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(71) Applicant: **RUTGERS, THE STATE UNIVERSITY OF NEW JERSEY** [US/US]; Old Queen's, Somerset Street, New Brunswick, NJ 08909 (US).

(72) Inventors: **TSE, Stephen**; 30 Casale Drive South, Warren, NJ 07059 (US). **XIONG, Gang**; 32 Cedar Lane, Apt. D, Highland Park, NJ 08904 (US). **ZHANG, Yiyang**.

(74) Agents: **BUTCH III, Peter, J.** et al.; Fox Rothschild LLP, 997 Lenox Drive, Building 3, Lawrenceville, NJ 08648-2311 (US).

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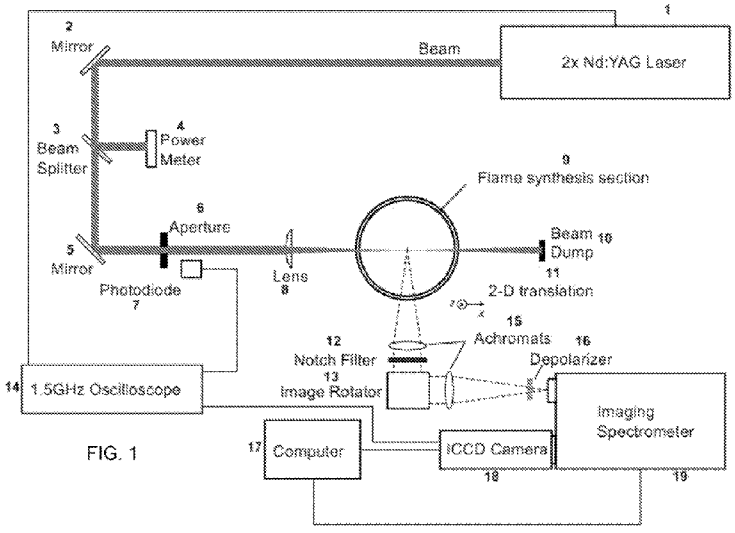

FIG. 1

(57) Abstract: A method of characterizing particles by excitation-intensity dependent Laser-Induced Breakdown Spectroscopy (LIBS), including providing a gaseous flow field comprising a gaseous phase and a particle phase, directing to the particle phase a series of laser pulses characterized by an excitation intensity effective to induce breakdown of the nanoparticles without breakdown of the gaseous phase, detecting the emission spectrum from the selective breakdown, and processing the spectrum to obtain measurements on various characteristics of the particles.

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METHODS FOR EXCITATION-INTENSITY-DEPENDENT PHASE-SELECTIVE LASER-INDUCED BREAKDOWN SPECTROSCOPY OF NANOPARTICLES AND APPLICATIONS THEREOF

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority under 35 U.S.C. § 119(e) to U.S. Provisional Patent Application Serial No. 61/917,991, filed on December 19, 2013, which is hereby incorporated by reference in its entirety.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH

[0002] This invention was made with government support under Grant Nos. W911NF-08-1-0417, W911NF-09-1-0138, and W911NF-10-1-0018 by the Army Research Office and through Grant No. N00014-09-1-0773 by the Office of Naval Research. Accordingly, the Government has certain rights in this invention.

FIELD OF THE DISCLOSURE

[0003] This invention describes methods of characterizing nanoparticles, including aerosols (e.g. elemental composition, size, volume fraction, etc.), which can be used, among other systems, during gas-phase synthesis or other particulate-monitoring systems.

BACKGROUND OF THE INVENTION

[0004] Nano-sized metal-oxide particles have great potential in a wide range of applications, including structural additives, purification of air and water, catalysis, chemical gas sensors, and energy-conversion devices. Gas-phase synthesis methods, including flame processes, are well known to produce metal-oxide nanoparticles less than 10 nm at high production rates with controllable sizes. Gas-phase processes allow for chemical conversion (homogeneous and heterogeneous) from precursor to metal-oxide monomers; coagulation and coalescence of metal-oxide nanoparticles; and deposition of particles driven by thermophoresis and diffusion. Fast time scales, along with steep temperature gradients, are well-suited for producing metastable phases, with the associated dynamics being far from equilibrium. As such, non-intrusive in-situ

diagnostics are essential in understanding growth mechanisms, as well as in process control during nanopowder manufacture via real-time feedback.

[0005] Although conventional laser-induced breakdown spectroscopy (LIBS) has been shown to be a quantitative technique for identifying particles, it cannot quantitatively characterize them substantially exclusively, as the molecules in the surrounding gas-phase are also broken down and excited. Accordingly, there is a strong need for better methods of mapping and characterizing nanoparticles during synthesis and other particulate-containing systems.

SUMMARY OF THE INVENTION

[0006] A novel excitation-intensity-dependent phase-selective laser-induced breakdown spectroscopy (LIBS) has been developed to characterize metal-oxide nanoparticles. In contrast to traditional application of LIBS on particles, the power used here is much lower; and no macroscopic spark is visually observed. Nevertheless, the low-intensity LIBS shows interesting selectivity—only exciting atoms in particle phase, with no breakdown emission occurring for gas molecules (e.g. metal-organic precursor, air). The emission intensity increases with particle size, plateauing as the particles reach a certain size, indicating the absorption efficiency to be size-dependent for small particles. Furthermore, by selecting the excitation wavelength to match the transition lines of the atoms, stronger emission intensity from the selected atoms can be produced to enhance the signal of the selected atoms without increasing the emission from other atoms. This method has been applied to make two-dimensional measurements of volume fraction of nanoparticles in both far and near wall conditions.

[0007] The selectivity of the low-intensity LIBS for such application can be advantageous for identifying nanoparticle composition, tracking nanoparticle formation and presence, and measuring nanoparticle volume fraction during gas-phase synthesis or particulate monitoring. The size-dependent absorption efficiency can be used to measure nanoparticle size in-situ.

[0008] This new method for detecting elements in nanoparticles, wherein only the nanoparticles are dissociated into their constituent atoms/ions (whose electrons are then excited) via laser without macroscopic visible spark, and where no delay time is needed to collect the

atomic emissions, presents many applications. It can be used for determining the progress rate of gas-to-particle transition processes; for determining the elemental portions in different substances in a gas or liquid dispensed mixture, for example, by changing laser fluence in-between different breakdown thresholds; for determining the particle concentration according to the breakdown threshold; for determining the particle concentration/volume-fraction according to the signal strength after saturation; for determining the particle size according to the different breakdown threshold; and for determining both the gas phase and particle phase concentrations by combining with conventional LIBS, as well as other laser-based diagnostics such as Raman spectroscopy, laser-induced fluorescence (LIF), laser-induced incandescence (LII), etc.

[0009] The broad suitability of the technique for other metal-oxides has been shown for different materials. Moreover, this method is applicable to small particles of a host of compositions other than metal oxides, such as nitrides, carbides, chlorides, pure metals, etc., albeit with differing requisite excitation power ranges and selectivity dependencies. Note that depending on the breakdown thresholds for the solid and gas phases, the particles may not be limited to nanoparticles and may be larger in size (e.g. microparticles). As such, the technique is particularly useful for small particle identification and monitoring for many systems, including those associated with pollutant emissions and atmospheric sciences. Moreover, the utilization of this diagnostic as an input into real-time feedback in modern control systems can be used to optimize and ensure quality in the large-scale commercial production of user-defined nanomaterials.

[0010] The present invention thus provides a method of characterizing nanoparticles by Laser-Induced Breakdown Spectroscopy (LIBS). The method comprises:

providing a gaseous flow field comprising a gaseous phase and a particle phase, wherein the particle phase comprises the particles to be characterized;

exciting the gaseous flow field with a series of laser pulses characterized by an excitation intensity effective to induce breakdown of the particle phase and excitation of the atoms within the particles without the breakdown of said gas phase and excitation of the atoms

within the gas phase, so that the excited atoms of the particles emit an atomic emission spectrum characteristic of the elements within the particles; and

detecting the emission spectrum produced by the excited atoms within the particles.

[0011] In some embodiments, the laser pulse comprises a pre-determined excitation wavelength matching an atomic transition line of an elemental species within the particles.

[0012] In some embodiments, the laser pulses are provided by a tunable laser and are characterized by a plurality of pre-determined excitation wavelengths matching the atomic transition line of more than one elemental species within the particles. The plurality of pre-determined excitation wavelengths can be generated sequentially or simultaneously.

[0013] In some embodiments, the laser pulses are provided by a plurality of lasers and are characterized by a plurality of pre-determined excitation wavelengths matching the atomic transition line of more than one elemental species within the particles. The plurality of pre-determined excitation wavelengths can be generated sequentially or simultaneously.

[0014] In some embodiments, the fluence of the laser is adjustable.

[0015] In some embodiments, the fluence of the laser is set at or above saturation of emission signals.

[0016] In some embodiments, the method of the present invention further comprises processing the emission spectrum to obtain a spatial measurement of the particles based on the emission intensity of the spectrum. In some embodiments, the spatial measurement obtained by processing the emission spectrum is a volume fraction measurement of the particles. In some embodiments, the laser pulses are in the form of a sheet and the emission spectrum is processed to obtain a planar volume fraction measurement of the particles.

[0017] In some embodiments, the method of the present invention further comprises processing the emission spectrum to obtain a temporal measurement of the nanoparticles.

[0018] In some embodiments, the method further comprises processing the emission spectrum to obtain a size measurement of the particles based on the emission intensity of the spectrum, provided that the concentration of the particles is known or constant.

[0019] In some embodiments, the method further comprises processing the emission spectrum to obtain a concentration measurement of the particles based on the emission intensity of the spectrum, provided that the size of the particles is known or constant.

[0020] In some embodiments, the method further comprises processing the emission spectrum to determine the elemental identity of the particles, wherein the fluence of the laser is optionally adjusted according to different breakdown thresholds. In some embodiments, the pre-determined excitation wavelengths match one or more atomic lines of known (reference) elements.

[0021] In some embodiments the particles comprise nanoparticles. In some aspects of this embodiment, the particles consist essentially of nanoparticles. In other embodiments the particles comprise microparticles. In some aspects of this embodiment, the particles consist essentially of nanoparticles.

[0022] In some embodiments, the gaseous flow field is sampled from a manufacturing process for producing the particles, and said method further comprises the steps of processing the emission spectrum to measure a characteristic of the particles and providing a feedback command according to the processed spectrum to the manufacturing process to control the measured characteristic of the particles.

[0023] In some embodiments, the particles are collected from a pollution source or a particulate-containing atmosphere.

BRIEF DESCRIPTION OF THE DRAWINGS

[0024] Embodiments will be described with reference to the following drawing figures, in which like numerals represent like items throughout the figures, and in which:

[0025] Figure 1 shows a typical schematic of the in-situ laser-based diagnostics as used during flame synthesis of nanoparticles. The setup is similar to that for conventional LIBS; however, the adjustment of laser-excitation intensity is critical in discriminating only the nanoparticle phases, with associated nanoparticle specific characterizations.

[0026] Figure 2 provides the typical low-intensity LIBS emission spectra acquired from a laser excitation of 532 nm (28 J/cm^2). Ti atomic spectra from NIST database is marked by red lines.

[0027] Figure 3A provides the integrated emission intensity (black squares) and calculated particle size (red line) as functions of distance from the tested burner exit, along the axis of symmetry.

[0028] Figure 3B provides the spectra collected at distances of 2 mm, 4 mm, 6 mm, 8 mm, and 14mm from the burner exit, respectively.

[0029] Figure 4 provides the emission intensities for different laser excitation powers at two different precursor loading rates. The measuring volume is at a distance of 14 mm from the burner exit.

[0030] Figure 5 provides the integrated emission intensity as a function of precursor concentration. The measuring volume is at a distance of 14 mm from the burner exit. The insets A and B are TEM photos of TiO_2 nanoparticles collected from substrate, when the gas-phase precursor loading concentrations are 116.4 ppm and 232.8 ppm respectively.

[0031] Figures 6A and 6B provides the emission spectra with 532 nm and 355 nm excitation, respectively, along with the given settings (e.g. the same laser power, detection settings, etc.).

[0032] Figure 7 provides the integrated emission intensity (black squares) from 532nm laser excitation, 355 nm excitation (blue circles), and calculated particle size (red line), as functions of distance from the burner exit, along the axis of symmetry.

[0033] Figure 8 .provides the intensity change with laser power for 497.534 nm emission, along with other emissions at 355 nm laser excitation. The inset shows the intensity change with laser power at 532 nm laser excitation.

[0034] Figure 9 provides the temporal evolution of emission intensity, as detected by photomultiplier tube (PMT) and recorded by digital oscilloscope.

[0035] Figure 10 provides the increase of signal intensity versus particle volume fraction. The line shows the linear fitting of the data with an intercept of 140 ppb.

[0036] Figure 11 provides the two-dimensional planar measurement of TiO_2 nanoparticle volume fraction produced by Bunsen flame synthesis, using phase-selective LIBS

[0037] Figure 12 provides the two-dimensional planar measurement of TiO_2 nanoparticle volume fraction in stagnation flame synthesis.

[0038] Figure 13 provides the application of the present invention in monitoring and controlling the production of nanoparticles.

[0039] Figure 14 provides the feedback mechanism for determining and refining the parameters for gas-phase synthesis of nanoparticles.

DETAILED DESCRIPTION

[0040] The instant invention describes methods for diagnosing nanoparticle characteristics (e.g., for metal- oxides, nitrides, carbides, chlorides, pure metals, or mixtures thereof), in-situ and ex-situ. By adjusting the excitation wavelength and laser fluence for laser-induced breakdown spectroscopy, only the particle phase undergoes breakdown and there is no macroscopic visible spark in the gas phase. As a result, high resolution spatial measurements of the particles can be accomplished. In addition, because no delay time is needed for the emission signal detection, high temporal resolution measurements can be achieved.

[0041] The methods can be adopted for the detection of nanoparticle composition of metal-oxides as well as other materials such as nitrides, carbides, chlorides, pure metals, etc., albeit with likely differing requisite excitation power ranges and selectivity dependencies, depending on the nature of the material. This can be determined by one of ordinary skill in the art without undue experimentation. In addition, depending on the breakdown thresholds for the solid and gas phases, the particles may not be limited to nanoparticles and may be larger in size (e.g. microparticles).

[0042] The methods of the present invention find broad applications in areas including particle measurement, process control, and environmental monitoring. For example, the methods are particularly useful for small particle identification and monitoring for many systems, including those associated with pollutant emissions and atmospheric sciences. Moreover, the

utilization of this diagnostic as an input into real-time feedback in modern control systems can be used to optimize and ensure quality in the large-scale commercial production of user-defined nanomaterials.

[0043] While the following text may reference or exemplify specific steps of a particle characterization process, it is not intended to limit the scope of the invention to such particular reference or examples. Various modifications may be made by those skilled in the art, in view of practical and economic considerations, such as the size and composition of the particles and the excitation wavelengths of the laser pulses. In order to more clearly and concisely describe the subject matter of the claims, the following definitions are intended to provide guidance as to the meaning of terms used herein.

[0044] The articles "a" and "an" as used herein mean "one or more" or "at least one," unless otherwise indicated. That is, reference to any element of the present invention by the indefinite article "a" or "an" does not exclude the possibility that more than one of the element is present.

[0045] The term "nanoparticle" used here includes solid phase particles as well as liquid phase particles (i.e., nanodroplets) and liquid phase-solid phase mixtures (i.e., nanoslurries).

[0046] The method of the present invention includes: providing a gaseous flow field comprising a gaseous phase and a particle phase, wherein the particle phase comprises the particles to be characterized; exciting the gaseous flow field with a series of laser pulses characterized by an excitation intensity effective to induce breakdown of the particle phase and excitation of the atoms within the particles without the breakdown of the gas phase and excitation of the atoms within the gas phase, so that the excited atoms of the particles emit an atomic emission spectrum characteristic of the elements within the particles; and detecting the emission spectrum produced by the excited atoms within the particles. The method may further include processing the emission spectrum to determine the characteristics of the particles.

[0047] Because the method includes using in-situ excitation-intensity-dependent laser induced breakdown of the particle phase without breaking down the gas phase in an aerosol, various characteristics can be obtained such as elemental particle information and concentration of particles, which are also useful for determining the progress rate of gas-to-particle transition

processes. By selecting the excitation wavelength to correspond to resonance of specific atomic lines, the limit of detection can be significantly lowered down. The wave-length can be chosen such that only the emission from the atom of interest is enhanced, thus achieving species selectivity. Since relatively low energy is required in this low-intensity LIBS process, species selectivity can be achieved via the use of a tunable laser, such as a dye laser or an array of tunable diode lasers. By selecting the laser fluence carefully according to the breakdown threshold(s), this method can be applied to various particle compositions to breakdown the particle phase only for detection, thus with high selectivity.

[0048] In some embodiments of the present invention, the series of laser pulses include one or more pre-determined excitation wavelengths which may be the same or different from the atomic line of known reference elements. Because each known element may have a set of corresponding atomic lines that can be the same as or overlapping with that of other elements, the number and range of the pre-determined wavelengths can be adjusted to suit the need for the detection of one or more elements. After detection and processing of the emission spectrum of the nanoparticles in comparison with that of the known reference elements, the elemental identification of the particle composition can be obtained. In some embodiments, the series of laser pulses includes one or more pre-determined excitation wavelengths that match an atomic transition of an elemental species within the particles to be characterized. The pre-determined wavelengths may also match two or more elemental species of the particles. The detection and processing of the resulting emission spectrum will not only serve to confirm the elemental identity of the particles, but also provide other information such as particle size, concentration, and volume fraction, with the advantage of very low detection thresholds. Moreover, the method of the present invention is characterized by lasing, affording extremely low threshold and directional detection at long distances from excitation/detection, using back-scatter configuration.

[0049] The excitation wavelengths may vary depending on the range of the particle size and other relevant parameters. For example, some wavelengths may be more suitable and sensitive than others for detecting smaller particles. As the size of the particles increases, a different wavelength may become more suitable. Accordingly, the wavelengths can be adjusted according

to the range of the particle size, which can be readily determined by one of ordinary skill in the art without undue experimentation.

[0050] The laser pulses can be generated from a single laser or multiple lasers. In some embodiments, the laser pulses have one or more pre-determined wavelengths that match the atomic transition lines of one or more known reference elements. The multiple lasers can be arranged in any suitable manner, including different angles from the particles to be characterized, different shape (e.g. beam or sheet), and different distance from the particles. In some embodiments, the laser pulses with one or more wavelengths can be generated from a tunable laser, such as a dye laser, or an array of tunable diode lasers. As described above, the laser pulses generated from the tunable laser can also have one or more pre-determined excitation wavelengths that match the atomic transition lines of one or more known reference elements. In some embodiments, the pre-determined wavelengths match the atomic lines of one or more elemental species of the nanoparticles to be characterized. In exemplary embodiments, the pre-determined wavelengths match more than one elemental species (e.g. 2, 3, 4, 5, 6, or more elemental species) as references or within the particles.

[0051] The pre-determined excitation wavelengths can be generated sequentially or simultaneously depending on the specific particles and the particular data to be collected. For example, multiple pre-determined excitation wavelengths generated at the same time can be used to detect or confirm the elemental identity of the particles. Meanwhile, multiple pre-determined excitation wavelengths generated sequentially find application on the monitoring of changing particle characteristics, such as particle growth and particle production. Sequential generation of pre-determined wavelengths also offer the benefit of lower intensity and therefore signal interference from the breakdown of surrounding mediums such as gas phase. However, methods using sequentially or simultaneously generated wavelengths are not mutually exclusive of each other and may both be employed in the same type of particle characterization.

[0052] The fluence of the laser can be adjusted depending on the particle size, the elemental composition of the particle, the excitation wavelength, and other parameters relating to breakdown thresholds. For example, while certain excitation wavelengths may be suitable for

detecting small particles within a certain range, the emission intensity can also be affected by laser fluence which will continue to excite more electrons as the power level increases and may lead to inconsistent results. Therefore, depending on the range of the particle size and the pre-determined wavelengths, adjustment of laser fluence is desirable. In some embodiments, the fluence remains constant. In some embodiments, the laser fluence is variable. In some embodiments, the laser fluence is set at a level that corresponds to the saturation of the emission signals. In some embodiments, the laser fluence corresponds to a level at or above the saturation of the emission signals. The exact extent of laser intensity above the signal saturation can be determined by one of ordinary skill in the art without undue experimentation. In general, keeping the laser fluence above the signal saturation level can help obtain consistent data. Meanwhile, it is still low enough to avoid the breakdown of the surrounding medium such as the gaseous phase.

[0053] The method of the present invention finds application in various aspects of particle detection. Because the low intensity laser does not affect substances or materials other than the particle phase, the emission spectrum resulting from the selective breakdown of the particles reflects a high spatial resolution measurement of the particles with zero or minimum interference from the surrounding medium (e.g. gaseous phase). For example, under low intensity laser condition, there is no visible macroscopic spark and the affected area (distinct nanoplasmas for each nanoparticle) is small compared to conventional laser induced breakdown spectroscopy. In addition, minimum delay time is required to detect the emission spectrum or signal because any possible Bremsstrahlung emissions dissipate quickly at nanosecond level so that nanosecond gating delays are sufficient to gate them out. Therefore, the method of the present invention also provides a high temporal resolution measurement of the particles.

[0054] In some embodiments, processing the emission spectrum of the laser induced breakdown of the particles provide a volume fraction measurement of the particles based on the emission intensity of the spectrum. In exemplary embodiments, the method comprises measuring the planar volume fraction of particles based on the atomic emission with a laser sheet at sufficiently high fluence to breakdown the particles locally. With the laser-generated nanoplasmas (as confirmed by ionic spectra) confined around each nanoparticle and inter-

particle distance sufficiently large, particle volume fraction can be determined with sufficient spatial resolution.

[0055] Depending on the range of the particle size, different intensity-particle volume fraction relationship has been observed. Accordingly, suitable equations can be extrapolated from experimental data for different ranges of particles with known characteristics. Processing the emission intensity against the extrapolated equations provides quantitative characterization of the particle volume fraction. In some embodiments, the particles to be characterized are above a cut-off size or within a certain size range, so that the emission intensity and the characteristic (e.g. particle volume fraction) to be measured are in a linear relationship. Exemplary cut-off sizes (particle diameter) include about 5.5 nm, about 6 nm, about 6.5 nm , about 7 nm, about 7.5 nm, about 8 nm, about 8.5 nm , about 9 nm, about 9.5 nm, about 10 nm, about 10.5 nm, about 11 nm, about 11.5 m, about 12 nm, about 12.5 nm. Similarly, in some embodiments, a cut-off volume fraction can be employed to obtain a linear relationship between the emission intensity of the particles and the particle volume fraction above the cut-off. Exemplary cut-off values of volume fraction include about 80 ppb, about 90 ppb, about 100 ppb, about 110 ppb, about 120 ppb, about 130 ppb, about 140 ppb, about 150 ppb, about 160 ppb, about 170 ppb, about 180 ppb, about 190 ppb, and about 200 ppb.

[0056] In some embodiments, the laser pulses are in the form of a sheet and processing of the emission spectrum provides a planar volume fraction measurement of the particles. The two-dimensional measurements of volume fraction of particles are applicable to both far and near wall conditions. The particle volume fraction measurement near walls provides a useful tool for monitoring various nanoparticle-related processes, such as particle deposition, which is important for the synthesis of nano-films.

[0057] In some embodiments, processing of the emission spectrum from the breakdown of the particles provides a size measurement of the particles based on the emission intensity of the spectrum provided that the concentration of the particles is known or constant.

[0058] In some embodiments, processing of the emission spectrum from the breakdown of the particles provides a concentration measurement of the particles based on the emission intensity of the spectrum provided that the size of the particles is known or constant.

[0059] In some embodiments, by increasing the intensity of laser fluence, from no breakdown, to particle-phase breakdown, to all matter breakdown (including gas phase) as a sequence, the concentrations of the particle phase as well as gas phase can both be determined. In exemplary embodiments, the particle-phase concentration is determined by low-intensity phase-selective LIBS, and the total concentration is determined by the normal LIBS, and the difference between them indicates the gas phase concentration.

[0060] In some embodiments, processing of the emission spectrum from the breakdown of the nanoparticles provides the elemental identity of the particles. In some embodiments, the emission spectrum reflects saturated signal strength. By comparing the characteristic peaks and intensity thereof with that of known reference elements, one of ordinary skill in the art can readily determine the presence or absence of certain elements in the particles. In particular, when the pre-determined excitation wavelengths matches one or more atomic lines of known (reference) elements, the pattern of the enhanced peaks are expected to be the same between the emission spectrum and the reference spectrum if the reference elements is present. The identity of multiple elements can also be determined in this manner.

[0061] In some embodiments, the laser fluence is optionally adjusted between different breakdown thresholds to suit the detection of individual or multiple elements. A laser pulse at any particular excitation wavelength may have a constant and changing fluence. Laser pulses with different excitation wavelengths, whether they are generated simultaneously or sequentially, may have the same or different laser fluences, which may change in the same or different patterns. In some embodiments, the fluence is set at or above a level which corresponds to the saturation point of the emission strength.

[0062] In some embodiments, the gaseous flow field is sampled from a manufacturing process for producing the particles. The method further includes the steps of processing the emission spectrum to measure a characteristic of the particles and providing a feedback

command according to the processed spectrum to the manufacturing process in order to control the measured characteristic of the particles. The feedback command may require process conditions to be maintained at current levels if the measured characteristic is nominal.

[0063] In some embodiments, the particles are collected from environments associated with pollution emissions or atmospheric sciences. For example, heavy metal-containing particles and other pollutant nanoparticles can be monitored in a particular environment. Regions or instances where gas-to-particle transitions occur (e.g. nucleation) can be identified. Accordingly, the methods of the present invention provide a convenient, accurate and efficient means of monitoring various environmental conditions.

[0064] The methods described herein can be applied to the detection of various types of particles. For example, extensions of the present methods to detect nanodroplets (liquid phase) and nanoslurries (liquid/solid mixtures) can be made by one of ordinary skill in the art without undue experimentation. There are also no particular restrictions on the state of the particles and extensions can be made to solid particles in fluids in general (e.g. surrounded by liquid phase rather than gas-phase). Further, the methods of the present invention can be applied to the detection of particles larger than nanoparticles such as microparticles. Exemplary sizes of nanoparticles and larger particles that can be characterized with the present invention include about 1-10 nm, about 1-25 nm, about 1-50 nm, about 1-100 nm, about 1-150 nm, about 1-200 nm, about 1-300 nm, about 1-400 nm, about 1-500 nm, about 1-1000 nm, or about 1-2000 nm.

EXAMPLE

Nanoparticle synthesis

[0065] The in-situ measurements of nanoparticles were performed on a stagnation swirl flame setup for TiO_2 synthesis. Briefly, the main parts of the setup included a stainless steel nozzle (burner) with 18 mm inner diameter, an internal swirler positioned 70 mm upstream of the nozzle outlet, and a water cooled substrate. Premixed gases of O_2, CH_4, and N_2, were fed into the burner, forming a stagnation swirl flame between the nozzle and substrate, with separation distance fixed at 19 mm. The precursor (titanium tetraisopropoxide, TTIP), was radiantly heated

in a bubbler to 353±1K with a temperature-controlled silicon controlled rectifier (SCR) and delivered to the burner by a nitrogen carrier gas flow.

[0066] The second harmonic (532 nm) and third harmonic (so-called 355 nm, which was actually 354.71 nm as measured for our system) of an Nd:YAG laser operating at 10Hz served as excitation source. The detector was an intensified charge coupled device (ICCD) camera, gated to minimize the interference from flame emissions and other sources. The typical gate width is 20 ns to 200 ns, and the typical collection time is 20 s to 400 s (200 shots to 4000 shots) for laser-induced emissions. The typical power used in the low-intensity LIBS measurement is 35 mJ/pulse, corresponding to a local fluence of 28 J/cm^2 at the focal point. A typical setup is shown in Figure 1. Components of the setup include: laser source generating laser pulses with suitable excitation wave-lengths (1); mirrors (2 and 5); beam splitter (3); power meter (4); aperture (6); photodiode (7); lengs (8); flame synthesis section (9); beam dump (10); 2-D translation (11); notch filter (12); image rotator (13); oscilloscope (14); achromats (15); depolarizer (16); computer (17); ICCD camera (18); imaging spectrometer (19).

Low-Intensity LIBS Emission Spectra

[0067] For the "low" laser intensity employed here, a selectivity of breakdown is manifested, where breakdown occurs only for nanoparticles but not for gas molecules. This technique is quite different from that for conventional LIBS, where all the atoms in the measuring volume are excited, eliminating all molecular information and discrimination of the source of atoms (e.g. particle or gas phase). Here, the selectivity makes the technique particularly attractive for any gas-phase synthesis process because the particle phase can be identified at low power with no breakdown in the gas phase where precursor species (that contain metal atoms) are present. Figure 2 provides the typical low-intensity LIBS emission spectra acquired from a laser excitation of 532 nm (28 J/cm^2). Ti atomic spectra from NIST database is marked by red lines. The selectivity is further evinced in Figure 3A, which shows emission intensity collected along the symmetry axis from distances of 2 mm to 16 mm downstream from the burner exit. No significant peaks were detected at distances less than 4 mm from the burner exit, where there was no particles or with particles smaller than 5 nm. The peaks started to appear at 4 mm, increased

in intensity up to 12 mm, and maintained approximately constant intensity at distances further than 12 mm. Figure 3B displayed emission spectra collected at distances of 2 mm, 4 mm, 6 mm, 8 mm, and 14 mm; and significant increase in peak intensity were discerned.

Emission Intensity and Laser Power

[0068] Saturation is observed when increasing laser power higher than 20 mJ/pulse, as shown in figure 4, suggesting that all Ti atoms in the particle phase are completely ablated from the nanoparticles and excited.

Emission Intensity and Precursor Concentration

[0069] The emission intensities for different precursor concentrations are shown in Figure 5. The measurement volume was located at a distance of 14 mm from the burner exit, using a laser power of 35 mJ/pulse, and was confirmed to be above the saturation power. The emission intensity increased fairly linearly with precursor concentration when the precursor concentration was larger than 150 ppm. The particles were smaller for small precursor concentrations, which reduced the absorption efficiency of the laser power. The linearity of the emission intensity curve after 150 ppm suggested that for particles larger than a certain size (~12 nm here), the absorption efficiency remained constant. The absorption efficiency increased with particle size and became constant for particles larger than ~12 nm. This effect can be used to determine particle volume fraction (single point or planer sheet) during synthesis, for particle sizes within a certain range.

Emission Intensity and Wavelength Selectivity

[0070] The emission spectra from the second harmonic (532nm) and from the third harmonic (354.71 nm) of an injection-seeded Nd:YAG are shown in figures 6A and 6B,respectively. The markedly strong emission at 497.534nm was from the resonant excitation where the 354.71nm laser broke down flame-synthesized titanium-dioxide nanoparticles into their elements and then excited the titanium electrons resonantly (from a ^{1}G state to $w^{1}F^{0}$ state, which is the upper state of transition line 497.534nm). In this way, by selecting the excitation wavelength, the limit of detection can be significantly lowered. Moreover, the wavelength can be chosen such that only emissions from the atoms of interest are enhanced, thus achieving species selectivity.

[0071] The emission intensity, along the axis of symmetry for the setup, from 532 nm and 355 nm laser excitation, are shown in Fig. 7. The intensity was calculated by integrating the emission from 497 nm to 502 nm. The emission intensities both showed a quick increase at 5-12 mm distance from burner exit where the flame was located, indicating phase change and particle growth. Nevertheless, it showed some differences for these two excitation wavelengths. With 532 nm excitation, there was no emission around 500 nm at 2 mm away from burner exit; however, with 355 nm excitation, the atomic emission was present even at 2 mm away from the burner exit, albeit with low intensity. Since in this low-swirl flame burner the gases and precursor were mixed at a distance prior to the burner exit to ensure uniform composition, the TTIP precursor encounters O_2; and there was some reaction in the gas phase at ~ 100 °C to form some TiO_2 clusters at the burner exit, eventually becoming TiO_2 particles at longer residence times. These clusters can somehow absorb the 355 nm laser light and became excited and broke down, while the 532 nm laser was not well absorbed, due to the absorption efficiency difference for wave-lengths. This different detection threshold for particle size can be used as a quantitative method for size characterization.

Emission Intensity and Laser Power

[0072] The emission intensity change with laser intensity was studied and compared to the case with 532 nm laser excitation, as shown in Fig. 8, with the inset showing the emission intensity change with 532 nm laser excitation. For both cases, the measured volume location and precursor concentration were set to 14 mm from the burner exit and 116 ppm, respectively, where the particle size was ~10 nm. With 355 nm excitation, the laser power changed from 0.5 mJ/pulse to 35 mJ/pulse, without gas-phase breakdown or visible plasma, which was not observed until ~40 mJ/pulse. With 532 nm excitation, the LIBS emission intensity saturated at a laser power of 20 mJ/pulse, and then remained at the plateau regime until gas broke down at ~70 mJ/pulse. Nevertheless, the emission intensities from 355 nm laser excitation exhibited no saturation until gas-phase broke down at 40 mJ/pulse. The saturation at 20 mJ/pulse with 532nm excitation corresponded to the complete ablation of the particles, while the low-intensity LIBS with 355 nm excitation continued to excite more electrons resonantly; and the upper state

transitions to other energy states, thus leading to the continuous increasing of the 497.534 nm emission, as well as other emissions.

Temporal Evolution of Emission Intensity

[0073] The detailed temporal evolution for different wavelengths as detected by PMT is illustrated in Fig. 9. The pulse width (FWHM, full width at half maximum) of the laser beam was fitted to be 10 ns, and the time when the laser pulse reached maximum was set to zero. The emissions around 497.53 nm (resonant emission) increased rapidly when the laser beam was present. However, the regular LIBS emission at 498.17 nm arose slowly but lasted for a longer time. With respect to the laser peak, the emissions around 497.53 nm came about 6 ns later, while the 498.17 nm emission reached its peak about 12 ns later. The emissions around 497.53 nm come 6 ns prior to the emission around 498.17 nm. Since the laser excited the electrons resonantly, it led to the fast increase of the emission at 497.53 nm; however, this emission was more dependent on the laser and decayed when the laser beam was not sufficiently strong. After the laser pulse ended at ~15 ns, the emissions around 497.53 nm lasted for another 15 ns, corresponding approximately to the transition decay time for the Ti (I) 497.534 nm line.

Emission Intensity and Particle Volume Fraction

[0074] The nanoparticle volume fraction measurement is demonstrated in Figure 10, where the particle volume fraction was controlled by different precursor loading rates. The 532nm laser power was 51.7 mJ/pulse, which was in the saturation regime. The linearity between signal intensity and nanoparticle volume fraction was quite good. Instead of a strictly proportional relation, there is an intercept due to the size dependent excitation efficiency. It appears that this effect can be well addressed by employing a cut-off volume fraction. Here, by linear extrapolation, the intercept value is determined to be 140 ppb, corresponding to a particle diameter of 5.6 nm at the measuring point. Below 140 ppb, the intensity significantly deviates from the linear fitting. From 140 ppb to 870 ppb, the linear fitting gives an average accuracy of 8% deviation, which is better for higher volume fraction. For even higher volume fraction in a similar environment, the relation should be even more linear since the size-dependence is weaker.

Two-Dimensional Planar Measurement of Volume Fraction

[0075] The two-dimensional planar LIBS for particle volume fraction measurement is demonstrated in figure 11. The laser beam was shaped to a sheet, and two 500 nm band-pass filters were installed in series in front of the ICCD camera, to assure that inference from elastic scattering is blocked. The whole image was composed of four snapshots at different heights above the Bunsen burner (HAB 7.5–23.5 mm), starting from 3 mm before flame tip to 13 mm downstream from the tip. The rapid formation of TiO_2 nanoparticles across the flame front was clearly seen, verifying the fast chemistry of TTIP reaction. The absence of signal before the flame zone demonstrated the phase-selectivity of this technique, showing no excitation when Ti atoms (e.g., as part of the TTIP precursor) were in the gas phase. The main increase of signal was accomplished within 1 mm of the flame zone, where particles grew to about 7 nm according to population balance modeling. This portion of the increase came from the size-dependent excitation. As the particles continued coagulating in the post-flame gases, the signal was fairly uniform and stable, indicating the conservation of nanoparticle volume fraction during the coagulation process. The signal decayed at the left and right edges represented the gradient of volume fraction due to diffusion and entrainment. The results further demonstrated the good preservation of spatial resolution. There was a slight increase downstream, which was mainly caused by gas contraction as the burned gas temperature slowly dropped.

[0076] In order to demonstrate the measurement near walls, where particle dynamics as affected by diffusion and thermophoresis is always of great interest, a substrate was placed perpendicularly to the issuing Bunsen flame; and the laser sheet was positioned to investigate the boundary layer. The image of nanoparticle volume fraction in the stagnation flame was shown in Fig. 12. The decay of signal downstream of the diverging flow showed the decrease of nanoparticle volume fraction due to the entrainment of ambient particle-free gas, as well as deposition loss to the substrate. The gradient in the boundary layer can be resolved. Interference from bright reflections from the substrate surface was blocked by two tandem band-pass filters. The measurement of nanoparticle volume fraction near walls is very useful for the study of nanoparticle deposition, which is important for the synthesis of nano-films.

Monitoring and Controlling the Production of Nanoparticles

[0077] Using excitation-intensity-dependent laser-induced breakdown spectroscopy, heavy metal-containing particles and other pollutant nanoparticles can be monitored in a particular environment. Regions or instances where gas-to-particle transitions occur (e.g. nucleation) can be identified.

[0078] Referring now to Figure 13, a method 1300 is provided. First, nanoparticles are produced using known gas-phase synthesis methods. For example, gas flow rates, ambient pressure, precursor loading, substrate temperature, and the like, are parameters that are involved to synthesize nanoparticles **1302**. In-situ low-intensity phase-selective LIBS measurement is conducted **1304**. The characteristics of the nanoparticles are determined **1306**. If the nanoparticle characteristics are in the proper range (**1308**: Yes) then the nanoparticle production process is concluded **1310**. If the nanoparticles are not in the proper range (**1308**: No), then the process returns to step **1302** for refinement of the parameters for gas-phase synthesis of nanoparticles. Details on the feedback mechanism for determining and refining the parameters for gas-phase synthesis of nanoparticles are provided in Figure 14.

CLAIMS

We claim:

1. A method of characterizing particles by Laser-Induced Breakdown Spectroscopy (LIBS), said method comprising:

providing a gaseous flow field comprising a gaseous phase and a particle phase, wherein said particle phase comprises the particles to be characterized;

exciting said gaseous flow field with a series of laser pulses characterized by an excitation intensity effective to induce breakdown of said particle phase and excitation of the atoms within said particles without the breakdown of said gas phase and excitation of the atoms within said gas phase, so that said excited atoms of said particles emit an atomic emission spectrum characteristic of the elements within said particles; and

detecting the emission spectrum produced by the excited atoms within said particles.

2. The LIBS method of claim 1, wherein said laser pulse comprises a pre-determined excitation wavelength matching an atomic transition line of an elemental species within said particles.

3. The LIBS method of claim 1, wherein said laser pulses are provided by a tunable laser and are characterized by a plurality of pre-determined excitation wavelengths matching the atomic transition line of more than one elemental species within said particles.

4. The LIBS method of claim 1, wherein said laser pulses are provided by a plurality of lasers and are characterized by a plurality of pre-determined excitation wavelengths matching the atomic transition line of more than one elemental species within said particles.

5. The LIBS method of claims 3 or 4, wherein said plurality of pre-determined excitation wavelengths are generated sequentially.

6. The LIBS method of claims 3 or 4, wherein said plurality of pre-determined excitation wavelengths are generated simultaneously.

7. The LIBS method of claim 1, wherein the fluence of the laser is adjustable.

8. The LIBS method of claim 1, wherein the fluence of the laser is set at or above saturation of emission signals.

9. The LIBS method of claim 1, further comprising processing the emission spectrum to obtain a spatial measurement of the particles based on the emission intensity of said spectrum.

10. The LIBS method of claim 1, further comprising processing the emission spectrum to obtain a temporal measurement of the particles.

11. The LIBS method of claim 9, wherein the spatial measurement obtained by processing said emission spectrum is a volume fraction measurement of said particles.

12. The LIBS method of claim 11, wherein the laser pulses are in the form of a sheet and the emission spectrum is processed to obtain a planar volume fraction measurement of the particles.

13. The LIBS method of claim 1, further comprising processing the emission spectrum to obtain a size measurement of the particles based on the emission intensity of said spectrum, provided that the concentration of the particles is known or constant.

14. The LIBS method of claim 1, further comprising processing the emission spectrum to obtain a concentration measurement of the particles based on the emission intensity of said spectrum, provided that the size of the particles is known or constant.

15. The LIBS method of claim 2, further comprising processing the emission spectrum to determine the elemental identity of the particles, wherein the fluence of the laser is optionally adjusted according to different breakdown thresholds.

16. The LIBS method of claim 15, wherein said pre-determined excitation wavelengths matches one or more atomic lines of known (reference) elements.

17. The LIBS method of claim 1, wherein said gaseous flow field is sampled from a manufacturing process for producing said particles, and said method further comprises the steps of processing the emission spectrum to measure a characteristic of said particles and providing a feedback command according to the processed spectrum to said manufacturing process to control the measured characteristic of the particles.

18. The LIBS method of claim 1, wherein the particles are collected from a pollution source or a particle-containing atmosphere.

19. The LIBS method of claim 1, wherein the particles are nanoparticles.

20. The LIBS method of claim 1, wherein the particles are microparticles.

FIGURES

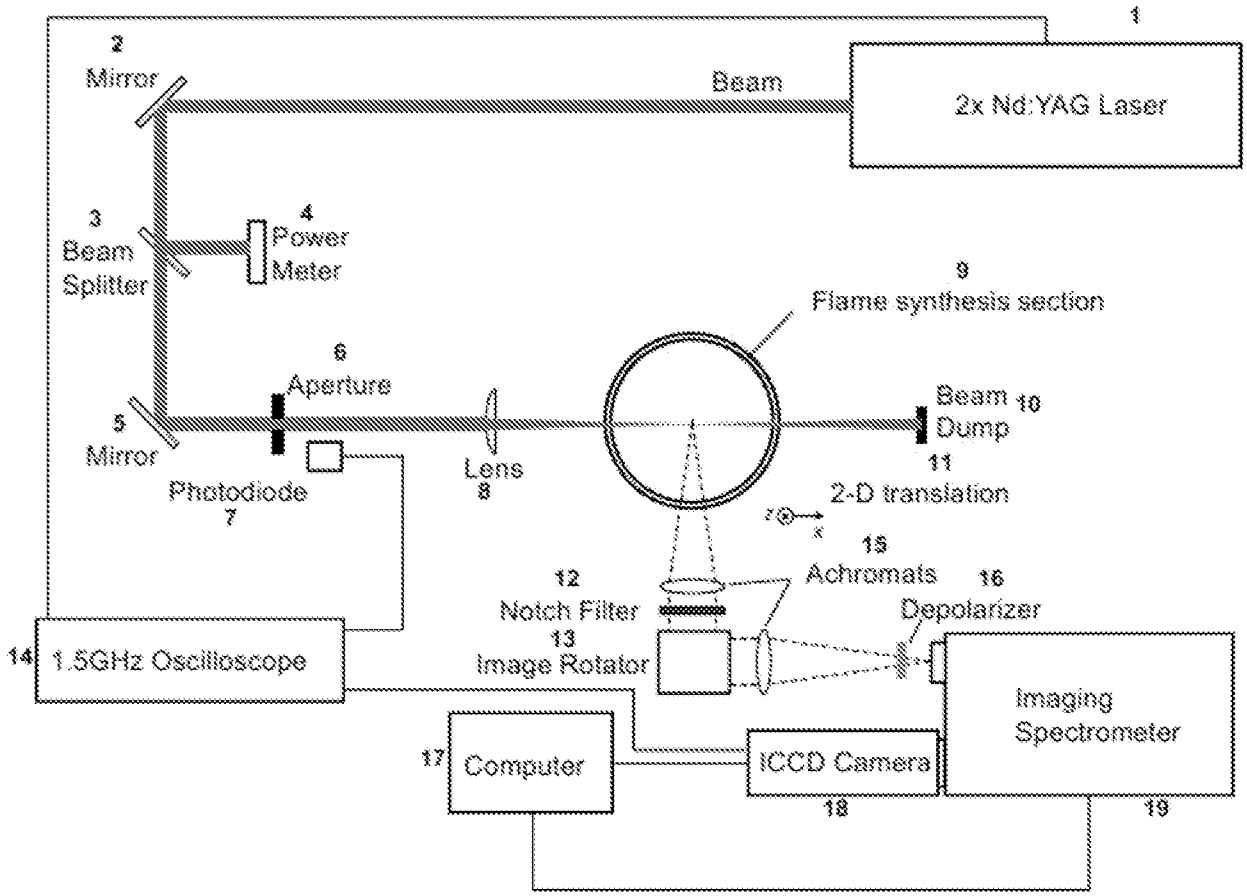

FIG. 1

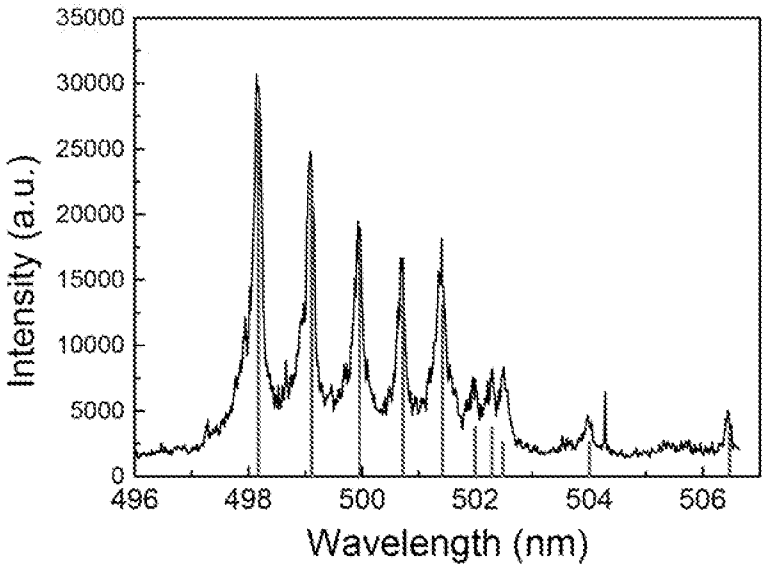
35000
30000
25000
20000
15000
10000
5000
0
Intensity (a.u.)
496
498
500
502
504
506
Wavelength (nm)

FIG. 2A

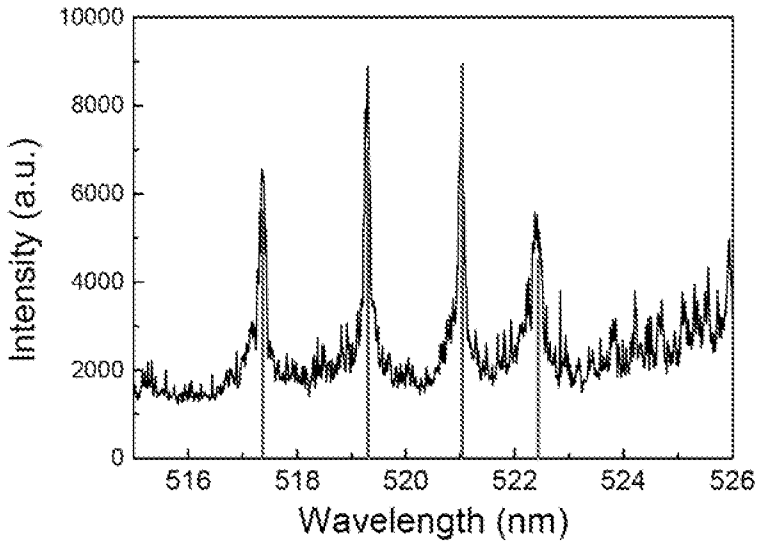
10000
8000
6000
4000
2000
0
Intensity (a.u.)
516
518
520
522
524
526
Wavelength (nm)

FIG 2B

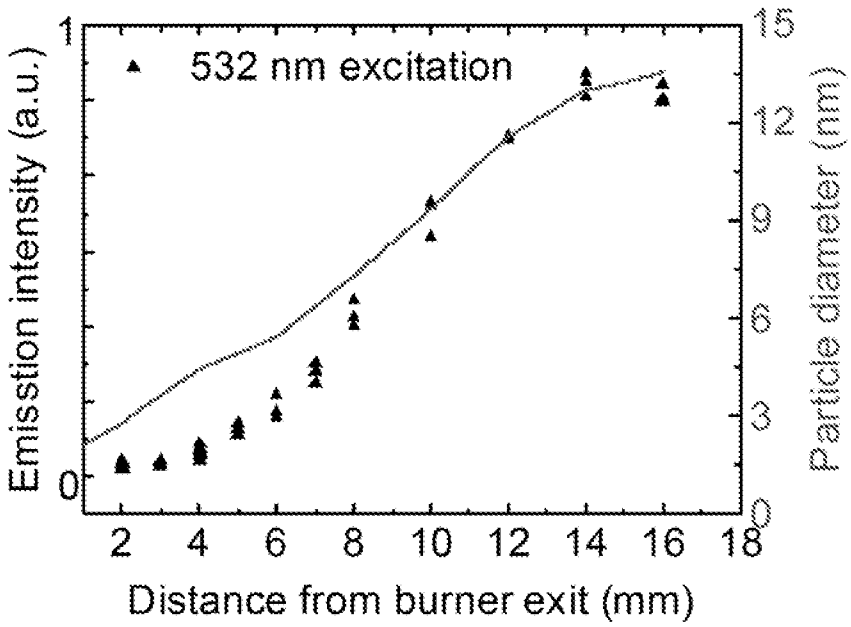
532 nm excitation
Emisstion intensity (a.u.)
Particle diameter (nm)
Distance from burner exit (mm)
0
1
0
3
6
9
12
15
2
4
6
8
10
12
14
16
18

FIG. 3A

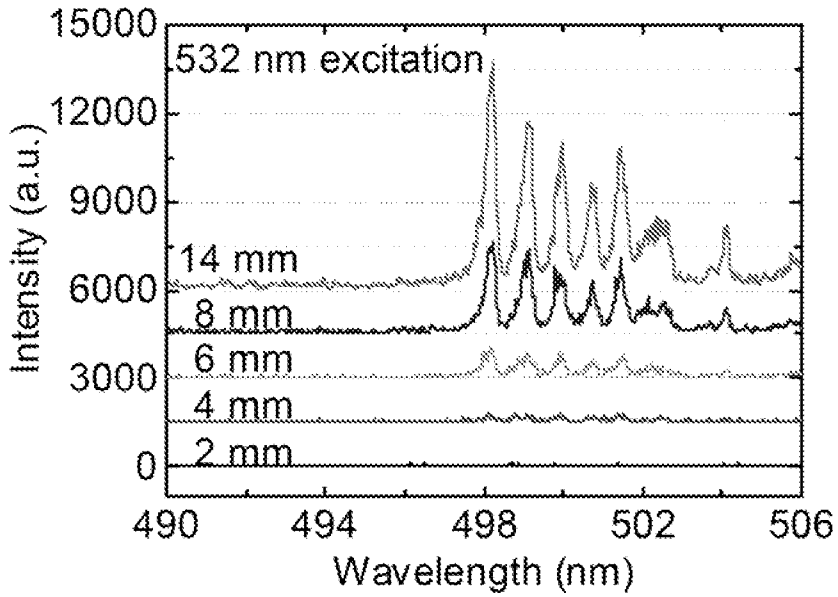
532 nm excitation
Intensity (a.u.)
Wavelength (nm)
14 mm
8 mm
6 mm
4 mm
2 mm
0
3000
6000
9000
12000
15000
490
494
498
502
506

FIG. 3B

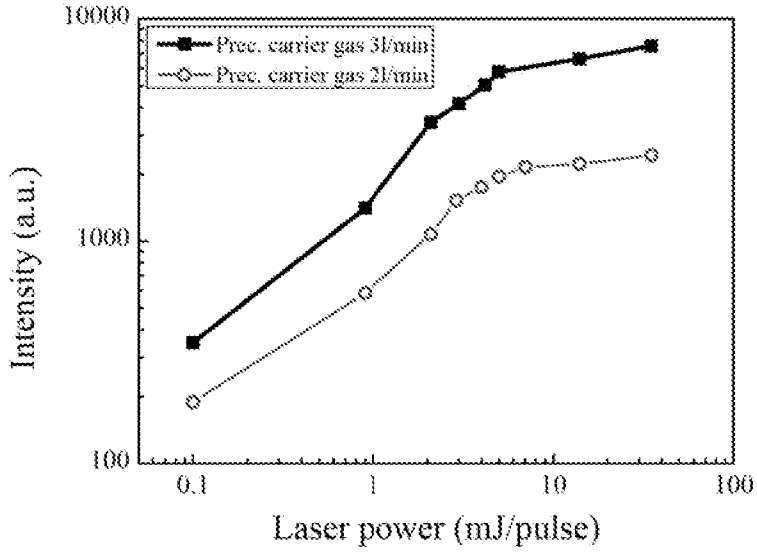
10000
1000
100
Intensity (a.u.)
Prec. carrier gas 3l/min
Prec. carrier gas 2l/min
0.1
1
10
100
Laser power (mJ/pulse)

FIG. 4

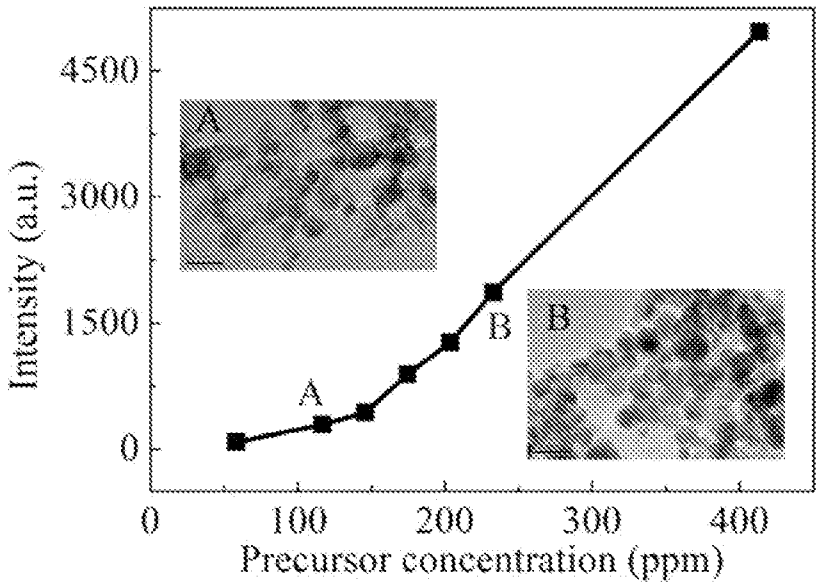
4500
3000
1500
0
Intensity (a.u.)
A
B
A
B
0
100
200
300
400
Precursor concentration (ppm)

FIG. 5

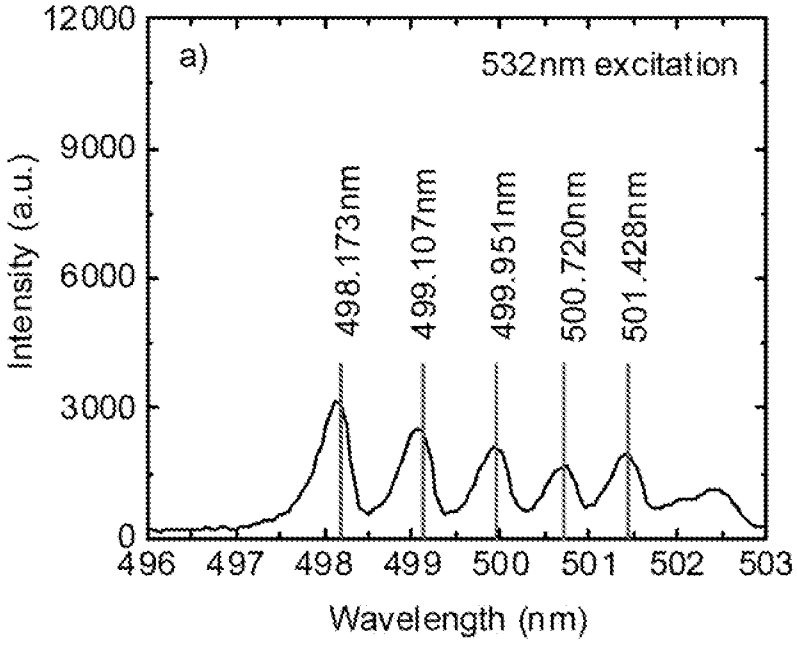
a)
532nm excitation
Intensity (a.u.)
12000
9000
6000
3000
0
498.173nm
499.107nm
499.951nm
500.720nm
501.428nm
496
497
498
499
500
501
502
503
Wavelength (nm)

FIG. 6A

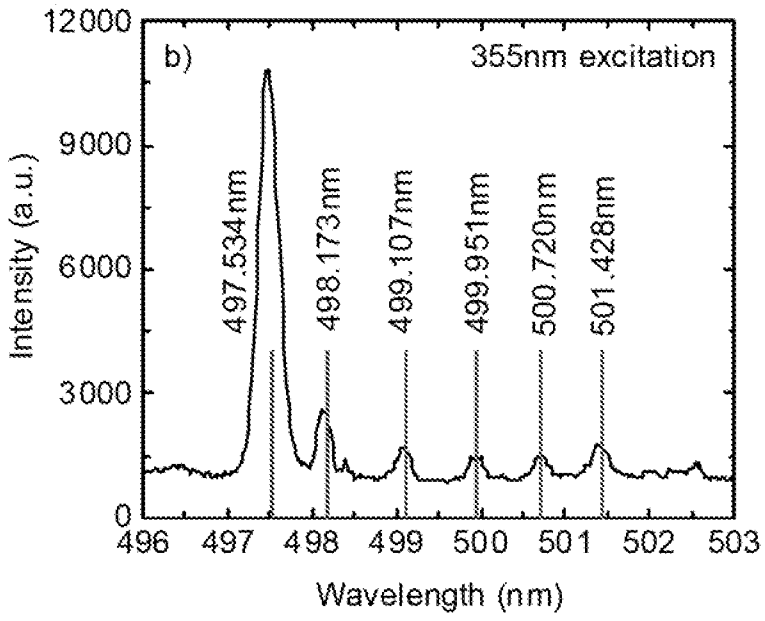
b)
355nm excitation
Intensity (a.u.)
12000
9000
6000
3000
0
497.534nm
498.173nm
499.107nm
499.951nm
500.720nm
501.428nm
496
497
498
499
500
501
502
503
Wavelength (nm)

FIG. 6B

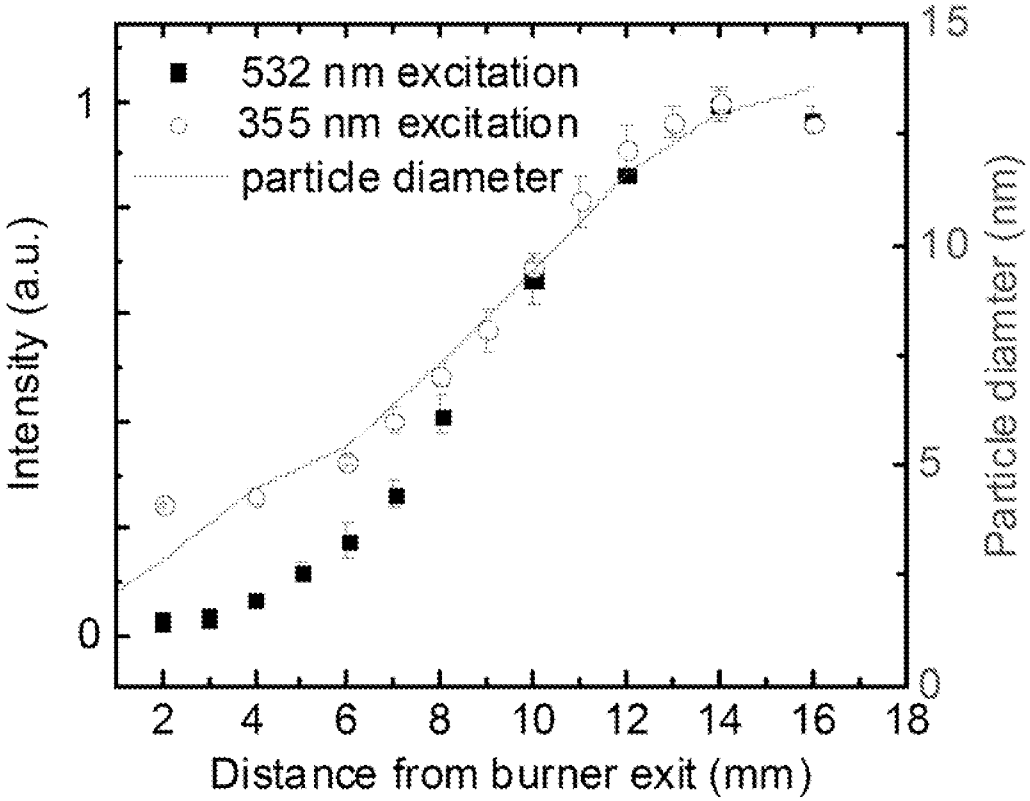
532 nm excitation
355 nm excitation
particle diameter
Intensity (a.u.)
Particle diamter (nm)
Distance from burner exit (mm)
0
1
0
5
10
15
2
4
6
8
10
12
14
16
18

FIG. 7

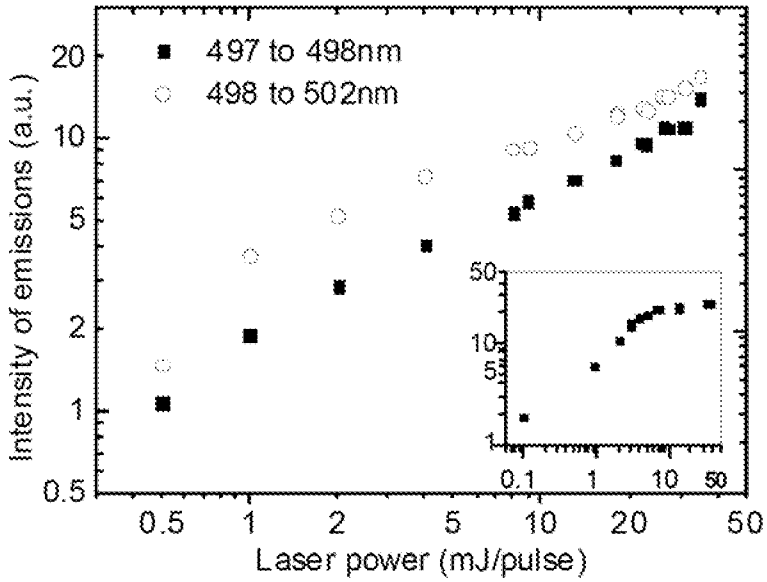
497 to 498nm
498 to 502nm
Intensity of emissions (a.u.)
Laser power (mJ/pulse)
0.5
1
2
5
10
20
50
0.1

FIG. 8

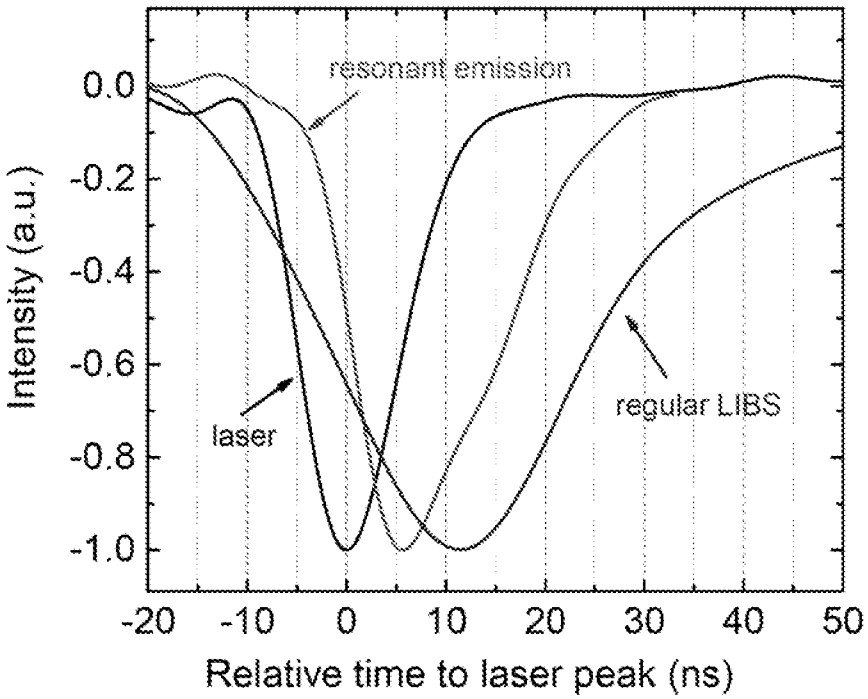
resonant emission
laser
regular LIBS
Intensity (a.u.)
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
-20
-10
0
10
20
30
40
50
Relative time to laser peak (ns)

FIG. 9

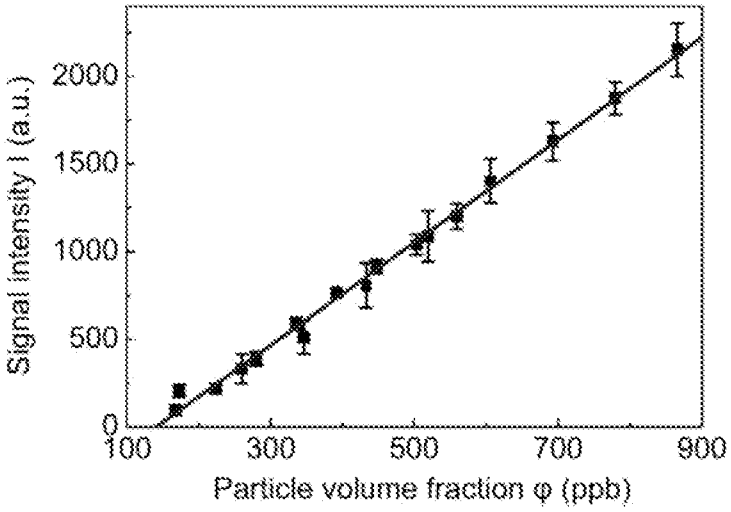
Signal intensity I (a.u.)
2000
1500
1000
500
0
100
300
500
700
900
Particle volume fraction φ (ppb)

FIG. 10

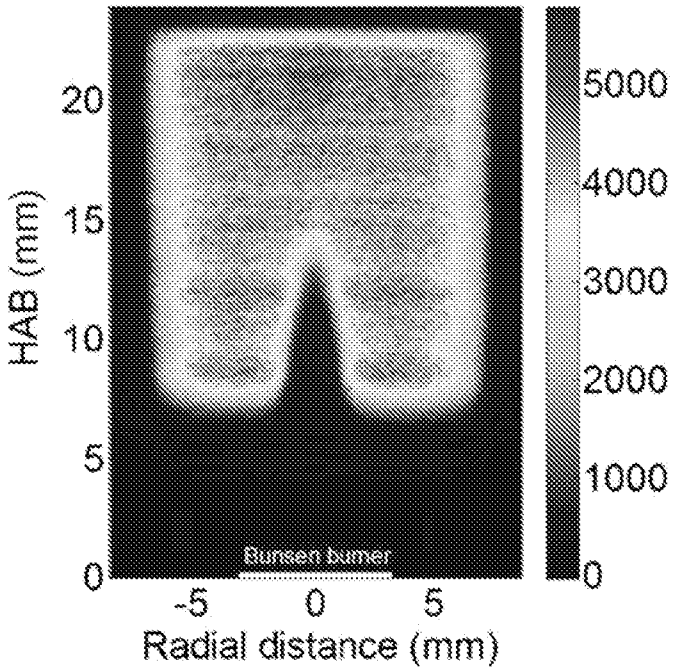
HAB (mm)
20
15
10
5
0
-5
0
5
Radial distance (mm)
Bunsen burner
5000
4000
3000
2000
1000
0

FIG. 11

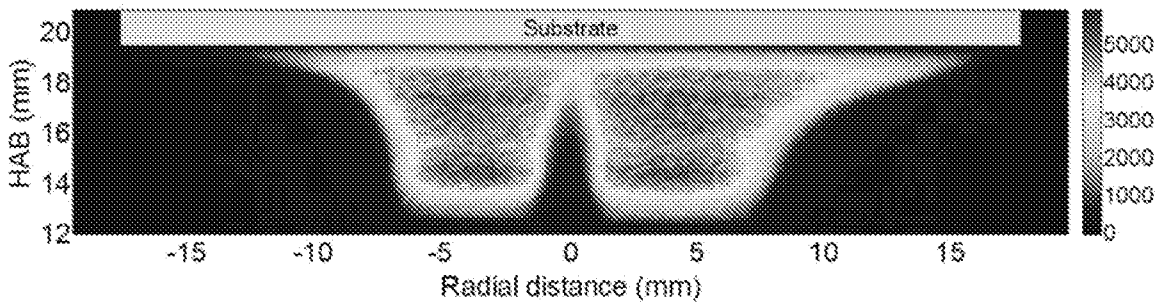
Substrate
HAB (mm)
20
18
16
14
12
-15
-10
-5
0
5
10
15
Radial distance (mm)
6000
4000
3000
2000
1000
0

FIG. 12

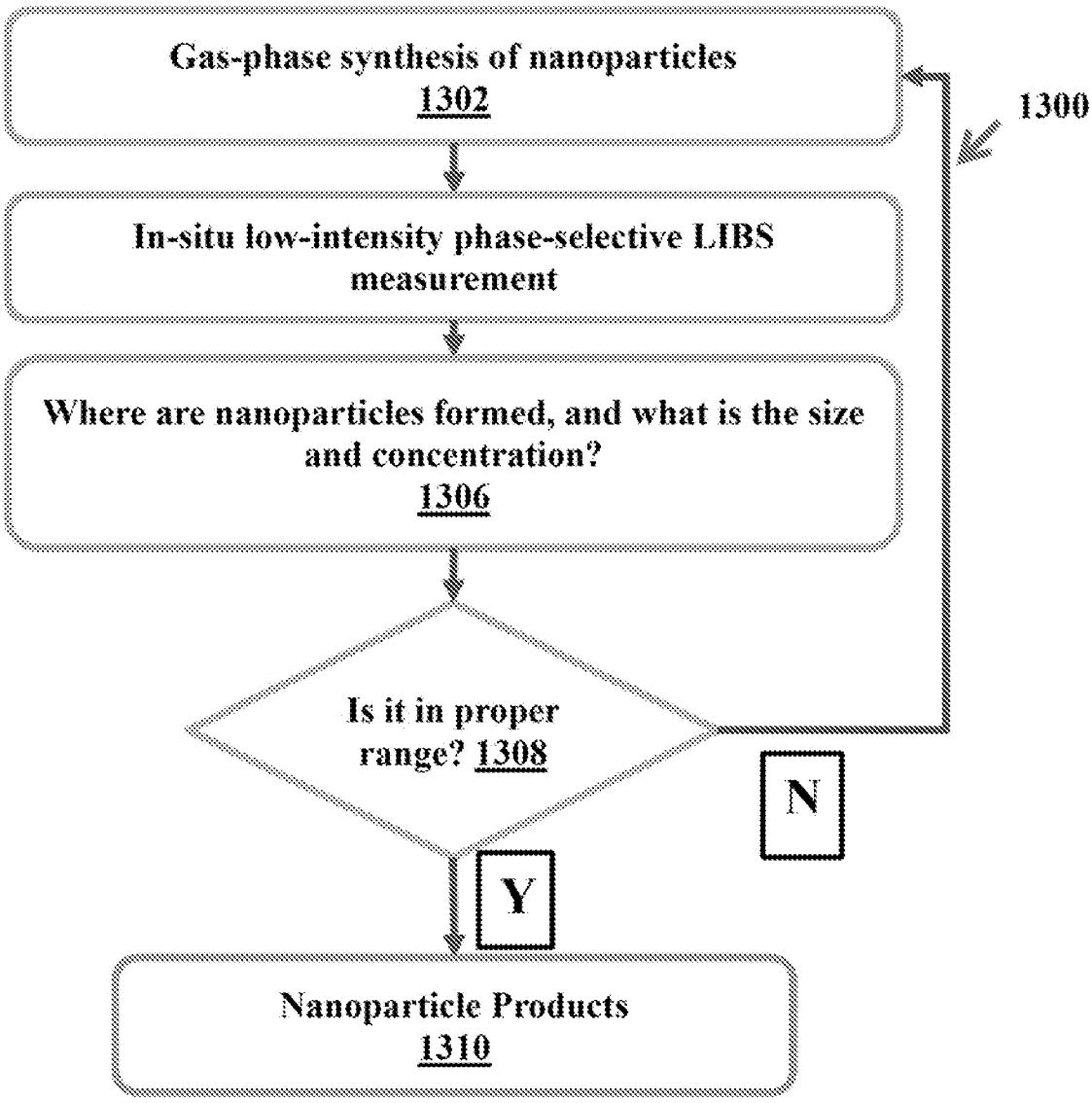
Gas-phase synthesis of nanoparticles
1302
In-situ low-intensity phase-selective LIBS measurement
Where are nanoparticles formed, and what is the size and concentration?
1306
Is it in proper range? 1308
N
Y
Nanoparticle Products
1310
1300

FIG. 13

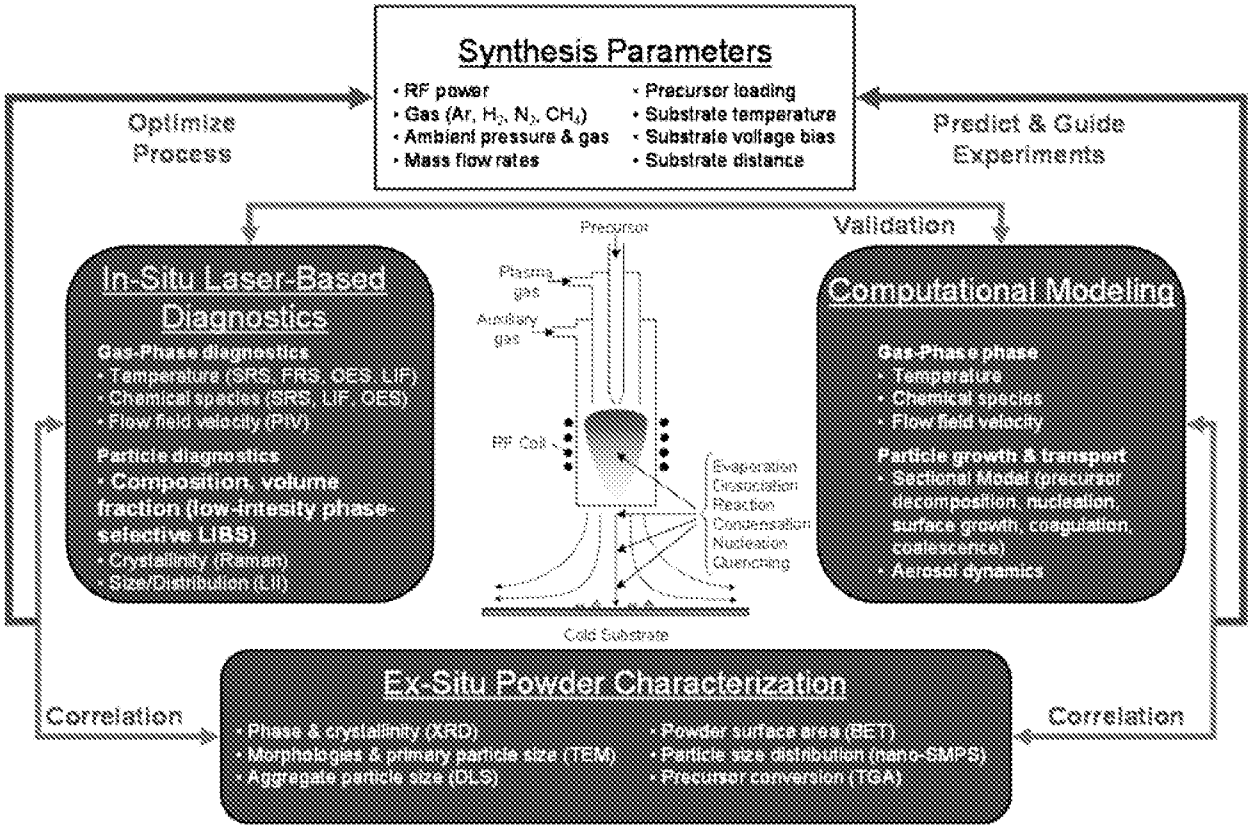
Synthesis Parameters
• RF power
• Gas (Ar, H_2, N_2, CH_4)
• Ambient pressure & gas
• Mass flow rates
• Precursor loading
• Substrate temperature
• Substrate voltage bias
• Substrate distance
Optimize Process
Predict & Guide Experiments
Validation
In-Situ Laser Based Diagnostics
Gas-Phase diagnostics
• Temperature (SRS, FRS, CES, LIF)
• Chemical species (SRS, LIF, CES)
• Flow field velocity (PIV)
Particle diagnostics
• Composition, volume fraction (low-intesity phase-selective LIBS)
• Crystallinity (Raman)
• Size/Distribution (ELS)
Precursor
Plasma gas
Auxiliary gas
RF Coil
Evaporation
Dissociation
Reaction
Condensation
Nucleation
Quenching
Cold Substrate
Computational Modeling
Gas-Phase phase
• Temperature
• Chemical species
• Flow field velocity
Particle growth & transport
• Sectional Model (precursor decomposition, nucleation, surface growth, coagulation, coalescence)
• Aerosol dynamics
Correlation
Correlation
Ex-Situ Powder Characterization
• Phase & crystallinity (XRD)
• Morphologies & primary particle size (TEM)
• Aggregate particle size (DLS)
• Powder surface area (BET)
• Particle size distribution (nano-SMPS)
• Precursor conversion (TGA)

FIG. 14

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2014/071704

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - G01J 3/30 (2015.01)
CPC - G01J 3/4406 (2015.04)
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC(8) - G01J 3/30, 3/40, 3/45 (2015.01)
USPC - 356/303, 318, 320, 437, 451, 456; 250/339.13

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
CPC - G01J 3/06, 3/42, 3/4406; G01N 21/718 (2015.04) (keyword delimited)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Orbit, Google Patents, ProQuest
Search terms used: laser induced breakdown spectroscopy, particles, gas, low intensity, laser pulses, feedback, concentration

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ----- Y	ZHANG et al. Novel Low-Intensity Phase-Selective Laser-Induced Breakdown Spectroscopy of TiO2 Nanoparticle Aerosols During Flame Synthesis. 20 December 2012. [31 July 2015] Retrieved from the internet: <URL: http://www.sciencedirect.com/science/article/pii/S0010218012003483> pages 725-733	1-2, 7-11, 13, 15-16, 19 ---------- 3-6, 12, 14, 17-18, 20
Y	US 2006/0197033 A1 (HAIRSTON et al) 07 September 2006 (07.09.2006) entire document	3-6, 18
Y	US 2004/0100999 A1 (LIU) 27 May 2004 (27.05.2004) entire document	12
Y	US 2006/0256330 A1 (LEIPERTZ) 16 November 2006 (16.11.2006) entire document	14
Y	US 2007/0176078 A1 (TAKAHASHI et al) 02 August 2007 (02.08.2007) entire document	17
Y	US 2012/0314214 A1 (ALEXANDER et al) 13 December 2012 (13.12.2012) entire document	20
A	US 2013/0265574 A1 (BUCKLEY et al) 10 October 2013 (10.10.2013) entire document	1-20
A	US 2009/0040505 A1 (ACKERMAN et al) 12 February 2009 (12.02.2009) entire document	1-20

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
03 August 2015	20 AUG 2015
Name and mailing address of the ISA/ Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer Blaine Copenheaver PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774