

**FILM, MID INFRARED DETECTION SYSTEM, METHODS OF FORMING AND
OPERATING THE SAME**

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of priority of Singapore application No. 10202302270S filed August 10, 2023, the contents of it being hereby incorporated by reference in its entirety for all purposes.

TECHNICAL FIELD

[0002] Various embodiments of this disclosure may relate to a film including nanostructures. Various embodiments of this disclosure may relate to a method of forming a film including nanostructures. Various embodiments of this disclosure may relate to a mid infrared detection system. Various embodiments of this disclosure may relate to a method of forming a mid infrared detection system. Various embodiments of this disclosure may relate to a method of operating a mid infrared detection system.

BACKGROUND

[0003] Mid infrared (MIR) detection is of particular research interest and technological importance for various applications including environment monitoring, homeland security, thermal imaging, standoff sensing etc. Typical MIR detector materials, like indium antimonide (InSb), mercury cadmium telluride (MCT) and type-II superlattices (T2SL) are not suitable to be included in compact, low cost and sensitive MIR optoelectronic devices, due to cryogenic cooling requirements as well as complex growth/processing techniques.

[0004] Due to complementary metal oxide semiconductor (CMOS) compatible, cost-effective silicon (Si) photonic systems, upconversion detection converting MIR or even far infrared (FIR) photons into visible (vis)/near infrared (NIR) radiation has attracted enormous interest and research efforts. Conventional upconversion techniques based on bulky nonlinear crystals suffer from phase match requirement and narrow band response. The molecular optomechanical nanocavities have recently been demonstrated for MIR upconversion, although its quantum efficiency remains quite low. Lanthanide-doped nanocrystals show promise in terms of ratiometric emission with MIR radiation, making them a potential platform for

upconversion detection. However, their performance still falls short due to the intrinsic insufficient MIR absorption (1%).

SUMMARY

[0005] Various embodiments may relate to a film. The film may include one or more types of nanostructures. The film may also include one or more types of ligands bonded to the one or more types of nanostructures. The one or more types of nanostructures may include neodymium (Nd) and ytterbium (Yb). A ratio of a molar concentration of neodymium (Nd) to a molar concentration of ytterbium (Yb) may be more than 1 : 1.

[0006] Various embodiments may relate to a mid infrared (MIR) detection system. The mid infrared (MIR) detection system may include a film. The film may include one or more types of nanostructures, and one or more types of ligands bonded to the one or more types of nanostructures. The mid infrared (MIR) detection system may also include a near infrared (NIR) source configured to provide near infrared (NIR) light to the film. The mid infrared (MIR) detection system may further include a detector. The one or more types of nanostructures may include neodymium (Nd) and ytterbium (Yb), wherein a ratio of a molar concentration of neodymium (Nd) to a molar concentration of ytterbium (Yb) is more than 1 : 1. The detector may be configured to determine a first emission at a first wavelength from the film when the film is under radiation of only the near infrared (NIR) light, and a second emission at the first wavelength from the film when the film is under radiation of both the near infrared (NIR) light and mid infrared (MIR) light, the mid infrared (MIR) light from a mid infrared (MIR) source. The detector may be further configured to determine a first emission at a second wavelength from the film when the film is under radiation of only the near infrared (NIR) light, and a second emission at the second wavelength from the film when the film is under radiation of both the near infrared (NIR) light and the mid infrared (MIR) light.

[0007] Various embodiments may relate to a method of forming a film. The method may include forming one or more types of nanostructures with one or more types of ligands bonded to the one or more types of nanostructures. The one or more types of nanostructures may include neodymium (Nd) and ytterbium (Yb). A ratio of a molar concentration of neodymium (Nd) to a molar concentration of ytterbium (Yb) may be more than 1 : 1.

[0008] Various embodiments may relate to a method of forming a mid infrared (MIR) detection system. The method may include forming a film as described herein. The film may

include one or more types of nanostructures, and one or more types of ligands bonded to the one or more types of nanostructures. The method may also include arranging or providing a near infrared (NIR) source configured to provide near infrared (NIR) light to the film. The method may further include arranging or providing a detector. The one or more types of nanostructures may include neodymium (Nd) and ytterbium (Yb). A ratio of a molar concentration of neodymium (Nd) to a molar concentration of ytterbium (Yb) may be more than 1 : 1. The detector may be configured to determine a first emission at a first wavelength from the film when the film is under radiation of only the near infrared (NIR) light, and a second emission at the first wavelength from the film when the film is under radiation of both the near infrared (NIR) light and mid infrared (MIR) light, the mid infrared (MIR) light from a mid infrared (MIR) source. The detector may be further configured to determine a first emission at a second wavelength from the film when the film is under radiation of only the near infrared (NIR) light, and a second emission at the second wavelength from the film when the film is under radiation of both the near infrared (NIR) light and the mid infrared (MIR) light.

[0009] Various embodiments may relate to a method of operating a mid infrared (MIR) detection system. The method may include providing only near infrared (NIR) light using a near infrared (NIR) source to a film and determining a first emission at a first wavelength and a first emission at a second wavelength from the film using a detector. The method may also include providing the near infrared (NIR) light using the near infrared (NIR) source and mid infrared (MIR) light using a mid infrared (MIR) source to the film and determining the second emission at the first wavelength and the second emission at the second wavelength from the film using the detector. The film may include one or more types of nanostructures, and one or more types of ligands bonded to the one or more types of nanostructures. The one or more types of nanostructures may include neodymium (Nd) and ytterbium (Yb). A ratio of a molar concentration of neodymium (Nd) to a molar concentration of ytterbium (Yb) may be more than 1 : 1.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] In the drawings, like reference characters generally refer to the same parts throughout the different views. The drawings are not necessarily drawn to scale, emphasis

instead generally being placed upon illustrating the principles of various embodiments. In the following description, various embodiments of the invention are described with reference to the following drawings.

FIG. 1 shows a general illustration of a film according to various embodiments

FIG. 2 shows a general illustration of a mid infrared (MIR) detection system according to various embodiments.

FIG. 3 shows a general illustration of a method of forming a film according to various embodiments.

FIG. 4 shows a general illustration of a method of forming a mid infrared (MIR) detection system according to various embodiments.

FIG. 5 shows a general illustration of a method of operating a mid infrared (MIR) detection system according to various embodiments.

FIG. 6A shows (left) a nanoparticle including neodymium (Nd) and ytterbium (Yb) according to various embodiments being pumped only by near infrared (NIR) light as well as an intensity plot illustrating light emissions due to neodymium (Nd) and ytterbium (Yb) under NIR pumping; and (right) the nanoparticles according to various embodiments being pumped by both near infrared (NIR) light and mid infrared (MIR) light as well as an intensity plot illustrating light emissions due to neodymium (Nd) and ytterbium (Yb) under NIR and MIR pumping. FIG. 6B illustrates the mechanism for enhanced mid infrared (MIR) upconversion of the nanoparticle according to various embodiments.

FIG. 6B illustrates the mechanism for enhanced mid infrared (MIR) upconversion of the nanoparticle according to various embodiments.

FIG. 7A shows a schematic of an experimental setup of mid infrared (MIR) sensing according to various embodiments.

FIG. 7B shows a plot of intensity (in arbitrary units or a.u.) as a function of wavelength (in nanometers or nm) illustrating change in ratiometric luminescence of the film $\text{NaYF}_4:\text{Nd}_{40}\text{Yb}_{15}$ (sodium yttrium tetra-fluoride nanoparticles doped with molar ratio of neodymium to ytterbium of 40 : 15) according to various embodiments with and without mid infrared radiation (6.3 μm , 35 mW).

FIG. 7C shows a plot of infrared (IR) sensitivity (per milli-Watts or /mW) /absorption (in arbitrary units or a.u.) as a function of wavenumber (per centimeter or cm^{-1}) illustrating the

Fourier Transform Infrared (FTIR) spectra as well as the mid infrared (MIR) sensitivity of the film according to various embodiments.

FIG. 8A shows a plot of absorption (in arbitrary units or a.u.)/infrared (IR) response as a function of wavenumber (per centimeter or cm^{-1}) illustrating the Fourier Transform Infrared (FTIR) spectra as well as the mid infrared (MIR) response of the film including tetraethyl orthosilicate (TEOS) ligands according to various embodiments.

FIG. 8B shows a plot of absorption (in arbitrary units or a.u.)/infrared (IR) response as a function of wavenumber (per centimeter or cm^{-1}) illustrating the Fourier Transform Infrared (FTIR) spectra as well as the mid infrared (MIR) response of the film including tetrafluoro-tetracyanoquinodimethane (F4TCNQ) ligands according to various embodiments.

FIG. 9A shows a plot of ratio of 806 nm wavelength emission to 980 nm wavelength emission (ratio (806/980)) as a function of temperature (in degrees Celsius) illustrating the variation of the rationmetric emission of the film according to various embodiments with temperature.

FIG. 9B shows a plot of ratio of 806 nm wavelength emission to 980 nm wavelength emission (ratio (806/980)) as a function of power (in milli-Watts or mW) illustrating the variation of the rationmetric emission of the film according to various embodiments with mid infrared (MIR) power.

FIG. 10A shows a plot of normalized photoluminescence (in arbitrary units or a.u.) as a function of time (in milliseconds or ms) illustrating the transient photoluminescence (PL) spectra of the 980 nm wavelength emission by the film according to various embodiments under different mid infrared laser powers (6.3 μm).

FIG. 10B shows a plot of normalized photoluminescence (in arbitrary units or a.u.) as a function of time (in milliseconds or ms) illustrating the transient photoluminescence (PL) spectra of the 866 nm wavelength emission by the film according to various embodiments under different mid infrared laser powers (6.3 μm).

FIG. 10C shows a plot of normalized photoluminescence (in arbitrary units or a.u.) as a function of time (in milliseconds or ms) illustrating the transient photoluminescence (PL) spectra of the 806 nm wavelength emission by the film according to various embodiments under different mid infrared laser powers (6.3 μm).

FIG. 10D shows a plot of lifetime (in microseconds or μs) as a function of mid infrared (MIR) power (in milli-Watts or mW) illustrating the calculated change in lifetimes for ytterbium ions (Yb^{3+}) $^4\text{F}_{7/2}$ energy level of the film according to various embodiments.

FIG. 10E shows a plot of lifetime (in microseconds or μs) as a function of mid infrared (MIR) power (in milli-Watts or mW) illustrating the calculated change in lifetimes for neodymium ions (Nd^{3+}) $^4\text{F}_{3/2}$ energy level of the film according to various embodiments.

FIG. 10F shows a plot of lifetime (in microseconds or μs) as a function of mid infrared (MIR) power (in milli-Watts or mW) illustrating the calculated change in lifetimes for neodymium ions (Nd^{3+}) $^4\text{F}_{5/2}$ energy level of the film according to various embodiments.

FIG. 11A shows a plot of voltage (in volts or V) as a function of time (in seconds or s) illustrating the time-resolved photovoltage responses of the film according to various embodiments under multiple periodic switches of laser illuminations from 35.8 mW to 2.5 mW.

FIG. 11B shows a plot of voltage (in volts or V) as a function of power (in milli-Watts or mW) illustrating the linear relationship between photovoltage generated by the photodetector and incident mid infrared (MIR) power provided to the film according to various embodiments.

FIG. 11C shows plots of normalized current (in arbitrary units or a.u.) as a function of time (in milliseconds or ms) illustrating the rise and fall times of the system according to various embodiments.

FIG. 11D shows a plot of noise (in nano-volts or nV) as a function of frequency (in Hertz or Hz) illustrating the frequency dependent noise level for the mid infrared (MIR) upconversion system according to various embodiments with and without 730 nm pumping.

FIG. 11E shows a plot of specific detectivity (in Jones) as a function of wavelength (in micrometers or μm) comparing the calculated detectivity of the system according to various embodiments with commercially available room temperature mid infrared (MIR) detectors.

FIG. 11F shows the resultant mid infrared (MIR) image generated by the system according to various embodiments.

DESCRIPTION

[0011] The following detailed description refers to the accompanying drawings that show, by way of illustration, specific details and embodiments in which the invention may be practiced. These embodiments are described in sufficient detail to enable those skilled in the art to practice the invention. Other embodiments may be utilized and structural, logical, and electrical changes may be made without departing from the scope of the invention. The various embodiments are not necessarily mutually exclusive, as some embodiments can be combined with one or more other embodiments to form new embodiments.

[0012] Features that are described in the context of an embodiment may correspondingly be applicable to the same or similar features in the other embodiments. Features that are described in the context of an embodiment may correspondingly be applicable to the other embodiments, even if not explicitly described in these other embodiments. Furthermore, 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.

[0013] 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.

[0014] 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, e.g., within 10% of the specified value.

[0015] As used herein, the term “and/or” includes any and all combinations of one or more of the associated listed items.

[0016] By “comprising” it is meant including, but not limited to, whatever follows the word “comprising”. Thus, use of the term “comprising” indicates that the listed elements are required or mandatory, but that other elements are optional and may or may not be present.

[0017] By “consisting of” is meant including, and limited to, whatever follows the phrase “consisting of”. Thus, the phrase “consisting of” indicates that the listed elements are required or mandatory, and that no other elements may be present.

[0018] Embodiments described in the context of one of the films/systems are analogously valid for the other films/systems. Similarly, embodiments described in the context of a method are analogously valid for a film/system, and vice versa.

[0019] FIG. 1 shows a general illustration of a film according to various embodiments. The film may include one or more types of nanostructures 102. The film may also include one or more types of ligands 104 bonded to the one or more types of nanostructures 102. The one or more types of nanostructures 102 may include neodymium (Nd) and ytterbium (Yb). A ratio of a molar concentration of neodymium (Nd) to a molar concentration of ytterbium (Yb) may be more than 1 : 1.

[0020] In other words, the film may include a nanostructure or nanostructures 102 of a single type (e.g., nanoparticles, nanowires, or nanoplates etc.) or multiple types. The nanostructure or nanostructures 102 may be bonded to a single type of ligands (e.g., butile ligands, tetraethyl orthosilicate (TEOS) ligands, tetrafluoro-tetracyanoquinodimethane

(F4TCNQ) ligands, oleic acid ligand, polydimethylsiloxane (PDMS) ligand, or polymethyl methacrylate (PMMA) ligand etc.) or multiple types of ligands. The nanostructure or nanostructures 102 may include neodymium (Nd) and ytterbium (Yb), with the molar concentration of Nb being more than the molar concentration of Yb.

[0021] For avoidance of doubt, FIG. 1 seeks to illustrate some features of the film according to various embodiments, and is not intended to limit, for instance, the number, shape, dimensions, orientation, arrangement etc. of such features. For instance, while FIG. 1 shows three nanostructures 102, with three ligands 104 bonded to each of the three nanostructures 102, various embodiments may include any suitable number of nanostructures 102, with any suitable number of ligands 104 bonded to any one (or more) of the nanostructures 102.

[0022] By having the ratio of Nd: Yb to be more than 1 : 1, the film may have improved sensitivity to mid infrared (MIR). In various embodiments, the ratio of the molar concentration of neodymium (Nd) to the molar concentration of ytterbium (Yb) may be equal to or more than 4 : 3, e.g., equal to or more than 8 : 3, e.g., equal to or more than 8 : 1.

[0023] In various embodiments, the one or more types of nanostructures 102 may include nanostructures of any suitable shape or shapes. As mentioned above, the one or more types of nanostructures 102 may include nanoparticles, nanowires, nanoplates or any combination thereof. Various embodiments may include any other types of nanostructures.

[0024] In various embodiments, the one or more types of nanostructures 102 may include or consist of any suitable material or materials. In various embodiments, the one or more types of nanostructures 102 may include one or more materials selected from a group consisting of sodium yttrium tetra-fluoride (NaYF₄), lanthanum trifluoride (LaF₃), sodium gadolinium fluoride (NaGdF₄), sodium lutetium fluoride (NaLuF₄), yttrium oxide (Y₂O₃), and zirconium oxide (ZrO₂). In various other embodiments, the one or more types of nanostructures 102 may include any other suitable material or materials. In various embodiments, different nanostructures 102 may include or consist of a same material, while in various other embodiments, different nanostructures 102 may include different materials.

[0025] In various embodiments, the one or more types of ligands 104 may include any suitable ligand or ligands. The one or more types of ligands 104 may be bonded to the surface(s) of the one or more types of nanostructures 102. For instance, as mentioned above, the one or more types of ligands 104 may be selected from a group consisting of butile ligands, tetraethyl orthosilicate (TEOS) ligands, tetrafluoro-tetracyanoquinodimethane (F4TCNQ) ligands, oleic

acid ligand, polydimethylsiloxane (PDMS) ligand, polymethyl methacrylate (PMMA) ligand and any combination thereof. In various other embodiments, the one or more types of ligands 104 may be or may include any other suitable ligands. In various embodiments, each nanostructure of the one or more types of nanostructures 102 included in the film may be bonded to one or more ligands of the one or more types of ligands 104.

[0026] In various embodiments, the 806 nm emission of the film may be enhanced with radiation of both near infrared (NIR) light and mid infrared (MIR) light (compared with radiation of only NIR light). Conversely, the 980 nm emission of the film may be suppressed with radiation of both NIR light and MIR light (compared with radiation of only NIR light). In other words, a first emission with a first wavelength of 806 nm by the film in response to the film under radiation of only the near infrared (NIR) light may be less than a second emission with the first wavelength of 806 nm by the film in response to the film under radiation of both the near infrared (NIR) light and the mid infrared (MIR) light. Further, a first emission with a second wavelength of 980 nm by the film in response to the film under radiation of only the near infrared (NIR) light may be more than a second emission with the second wavelength of 980 nm by the film in response to the film under radiation of both the near infrared (NIR) light and the mid infrared (MIR) light.

[0027] In various embodiments, a ratio of the second emission of the first wavelength of 806 nm to the second emission of the second wavelength of 980 nm when the film is under radiation of both the near infrared (NIR) light and the mid infrared (MIR) light is increased by more than 175 times, e.g., approximately 177 times, compared to a ratio of the first emission of the first wavelength of 806 nm to the first emission of the second wavelength of 980 nm when the film is under radiation of only the near infrared (NIR) light.

[0028] An increase of the ratio of the second emission of the first wavelength of 806 nm to the second emission of the second wavelength of 980 nm compared to the ratio of the first emission of the first wavelength of 806 nm to the first emission of the second wavelength of 980 nm may be due to multi-phonon relaxation of the one or more types of ligands 104.

[0029] In various embodiments, the 866 nm emission of the film may be enhanced with radiation of both near infrared (NIR) light and mid infrared (MIR) light (but by a magnitude less than that of the 806 nm emission), compared with radiation of only NIR light. In various other embodiments, the 866 nm emission of the film may be decreased with radiation of both near infrared (NIR) light and mid infrared (MIR) light, compared with radiation of only NIR

light. In other words, in various embodiments, a first emission with a third wavelength of 866 nm by the film in response to the film under radiation of only the near infrared (NIR) light may be less than a second emission with the third wavelength of 866 nm by the film in response to the film under radiation of both the near infrared (NIR) light and the mid infrared (MIR) light, while in various other embodiments, a first emission with a third wavelength of 866 nm by the film in response to the film under radiation of only the near infrared (NIR) light may be more than a second emission with the third wavelength of 866 nm by the film in response to the film under radiation of both the near infrared (NIR) light and the mid infrared (MIR) light.

[0030] In various embodiments, the film is configured to exhibit a room temperature detection of a mid infrared (MIR) wavelength of 6.3 μm with a specific detectivity of 5×10^8 Jones.

[0031] In various embodiments, the near infrared (NIR) light may have a wavelength (i.e., a single wavelength NIR light) or a range of wavelengths (i.e., a broadband NIR light) selected from a range from 700 nm to 1400 nm. For instance, the NIR light may be a 730 nm NIR light emitted by a single wavelength laser source. In various embodiments, the mid infrared (MIR) light may have a wavelength (i.e., a single wavelength MIR light) or a range of wavelengths (i.e., a broadband MIR light) selected from a range from 3 μm to 11 μm . For instance, the MIR light may be a broadband 4 – 11 μm MIR light emitted by a tunable quantum cascade laser (QCL).

[0032] FIG. 2 shows a general illustration of a mid infrared (MIR) detection system according to various embodiments. The mid infrared (MIR) detection system may include a film 202 as described herein, e.g., the film as shown in FIG. 1. The film may include one or more types of nanostructures, and one or more types of ligands bonded to the one or more types of nanostructures. The mid infrared (MIR) detection system may also include a near infrared (NIR) source 204 configured to provide near infrared (NIR) light to the film 202. The mid infrared (MIR) detection system may further include a detector 206. The one or more types of nanostructures may include neodymium (Nd) and ytterbium (Yb), wherein a ratio of a molar concentration of neodymium (Nd) to a molar concentration of ytterbium (Yb) is more than 1 : 1. The detector 206 may be configured to determine a first emission at a first wavelength from the film 202 when the film 202 is under radiation of only the near infrared (NIR) light, and a second emission at the first wavelength from the film 202 when the film 202 is under radiation of both the near infrared (NIR) light and mid infrared (MIR) light, the mid infrared (MIR) light

from a mid infrared (MIR) source. The detector 206 may be further configured to determine a first emission at a second wavelength from the film 202 when the film 202 is under radiation of only the near infrared (NIR) light, and a second emission at the second wavelength from the film 202 when the film 202 is under radiation of both the near infrared (NIR) light and the mid infrared (MIR) light.

[0033] In other words, the mid infrared (MIR) detection system may include a film 202 as described herein, a NIR source 204 and a detector 204. The film 202 may be configured to provide a first emission at a first wavelength and a first emission at a second wavelength when only NIR light from the NIR source 204 is provided to the film 202. The film 202 may also be configured to provide a second emission at a first wavelength and a second emission at a second wavelength when MIR light from a MIR source as well as NIR light from the NIR source 204 is provided to the film 202. The detector 204 may be configured to measure or detect the emissions (i.e., the first emission and the second emission) at the first wavelength as well as the emissions (i.e., the first emission and the second emission) at the second wavelength.

[0034] For avoidance of doubt, FIG. 2 seeks to illustrate some features of the mid infrared (MIR) detection system according to various embodiments, and is not intended to limit, for instance, the shape, dimensions, orientation, arrangement etc. of such features.

[0035] In various embodiments, the mid infrared (MIR) source may be a blackbody or a mid infrared (MIR) laser. In various embodiments, the mid infrared (MIR) detection system may include the mid infrared (MIR) source.

[0036] In various embodiments, the first wavelength may be 806 nm and the second wavelength may be 980 nm.

[0037] Generally speaking, the mid infrared (MIR) detection system may include a suitable optical system configured to direct the mid infrared (MIR) light from the mid infrared (MIR) source to the film 202, and to direct the near infrared (NIR) light from the near infrared (NIR) source 204 to the film 202. The suitable optical system may also be configured to direct the emissions (i.e., the first emission and the second emission) of the first wavelength and the emissions (i.e., the first emission and the second emission) of the second wavelength from the film 202 to the detector 206.

[0038] In various embodiments, the mid infrared (MIR) detection system may include a first lens configured to direct the mid infrared (MIR) light from the mid infrared (MIR) source to the film 202. The mid infrared (MIR) detection system may further include a beam splitter.

The mid infrared (MIR) detection system may additionally include a second lens. The beam splitter may be configured to direct the near infrared (NIR) light from the near infrared (NIR) source 204 to the second lens. The second lens may be configured to direct the near infrared (NIR) light from the beam splitter to the film 202.

[0039] In various embodiments, the mid infrared (MIR) detection system may further include a third lens configured to direct the emission of the first wavelength and the emission of the second wavelength from the film 202 to the detector 206.

[0040] In various embodiments, the detector 206 may be or may include a spectrometer. The detector 206 may include a bandpass filter. The bandpass filter may be configured to filter out the desired wavelength for transmission to the spectrometer. The spectrometer may include a processor (e.g. an on-board processor) configured to determine or calculate the emissions (i.e., the first emission and the second emission) of the first wavelength and the emissions (i.e., the first emission and the second emission) of the second wavelength.

[0041] The detector 206 or the processor may be configured to determine, compare or calculate a first emission with a first wavelength of 806 nm by the film 202 in response to the film 202 under radiation of only the near infrared (NIR) light, and a second emission with the first wavelength of 806 nm by the film 202 in response to the film 202 under radiation of both the near infrared (NIR) light and the mid infrared (MIR) light.

[0042] The detector 206 or the processor may also be configured to determine, compare or calculate a first emission with a second wavelength of 980 nm by the film 202 in response to the film 202 under radiation of only the near infrared (NIR) light and a second emission with the second wavelength of 980 nm by the film 202 in response to the film 202 under radiation of both the near infrared (NIR) light and the mid infrared (MIR) light.

[0043] The detector or the processor may further be configured to determine, compare or calculate the ratio of the second emission of the first wavelength of 806 nm to the second emission of the second wavelength of 980 nm (i.e., when the film is under radiation of both the near infrared (NIR) light and the mid infrared (MIR) light) to a ratio of the first emission of the first wavelength of 806 nm to the first emission of the second wavelength of 980 nm (when the film is under radiation of only the near infrared (NIR) light).

[0044] FIG. 3 shows a general illustration of a method of forming a film according to various embodiments. The method may include, in 302, forming one or more types of nanostructures with one or more types of ligands bonded to the one or more types of

nanostructures. The one or more types of nanostructures may include neodymium (Nd) and ytterbium (Yb). A ratio of a molar concentration of neodymium (Nd) to a molar concentration of ytterbium (Yb) may be more than 1 : 1.

[0045] In various embodiments, the one or more types of nanostructures comprise one or more materials selected from a group consisting of sodium yttrium tetra-fluoride (NaYF_4), lanthanum trifluoride (LaF_3), sodium gadolinium fluoride (NaGdF_4), sodium lutetium fluoride (NaLuF_4), yttrium oxide (Y_2O_3), and zirconium oxide (ZrO_2). In various embodiments, the one or more types of nanostructures may include nanoparticles, nanowires, nanoplates or any combination thereof.

[0046] In various embodiments, the ratio of the molar concentration of neodymium (Nd) to the molar concentration of ytterbium (Yb) may be equal to or more than 4 : 3, e.g., equal to or more than 8 : 3, e.g., equal to or more than 8 : 1.

[0047] In various embodiments, the one or more types of ligands may be selected from a group consisting of butile ligands, tetraethyl orthosilicate (TEOS) ligands, tetrafluoro-tetracyanoquinodimethane (F4TCNQ) ligands, oleic acid ligand, polydimethylsiloxane (PDMS) ligand, polymethyl methacrylate (PMMA) ligand and any combination thereof.

[0048] In various embodiments, a first emission with a first wavelength of 806 nm by the film in response to the film under radiation of only the near infrared (NIR) light may be less than a second emission with the first wavelength of 806 nm by the film in response to the film under radiation of both the near infrared (NIR) light and the mid infrared (MIR) light. A first emission with a second wavelength of 980 nm by the film in response to the film under radiation of only the near infrared (NIR) light may be more than a second emission with the second wavelength of 980 nm by the film in response to the film under radiation of both the near infrared (NIR) light and the mid infrared (MIR) light.

[0049] In various embodiments, a ratio of the second emission of the first wavelength of 806 nm to the second emission of the second wavelength of 980 nm when the film is under radiation of both the near infrared (NIR) light and the mid infrared (MIR) light may be increased by more than 175 times, e.g., approximately 177 times, compared to a ratio of the first emission of the first wavelength of 806 nm to the first emission of the second wavelength of 980 nm when the film is under radiation of only the near infrared (NIR) light.

[0050] In various embodiments, an increase of the ratio of the second emission of the first wavelength of 806 nm to the second emission of the second wavelength of 980 nm compared

to the ratio of the first emission of the first wavelength of 806 nm to the first emission of the second wavelength of 980 nm may be due to multi-phonon relaxation of the one or more types of ligands.

[0051] In various embodiments, a first emission with a third wavelength of 866 nm by the film in response to the film under radiation of only the near infrared (NIR) light may be less than a second emission with the third wavelength of 866 nm by the film in response to the film under radiation of both the near infrared (NIR) light and the mid infrared (MIR) light.

[0052] In various other embodiments, a first emission with a third wavelength of 866 nm by the film in response to the film under radiation of only the near infrared (NIR) light may be more than a second emission with the third wavelength of 866 nm by the film in response to the film under radiation of both the near infrared (NIR) light and the mid infrared (MIR) light.

[0053] In various embodiments, the film may be configured to exhibit a room temperature detection of a mid infrared (MIR) wavelength of 6.3 μm with a specific detectivity of 5×10^8 Jones.

[0054] FIG. 4 shows a general illustration of a method of forming a mid infrared (MIR) detection system according to various embodiments. The method may include, in 402, forming a film as described herein. The film may include one or more types of nanostructures, and one or more types of ligands bonded to the one or more types of nanostructures. The method may also include, in 404, arranging or providing a near infrared (NIR) source configured to provide near infrared (NIR) light to the film. The method may further include, in 406, arranging or providing a detector. The one or more types of nanostructures may include neodymium (Nd) and ytterbium (Yb). A ratio of a molar concentration of neodymium (Nd) to a molar concentration of ytterbium (Yb) may be more than 1 : 1. The detector may be configured to determine a first emission at a first wavelength from the film when the film is under radiation of only the near infrared (NIR) light, and a second emission at the first wavelength from the film when the film is under radiation of both the near infrared (NIR) light and mid infrared (MIR) light, the mid infrared (MIR) light from a mid infrared (MIR) source. The detector may be further configured to determine a first emission at a second wavelength from the film when the film is under radiation of only the near infrared (NIR) light, and a second emission at the second wavelength from the film when the film is under radiation of both the near infrared (NIR) light and the mid infrared (MIR) light.

[0055] For avoidance of doubt, FIG. 4 illustrates some steps in according to various embodiments, and is not intended to limit the sequence of the various embodiments. For instance, in various embodiments, the NIR source may be provided or arranged before providing or arranging the detector, while in various other embodiments, the NIR source may be provided after or at the same time as providing or arranging the detector.

[0056] In various embodiments, the mid infrared (MIR) source may be a blackbody or a mid infrared (MIR) laser. In various embodiments, the method may include providing or arranging the mid infrared (MIR) source.

[0057] In various embodiments, the method may include providing a suitable optical system configured to direct the mid infrared (MIR) light from the mid infrared (MIR) source to the film, and to direct the near infrared (NIR) light from the near infrared (NIR) source 204 to the film. The suitable optical system may also be configured to direct the emissions of the first wavelength and the emissions of the second wavelength from the film to the detector.

[0058] For instance, the method may include providing or arranging a first lens configured to direct the mid infrared (MIR) light from the mid infrared (MIR) source to the film. The method may also include providing or arranging a beam splitter. The method may additionally include providing or arranging a second lens. The beam splitter may be configured to direct the near infrared (NIR) light from the near infrared (NIR) source to the second lens. The second lens may be configured to direct the near infrared (NIR) light from the beam splitter to the film.

[0059] In various embodiments, the method may include providing a third lens configured to direct the emission of the first wavelength and the emission of the second wavelength from the film to the detector.

[0060] In various embodiments, the detector may be or may include a spectrometer. The detector may include a bandpass filter.

[0061] FIG. 5 shows a general illustration of a method of operating a mid infrared (MIR) detection system according to various embodiments. The method may include, in 502, providing only near infrared (NIR) light using a near infrared (NIR) source to a film and determining a first emission at a first wavelength and a first emission at a second wavelength from the film using a detector. The method may also include, in 504, providing the near infrared (NIR) light using the near infrared (NIR) source and mid infrared (MIR) light using a mid infrared (MIR) source to the film and determining the second emission at the first wavelength and the second emission at the second wavelength from the film using the detector. The film

may include one or more types of nanostructures, and one or more types of ligands bonded to the one or more types of nanostructures. The one or more types of nanostructures may include neodymium (Nd) and ytterbium (Yb). A ratio of a molar concentration of neodymium (Nd) to a molar concentration of ytterbium (Yb) may be more than 1 : 1.

[0062] In various embodiments, step 502 may occur before step 504, while in various other embodiments step 502 may occur after step 504.

[0063] In various embodiments, the method may also include determining a change between a ratio of the first emission at the first wavelength to the first emission at the second wavelength when the film is under radiation of only the near infrared (NIR) light, and a ratio of the second emission at the first wavelength to the second emission at the second wavelength when the film is under radiation of both the near infrared (NIR) light and the mid infrared (MIR) light.

[0064] The surface ligands are known to modulate the emission of the lanthanide nanophosphors by the multi-phonon relaxation, whose efficiency is influenced by the ambient temperature. Typically, the mechanism of energy transfer and back transfer between Nd^{3+} and Yb^{3+} are well established for temperature sensor. It may be demonstrated herein for the first time that the IR absorption of the ligand can activate/deactivate this process. FIG. 6A shows (left) a nanoparticle including neodymium (Nd) and ytterbium (Yb) according to various embodiments being pumped only by near infrared (NIR) light as well as an intensity plot illustrating light emissions due to neodymium (Nd) and ytterbium (Yb) under NIR pumping; and (right) the nanoparticles according to various embodiments being pumped by both near infrared (NIR) light and mid infrared (MIR) light as well as an intensity plot illustrating light emissions due to neodymium (Nd) and ytterbium (Yb) under NIR and MIR pumping. FIG. 6B illustrates the mechanism for enhanced mid infrared (MIR) upconversion of the nanoparticle according to various embodiments.

[0065] As shown in FIGS. 6A-B, the simultaneous pumping of Nd-Yb codoped NaYF_4 nanoparticles by the NIR (740 nm) and MIR (5 μm - 11 μm) lasers may realize the ratiometric emission located at around 806 nm ($^4\text{F}_{5/2}$ to $^4\text{I}_{9/2}$) for Nd^{3+} and emission located at around 980 nm ($^4\text{F}_{7/2}$ to $^4\text{F}_{5/2}$) for Yb^{3+} . For the case of sole NIR pumping, the weak emission around 806 nm is due to the rapid nonradiative depopulation of $^4\text{F}_{5/2}$ to $^4\text{F}_{3/2}$ energy level, while the strong emission at 980 nm is due to efficient energy transfer from Nd $^4\text{F}_{3/2}$ to Yb $^4\text{F}_{7/2}$ level. Upon NIR-MIR co-radiation, the molecular vibration of the surface ligand can be activated as a

pathway, which facilitates the energy back transfer from Yb^{3+} to Nd^{3+} . Therefore, the 980 nm emission may be suppressed, while the 806 nm emission may be enhanced due to the back pumping process ($^4\text{F}_{3/2}$ to $^4\text{F}_{5/2}$). The MIR radiation may activate the energy transfer from Yb^{3+} $^4\text{F}_{7/2}$ to Nd^{3+} $^4\text{F}_{5/2}$ and $^4\text{F}_{3/2}$ with surface ligand absorption.

[0066] In order to demonstrate the above, the lanthanide particles may be included into a thin film and tested in a simple fluorescence measurement system. A particle solution including the lanthanide particles and the surface ligands may first be formed. The particle solution may be formed by mixing the lanthanide particles and the surface ligands in a suitable solvent. The particle solution may then be made into thin film by repeated drop casting method to reach the desired thickness. In the measurement system, the NIR light and the MIR light may concentrate and converge on the film from two directions. FIG. 7A shows a schematic of an experimental setup of mid infrared (MIR) sensing according to various embodiments. The setup may include a film 702 including one or more types of nanostructures (e.g., nanoparticles) and one or more types of ligands bonded to the one or more types of nanostructures. The setup may also include a near infrared (NIR) source 704, e.g., a NIR pumping laser, configured to provide near infrared (NIR) light (e.g., of 730 nm) to the film 702. The setup may further include a detector 706. The setup may additionally include a mid infrared source 708, e.g., a tunable quantum cascade laser (QCL), providing mid infrared (MIR) light (e.g., of 4 – 11 μm). The detector 706 may be configured to determine a first emission at a first wavelength from the film 702 when the film 702 is under radiation of only the near infrared (NIR) light, and a second emission at the first wavelength from the film 702 when the film 702 is under radiation of both the near infrared (NIR) light and the mid infrared (MIR) light. The detector 706 may be further configured to determine a first emission at a second wavelength from the film 702 when the film 702 is under radiation of only the near infrared (NIR) light, and a second emission at the second wavelength from the film 702 when the film 702 is under radiation of both the near infrared (NIR) light and the mid infrared (MIR) light.

[0067] The setup may also include a first lens 710 configured to direct the mid infrared (MIR) light from the mid infrared (MIR) source 708 to the film 702. The setup may also include a beam splitter 712. The setup may additionally include a second lens 714. The beam splitter 712 may be configured to direct the near infrared (NIR) light from the near infrared (NIR) source 704 to the second lens 714, and the second lens 714 may be configured to direct the near infrared (NIR) light from the beam splitter 712 to the film 702. The setup may also include

a third lens 716 configured to direct the emissions (i.e., the first emission and the second emission) of the first wavelength and the emissions (i.e., the first emission and the second emission) of the second wavelength from the film 702 to the detector 706. The emissions of the first wavelength and the emissions of the second wavelength emitted from the film 702 may be directed from the second lens 714 to the beam splitter 712, and from the beam splitter 712 to the third lens 716, before being directed from the third lens 716 to the detector 706.

[0068] The doping concentrations may be tuned or adjusted to vary the strength of emission and MIR sensitivity. FIG. 7B shows a plot of intensity (in arbitrary units or a.u.) as a function of wavelength (in nanometers or nm) illustrating change in ratiometric luminescence of the film $\text{NaYF}_4:\text{Nd}_{40}\text{Yb}_{15}$ (sodium yttrium tetra-fluoride nanoparticles doped with molar ratio of neodymium to ytterbium of 40 : 15) according to various embodiments with and without mid infrared radiation (6.3 μm , 35 mW). As shown in FIG. 7B, the NIR pumping (740 nm) may excite three emission bands, which correspond to the two Stokes emission peaks (806 and 866 nm) for Nd^{3+} as well as the 980 nm emission from Yb^{3+} . Upon the co-radiation with MIR laser (1250 cm^{-1}), the Yb^{3+} emission peak may be suppressed drastically, and may be almost completely suppressed under intensive MIR radiation, while the 806 nm emission may be greatly enhanced due to the back pumping mechanism. This may lead to a remarkable enhancement of ratiometric emission, increasing it from 0.03 to 5.22, which is approximately 177 times higher.

[0069] Alternatively, in the ligand-free (LF) samples, the MIR radiation can introduce change for the two emission peaks for Nd^{3+} , while the 980 nm emission peak may only undergo a small reduction. Without the assistance of the surface phonon relaxation, the energy transfer rate between Nd and Yb may be reduced. To further demonstrate the function of the surface ligand, Fourier Transform Infrared (FTIR) measurements may be performed and the MIR wavelength dependent emission ratio (806 nm/980 nm) may be recorded by adjusting the wavelength of MIR light provided using the broadband tunable quantum cascade laser (QCL). FIG. 7C shows a plot of infrared (IR) sensitivity (per milli-Watts or /mW) /absorption (in arbitrary units or a.u.) as a function of wavenumber (per centimeter or cm^{-1}) illustrating the Fourier Transform Infrared (FTIR) spectra as well as the mid infrared (MIR) sensitivity of the film according to various embodiments.

[0070] Notably, the butile modified nanotransducer thin film shows a peak absorption of 36% at 1300 cm^{-1} , which is a great enhancement compared with pristine thin film (<1%). As

shown in FIG. 7C, the emission ratio may follow the same trend as the FTIR spectra, which may indicate that the change of the emissions mainly comes from the ligand absorption. Meanwhile, samples capped with different ligands, including tetraethyl orthosilicate (TEOS) ligands and tetrafluoro-tetracyanoquinodimethane (F4TCNQ) ligands, may be fabricated.

[0071] FIG. 8A shows a plot of absorption (in arbitrary units or a.u.)/infrared (IR) response as a function of wavenumber (per centimeter or cm^{-1}) illustrating the Fourier Transform Infrared (FTIR) spectra as well as the mid infrared (MIR) response of the film including tetraethyl orthosilicate (TEOS) ligands according to various embodiments. FIG. 8B shows a plot of absorption (in arbitrary units or a.u.)/infrared (IR) response as a function of wavenumber (per centimeter or cm^{-1}) illustrating the Fourier Transform Infrared (FTIR) spectra as well as the mid infrared (MIR) response of the film including tetrafluoro-tetracyanoquinodimethane (F4TCNQ) ligands according to various embodiments.

[0072] FIGS. 8A-B show that the trend of the FTIR absorption spectra and the trend of wavelength dependent emission ratio for different samples match well with each other.

[0073] Since the energy transfer in the Yb-Nd doping system is quite sensitive to the ambient temperature, it may be important to evaluate the contribution of the temperature vibration to the fluorescence emission during MIR radiation. FIG. 9A shows a plot of ratio of 806 nm wavelength emission to 980 nm wavelength emission (ratio (806/980)) as a function of temperature (in degrees Celsius) illustrating the variation of the rationmetric emission of the film according to various embodiments with temperature. FIG. 9B shows a plot of ratio of 806 nm wavelength emission to 980 nm wavelength emission (ratio (806/980)) as a function of power (in milli-Watts or mW) illustrating the variation of the rationmetric emission of the film according to various embodiments with mid infrared (MIR) power.

[0074] FIG. 9A shows that the emission ratios for various films vary exponentially with temperature, consistent with previous results. It may be worth noting that the emission ratio remains almost unchanged at around 20 degrees Celsius to 60 degrees Celsius, but may reach 1.6 at 150 degrees Celsius. The emission ratios also show a linear relationship with the incident MIR power, as displayed in FIG. 9B. A ratio of around 6.8 may be reached under 65 mW of MIR radiation (8.1 μm) for $\text{Nd}_{40}\text{Yb}_5$ thin film. The thermal camera recorded temperature vibration for samples (both ligand free and ligand capped) under MIR radiation. The butile-capped samples and the ligand free (LF) sample show slightly increased temperatures that are above the ambient temperature. Therefore, the change of the temperature may play a trivial

role in modulating the emission ratio upon MIR radiation, and the greatly enhanced ratio may be due to the phonon assisted energy transfer.

[0075] The transient photoluminescence (PL) spectra measured for lanthanide thin film both with and without MIR radiation. FIG. 10A shows a plot of normalized photoluminescence (in arbitrary units or a.u.) as a function of time (in milliseconds or ms) illustrating the transient photoluminescence (PL) spectra of the 980 nm wavelength emission by the film according to various embodiments under different mid infrared laser powers (6.3 μm). FIG. 10B shows a plot of normalized photoluminescence (in arbitrary units or a.u.) as a function of time (in milliseconds or ms) illustrating the transient photoluminescence (PL) spectra of the 866 nm wavelength emission by the film according to various embodiments under different mid infrared laser powers (6.3 μm). FIG. 10C shows a plot of normalized photoluminescence (in arbitrary units or a.u.) as a function of time (in milliseconds or ms) illustrating the transient photoluminescence (PL) spectra of the 806 nm wavelength emission by the film according to various embodiments under different mid infrared laser powers (6.3 μm). FIG. 10D shows a plot of lifetime (in microseconds or μs) as a function of mid infrared (MIR) power (in milli-Watts or mW) illustrating the calculated change in lifetimes for ytterbium ions (Yb^{3+}) $^4\text{F}_{7/2}$ energy level of the film according to various embodiments. FIG. 10E shows a plot of lifetime (in microseconds or μs) as a function of mid infrared (MIR) power (in milli-Watts or mW) illustrating the calculated change in lifetimes for neodymium ions (Nd^{3+}) $^4\text{F}_{3/2}$ energy level of the film according to various embodiments. FIG. 10F shows a plot of lifetime (in microseconds or μs) as a function of mid infrared (MIR) power (in milli-Watts or mW) illustrating the calculated change in lifetimes for neodymium ions (Nd^{3+}) $^4\text{F}_{5/2}$ energy level of the film according to various embodiments. As shown in FIG. 10D, there is a significant decrease from 250 μs to 80 μs of the $^4\text{F}_{7/2}$ (Yb^{3+}) lifetime observed with increasing MIR radiation, while the lifetime for $^4\text{F}_{5/2}$ and $^4\text{F}_{3/2}$ (Nd^{3+}) both increase from 15 μs to around 200 μs . This may suggest energy transfer from Yb^{3+} to Nd^{3+} with the assistance of MIR radiation, contributing to the significantly suppressed 980 nm emission as well as the enhanced Nd^{3+} emission bands at 806 and 866 nm. The transient PL spectra for purely Nd^{3+} doped sample also show increased lifetime for $^4\text{F}_{5/2}$ and slightly decreased lifetime for $^4\text{F}_{3/2}$ energy level under MIR radiation. Therefore, the MIR light may also contribute to the energy flux from $^4\text{F}_{3/2}$ to $^4\text{F}_{5/2}$ (Nd^{3+}).

[0076] In order to quantitatively analysis the MIR detection performance, the spectrometer may be replaced with a silicon (Si) avalanche photodetector (APD) (responsivity 7.5E5 V/W),

spectrally filtering the emission peak around 980 nm. FIG. 11A shows a plot of voltage (in volts or V) as a function of time (in seconds or s) illustrating the time-resolved photovoltage responses of the film according to various embodiments under multiple periodic switches of laser illuminations from 35.8 mW to 2.5 mW. As shown in FIG. 11A, the time-resolved photovoltage responses were recorded under multiple periodic switches of laser illuminations from 35.8 mW to 2.5 mW, in which the rapid and reproducible photovoltage V_{ph} responses may imply a good photodetection stability and show a responsivity of 170 V/W. The almost linear relationship of the power dependent photoresponse at 6.3 μm is displayed in FIG. 11B, from which the ideal factor (α of 0.9) may be obtained (fitted by power law: $V_{ph} \propto P_o^\alpha$). FIG. 11B shows a plot of voltage (in volts or V) as a function of power (in milli-Watts or mW) illustrating the linear relationship between photovoltage generated by the photodetector and incident mid infrared (MIR) power provided to the film according to various embodiments. This value is very close to the ideal value ($\alpha = 1$), suggesting the superior quality of the film. The quantum efficiency (QE) of the film may then be estimated by calculating the decreased up-conversion emission. Typically, the decreased photovoltage for $\text{Nd}_{40}\text{Yb}_{15}$ sample at 6.3 μm (35.8 mW) illumination is 6.9 V, corresponding to 9.2 μW MIR induced emission decrease. Considering that only 6.5% of the emission power is collected by the objective lens, the total emission change from the film is around 141 μW . Then, the estimated $\text{QE} = (P_{vis}/h\nu_{vis})/(P_{IR}/h\nu_{IR})$ is around 10^{-3} . Meanwhile, the response time of the film may be investigated by a high-resolution time resolved photovoltage V_{ph} response at 6.3 μm (FIG. 11C). FIG. 11C shows plots of normalized current (in arbitrary units or a.u.) as a function of time (in milliseconds or ms) illustrating the rise and fall times of the system according to various embodiments. The rise and fall times are estimated to be 2.2 ms and 2.1 ms by calculating the time interval of rising edge and falling edge. The detectivity of the MIR upconversion system may be estimated by measuring the noise equivalent power (NEP) as an important figure-of-merit for photodetectors. FIG. 11D shows a plot of noise (in nano-volts or nV) as a function of frequency (in Hertz or Hz) illustrating the frequency dependent noise level for the mid infrared (MIR) upconversion system according to various embodiments with and without 730 nm pumping. The Si APD contributes to a remarkable low noise below 5 nV (>100 Hz). The application of 730 nm pumping laser may introduce extra noise to the system, which is around one order higher than dark noise (without NIR radiation). Since the system has a response time of 2 ms to the MIR radiation, the noise level for the MIR upconversion system

may be estimated to be around to be 44 nV. The detectivity may then be calculated to be 5 E8 Jones for 6.3 μm .

[0077] FIG. 11E shows a plot of specific detectivity (in Jones) as a function of wavelength (in micrometers or μm) comparing the calculated detectivity of the system according to various embodiments with commercially available room temperature mid infrared (MIR) detectors. The upconversion detection system shows superior detectivity especially at long wavelength infrared (LWIR) region, which surpass those of room temperature mercury cadmium telluride (MCT) detectors.

[0078] Furthermore, the upconversion system exhibits exceptional sensitivity, enabling the detection of low-power mid-infrared (MIR) radiation. The thin film has been successfully applied in thermal imaging, utilizing a blackbody radiation source. The imaging target is positioned in front of the blackbody source (at 600K), and a germanium (Ge) window is used to filter out visible light. FIG. 11F shows the resultant mid infrared (MIR) image generated by the system according to various embodiments. The image may be obtained based on the reduced intensity captured by a CMOS camera equipped with a 980 nm bandpass filter. The image obtained shows clear details with a resolution of approximately 200 micrometers. To enhance the overall performance of MIR imaging, further optimization of the lanthanide film may be carried out to improve its quality and sensitivity. Such improvements may lead to higher-quality MIR imaging results.

[0079] Various embodiments may relate to a mechanism that can increase MIR upconversion response with surface phonon modulation. Various embodiments may relate to the upconversion process of a NdYb co-doped system. The obtained detectivity may be comparable (or may be better) with commercial room temperature MCTs. This exciting development may open possibilities for the creation of upconversion MIR cameras/sensors for various applications.

Claims

1. A film comprising:
 - one or more types of nanostructures; and
 - one or more types of ligands bonded to the one or more types of nanostructures;
 - wherein the one or more types of nanostructures comprise neodymium (Nd) and ytterbium (Yb); and
 - wherein a ratio of a molar concentration of neodymium (Nd) to a molar concentration of ytterbium (Yb) is more than 1 : 1.
2. The film according to claim 1,
 - wherein the one or more types of nanostructures comprise one or more materials selected from a group consisting of sodium yttrium tetra-fluoride (NaYF_4), lanthanum trifluoride (LaF_3), sodium gadolinium fluoride (NaGdF_4), sodium lutetium fluoride (NaLuF_4), yttrium oxide (Y_2O_3), and zirconium oxide (ZrO_2).
3. The film according to claim 1 or claim 2,
 - wherein the ratio of the molar concentration of neodymium (Nd) to the molar concentration of ytterbium (Yb) is equal to or more than 4 : 3.
4. The film according to any one of claims 1 to 3,
 - wherein the ratio of the molar concentration of neodymium (Nd) to the molar concentration of ytterbium (Yb) is equal to or more than 8 : 3.
5. The film according to any one of claims 1 to 4,

wherein the ratio of the molar concentration of neodymium (Nd) to the molar concentration of ytterbium (Yb) is equal to or more than 8 : 1.

6. The film according to any one of claims 1 to 5,
wherein the one or more types of ligands are selected from a group consisting of butile ligands, tetraethyl orthosilicate (TEOS) ligands, tetrafluoro-tetracyanoquinodimethane (F4TCNQ) ligands, oleic acid ligand, polydimethylsiloxane (PDMS) ligand, polymethyl methacrylate (PMMA) ligand and any combination thereof.
7. The film according to any one of claims 1 to 6,
wherein a first emission with a first wavelength of 806 nm by the film in response to the film under radiation of only the near infrared (NIR) light is less than a second emission with the first wavelength of 806 nm by the film in response to the film under radiation of both the near infrared (NIR) light and the mid infrared (MIR) light; and
wherein a first emission with a second wavelength of 980 nm by the film in response to the film under radiation of only the near infrared (NIR) light is more than a second emission with the second wavelength of 980 nm by the film in response to the film under radiation of both the near infrared (NIR) light and the mid infrared (MIR) light.
8. The film according to claim 7,
wherein a ratio of the second emission of the first wavelength of 806 nm to the second emission of the second wavelength of 980 nm when the film is under radiation of both the near infrared (NIR) light and the mid infrared (MIR) light is increased by more than 175 times compared to a ratio of the first emission of the first wavelength of 806 nm to the first emission of the second wavelength of 980 nm when the film is under radiation of only the near infrared (NIR) light.
9. The film according to claim 8,

wherein an increase of the ratio of the second emission of the first wavelength of 806 nm to the second emission of the second wavelength of 980 nm compared to the ratio of the first emission of the first wavelength of 806 nm to the first emission of the second wavelength of 980 nm is due to multi-phonon relaxation of the one or more types of ligands.

10. The film according to any one of claims 1 to 9,

wherein a first emission with a third wavelength of 866 nm by the film in response to the film under radiation of only the near infrared (NIR) light is less than a second emission with the third wavelength of 866 nm by the film in response to the film under radiation of both the near infrared (NIR) light and the mid infrared (MIR) light.

11. The film according to any one of claims 1 to 9,

wherein a first emission with a third wavelength of 866 nm by the film in response to the film under radiation of only the near infrared (NIR) light is more than a second emission with the third wavelength of 866 nm by the film in response to the film under radiation of both the near infrared (NIR) light and the mid infrared (MIR) light.

12. The film according to any one of claims 1 to 11,

wherein the film is configured to exhibit a room temperature detection of a mid infrared (MIR) wavelength of 6.3 μm with a specific detectivity of 5×10^8 Jones.

13. The film according to any one of claims 1 to 12,

wherein the one or more types of nanostructures comprise nanoparticles, nanowires, nanoplates or any combination thereof.

14. A mid infrared (MIR) detection system comprising:

a film comprising:

one or more types of nanostructures; and
one or more types of ligands bonded to the one or more types of nanostructures;
a near infrared (NIR) source configured to provide near infrared (NIR) light to the film; and
a detector;
wherein the one or more types of nanostructures comprise neodymium (Nd) and ytterbium (Yb);
wherein a ratio of a molar concentration of neodymium (Nd) to a molar concentration of ytterbium (Yb) is more than 1 : 1;
wherein the detector is configured to determine a first emission at a first wavelength from the film when the film is under radiation of only the near infrared (NIR) light, and a second emission at the first wavelength from the film when the film is under radiation of both the near infrared (NIR) light and mid infrared (MIR) light, the mid infrared (MIR) light from a mid infrared (MIR) source; and
wherein the detector is further configured to determine a first emission at a second wavelength from the film when the film is under radiation of only the near infrared (NIR) light, and a second emission at the second wavelength from the film when the film is under radiation of both the near infrared (NIR) light and the mid infrared (MIR) light.

15. The mid infrared (MIR) detection system according to claim 14,
wherein the mid infrared (MIR) source is a blackbody or a mid infrared (MIR) laser.
16. The mid infrared (MIR) detection system according to claim 14 or claim 15,
wherein the first wavelength is 806 nm and the second wavelength is 980 nm.

17. The mid infrared (MIR) detection system according to any one of claims 14 to 16, further comprising:

the mid infrared (MIR) source.

18. The mid infrared (MIR) detection system according to any one of claims 14 to 17, further comprising:

a first lens configured to direct the mid infrared (MIR) light from the mid infrared (MIR) source to the film;

a beam splitter; and

a second lens;

wherein the beam splitter is configured to direct the near infrared (NIR) light from the near infrared (NIR) source to the second lens; and

wherein the second lens is configured to direct the near infrared (NIR) light from the beam splitter to the film.

19. The mid infrared (MIR) detection system according to claim 18, further comprising:

a third lens configured to direct the emission of the first wavelength and the emission of the second wavelength from the film to the detector.

20. The mid infrared (MIR) detection system according to any one of claims 14 to 19, wherein the detector is a spectrometer.

21. The mid infrared (MIR) detection system according to any one of claims 14 to 20, wherein the detector comprises a bandpass filter.

22. A method of forming a film, the method comprising:

forming one or more types of nanostructures with one or more types of ligands bonded to the one or more types of nanostructures;
wherein the one or more types of nanostructures comprise neodymium (Nd) and ytterbium (Yb); and
wherein a ratio of a molar concentration of neodymium (Nd) to a molar concentration of ytterbium (Yb) is more than 1 : 1.

23. The method according to claim 22,
wherein the one or more types of nanostructures comprise one or more materials selected from a group consisting of sodium yttrium tetra-fluoride (NaYF_4), lanthanum trifluoride (LaF_3), sodium gadolinium fluoride (NaGdF_4), sodium lutetium fluoride (NaLuF_4), yttrium oxide (Y_2O_3), and zirconium oxide (ZrO_2).
24. The method according to claim 22 or claim 23,
wherein the ratio of the molar concentration of neodymium (Nd) to the molar concentration of ytterbium (Yb) is equal to or more than 4 : 3.
25. The method according to any one of claims 22 to 24,
wherein the ratio of the molar concentration of neodymium (Nd) to the molar concentration of ytterbium (Yb) is equal to or more than 8 : 3.
26. The method according to any one of claims 22 to 25,
wherein the ratio of the molar concentration of neodymium (Nd) to the molar concentration of ytterbium (Yb) is equal to or more than 8 : 1.
27. The method according to any one of claims 22 to 26,
wherein the one or more types of ligands are selected from a group consisting of butile ligands, tetraethyl orthosilicate (TEOS) ligands, tetrafluoro-tetracyanoquinodimethane (F_4TCNQ) ligands, oleic acid ligand,

polydimethylsiloxane (PDMS) ligand, polymethyl methacrylate (PMMA) ligand and any combination thereof.

28. The method according to any one of claims 22 to 27,

wherein a first emission with a first wavelength of 806 nm by the film in response to the film under radiation of only the near infrared (NIR) light is less than a second emission with the first wavelength of 806 nm by the film in response to the film under radiation of both the near infrared (NIR) light and the mid infrared (MIR) light; and

wherein a first emission with a second wavelength of 980 nm by the film in response to the film under radiation of only the near infrared (NIR) light is more than a second emission with the second wavelength of 980 nm by the film in response to the film under radiation of both the near infrared (NIR) light and the mid infrared (MIR) light.

29. The method according to claim 28,

wherein a ratio of the second emission of the first wavelength of 806 nm to the second emission of the second wavelength of 980 nm when the film is under radiation of both the near infrared (NIR) light and the mid infrared (MIR) light is increased by more than 175 times compared to a ratio of the first emission of the first wavelength of 806 nm to the first emission of the second wavelength of 980 nm when the film is under radiation of only the near infrared (NIR) light.

30. The method according to claim 29,

wherein an increase of the ratio of the second emission of the first wavelength of 806 nm to the second emission of the second wavelength of 980 nm compared to the ratio of the first emission of the first wavelength of 806 nm to the first emission of the second wavelength of 980 nm is due to multi-phonon relaxation of the one or more types of ligands.

31. The method according to any one of claims 22 to 30,
wherein a first emission with a third wavelength of 866 nm by the film in response to the film under radiation of only the near infrared (NIR) light is less than a second emission with the third wavelength of 866 nm by the film in response to the film under radiation of both the near infrared (NIR) light and the mid infrared (MIR) light.
32. The method according to any one of claims 22 to 30,
wherein a first emission with a third wavelength of 866 nm by the film in response to the film under radiation of only the near infrared (NIR) light is more than a second emission with the third wavelength of 866 nm by the film in response to the film under radiation of both the near infrared (NIR) light and the mid infrared (MIR) light.
33. The method according to any one of claims 22 to 32,
wherein the film is configured to exhibit a room temperature detection of a mid infrared (MIR) wavelength of 6.3 μm with a specific detectivity of 5×10^8 Jones.
34. The method according to any one of claims 22 to 33,
wherein the one or more types of nanostructures comprise nanoparticles, nanowires, nanoplates or any combination thereof.
35. A method of forming a mid infrared (MIR) detection system, the method comprising:
forming a film comprising:
one or more types of nanostructures; and
one or more types of ligands bonded to the one or more types of nanostructures;
arranging a near infrared (NIR) source configured to provide near infrared (NIR) light to the film; and

providing a detector;
wherein the one or more types of nanostructures comprise neodymium (Nd) and ytterbium (Yb);
wherein a ratio of a molar concentration of neodymium (Nd) to a molar concentration of ytterbium (Yb) is more than 1 : 1;
wherein the detector is configured to determine a first emission at a first wavelength from the film when the film is under radiation of only the near infrared (NIR) light, and a second emission at the first wavelength from the film when the film is under radiation of both the near infrared (NIR) light and mid infrared (MIR) light, the mid infrared (MIR) light from a mid infrared (MIR) source; and
wherein the detector is further configured to determine a first emission at a second wavelength from the film when the film is under radiation of only the near infrared (NIR) light, and a second emission at the second wavelength from the film when the film is under radiation of both the near infrared (NIR) light and the mid infrared (MIR) light.

36. The method according to claim 35,
wherein the mid infrared (MIR) source is a blackbody or a mid infrared (MIR) laser.
37. The method according to claim 35 or claim 36,
wherein the first wavelength is 806 nm and the second wavelength is 980 nm.
38. The method according to any one of claims 35 to 37, further comprising:
providing the mid infrared (MIR) source.
39. The method according to any one of claims 35 to 38, further comprising:

providing a first lens configured to direct the mid infrared (MIR) light from the mid infrared (MIR) source to the film;
providing a beam splitter; and
providing a second lens;
wherein the beam splitter is configured to direct the near infrared (NIR) light from the near infrared (NIR) source to the second lens; and
wherein the second lens is configured to direct the near infrared (NIR) light from the beam splitter to the film.

40. The method according to claim 39, further comprising:
providing a third lens configured to direct the emission of the first wavelength and the emission of the second wavelength from the film to the detector.
41. The method according to any one of claims 35 to 40,
wherein the detector is a spectrometer.
42. The method according to any one of claims 35 to 41,
wherein the detector comprises a bandpass filter.
43. A method of operating a mid infrared (MIR) detection system, the method comprising:
providing only near infrared (NIR) light using a near infrared (NIR) source to a film and determining a first emission at a first wavelength and a first emission at a second wavelength from the film using a detector; and
providing the near infrared (NIR) light using the near infrared (NIR) source and mid infrared (MIR) light using a mid infrared (MIR) source to the film and determining the second emission at the first wavelength and the second emission at the second wavelength from the film using the detector;
wherein the film comprises:
one or more types of nanostructures; and

one or more types of ligands bonded to the one or more types of nanostructures;
wherein the one or more types of nanostructures comprise neodymium (Nd) and ytterbium (Yb); and
wherein a ratio of a molar concentration of neodymium (Nd) to a molar concentration of ytterbium (Yb) is more than 1 : 1.

44. The method according to claim 43, further comprising:
determining a change between a ratio of the first emission at the first wavelength to the first emission at the second wavelength when the film is under radiation of only the near infrared (NIR) light, and a ratio of the second emission at the first wavelength to the second emission at the second wavelength when the film is under radiation of both the near infrared (NIR) light and the mid infrared (MIR) light.