating being configured to be hydrophobic and/or anti-fouling.

7. The sensor probe as recited in claim any one of claims 4 to 6, wherein the cover comprises an electromagnetic control unit, the electromagnetic control unit being configured to change the state of the cavity between the closed state and the open state.

8. The sensor probe as recited in claim 4, comprising:

- an electromagnetic control unit, the electromagnetic control unit including a coil and a magnetic component, the magnetic component being displaceable under an electromagnetic force generated by the electromagnetic control unit; and

- a membrane, the magnetic component being coupled to the membrane, the membrane being elastically deformable in response to the magnetic component being displaced.

9. The sensor probe as recited in any one of claims 2 to 8, wherein the collimation-and-focusing sub-system comprises:

- a double-cemented lens, the double-cemented lens being two lenses of different refractive indices arranged to form a parallel beam of light; and

- an aspheric lens, the aspheric lens defining a fixed distance between the collimation-and-focusing sub-system and the sensing window.

10. The sensor probe as recited in claim 9, wherein the collimation-and-focusing sub-system further comprises:

a prism lens, the prism lens being disposed to deflect the parallel beam between the double-cemented lens and the aspheric lens.

11. The sensor probe as recited in any one of claims 2 to 10, wherein the sensing window is disposed at any one of a side wall of the casing and a terminal wall of the casing.

12. The sensor probe as recited in any one of claims 2 to 11, wherein the one or more optical fibers extend longitudinally straight through the elongate member to the sensor head.

13. The sensor probe as recited in any one of claims 2 to 12, wherein the cavity is any one of a hemispherical shape, a frustoconical shape, a cylindrical shape, and a triangular prism shape.

14. The sensor probe as recited in any one of claims 2 to 13, wherein the sensing window comprises a sapphire lens.

15. An in-situ fiber-optic laser-induced breakdown spectroscopy (FO-LIBS) system comprising:

a laser source;

a spectrometer;

one or more optical fibers; and

the sensor probe according to any one of claims 2 to 14, wherein a plasma plume formed by laser irradiation of an in-situ sample is at least partially receivable in the cavity and detectable via the sensing window.