(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
20 July 2017 (20.07.2017)

WIPO | PCT

(10) International Publication Number
WO 2017/123774 A1

(51) International Patent Classification:
B01D 53/86 (2006.01) *B82Y 30/00* (2011.01)
B01J 37/08 (2006.01) *B82Y 40/00* (2011.01)
C01B 31/04 (2006.01)

(21) International Application Number:
PCT/US2017/013210

(22) International Filing Date:
12 January 2017 (12.01.2017)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
62/277,781 12 January 2016 (12.01.2016) US

(71) Applicant: **THE BOARD OF REGENTS, THE UNIVERSITY OF TEXAS SYSTEM** [US/US]; 201 West 7th Street, Austin, TX 78701 (US).

(72) Inventors: **CHEN, Wei**; 2604 Park Run Drive, Arlington, TX 76016 (US). **MA, Lun**; 1020 West Abram Street, #108, Arlington, Texas 75013 (US).

(74) Agent: **ECHLER, Richard, S.**; 118 Highlands Drive, Woodstock, GA 30188 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

WO 2017/123774 A1

(54) Title: NANOPHOSPHORS FOR VISIBLE LIGHT ENHANCEMENT

(57) Abstract: Disclosed herein are composite materials that comprise one or more nanophosphors capable of converting higher frequency, lower wavelength radiation into visible light. As used, the produced visible light enhances the amount of visible light already present from natural or artificial sources. The disclosed composite materials provide a source of strong white light that can be used for solid-state lighting, full color displays, and as a light source for plant growth, crop improvement and interior lighting.

NANOPHOSPHORS FOR VISIBLE LIGHT ENHANCEMENT

FIELD OF THE DISCLOSURE

Disclosed herein are composite materials that comprise one or more nanophosphors capable of converting higher frequency, lower wavelength radiation into visible light. As used, the produced visible light enhances the amount of visible light already present from natural or artificial sources.

BACKGROUND

It is projected that the world population will be about 10 billion before reaching a plateau in the later part of this century, and increasing economic prosperity of the developing world is forecast to soon place even greater demands on agricultural production than will population growth. With very few prospects to sustainably expand the 1.5 billion ha of cropland currently under cultivation, a doubling of productivity will be needed to meet the increasing demand before the end of this century.[1, 2] In the last ten years, increases in yield for some major crops such as rice have shown little improvement.[3] In 2008, the world saw the lowest wheat stockpiles of the past 30 years and fears of a rice shortage incited riots in some countries.[4] Adding to this, the rapid growth in the Chinese and Indian economies has resulted in never before seen demands on grain supplies.[3] Increasing grain crop productivity is the foremost challenge facing agricultural research. Globally, rice is the world's most important crop in terms of the number of people who depend upon it as their major source of calories and nutrition. After rapid increases in yield over the latter half of the twentieth century, further yield increases appear harder to obtain. This indicates that human will be facing the crisis of food supplies in the near future and a boost in food production is urgently demanded.

The other challenge facing the world is an energy crisis. Our present oil reserves will last 40 years at most and will decline significantly well before then. Globally, experts are working hard to find out how renewable sources of energy can be used to better fulfill our energy needs. Today, when we talk about renewable energy sources we usually mean solar energy, wind power and water (hydroelectric or watermill) power. Renewable energy sources by their very nature will never be exhausted. The great thing about solar energy is that there is an unlimited supply and it is relatively easy and straightforward to implement. Solar energy doesn't pollute the environment and produces so much energy that the total amount of light and heat energy that hits the earth every hour is enough to meet the entire energy needs of the planet for a whole year. The use of nanophosphors to convert UV

sunshine to blue and red light for photosynthesis improvement can provide a good solution not only for food need but also for other purposes that will help with the energy crisis.

Numerous efforts have been dedicated to the research and development of luminescence materials for these applications and most phosphors are rare earth based materials. For example, the three basic phosphors for solid-state lighting are materials doped with Eu^{3+} (red), Tb^{3+} (green) and Eu^{2+} (blue). The most tested luminescence or light converting materials for photosynthesis improvement are Eu^{2+} doped sulfates and silicate phosphors. The advantage is that these materials have a high light output that can meet the requirement for these applications. However, the challenging issue is that rare earths are very expensive and their resources are limited due to the extremely low abundance of these elements on earth.

There is, therefore, a long felt need for alternative solutions. One alternative is the use of non-rare earth materials that can fulfill these requirements of practical applications, an alternative that is inexpensive, practical, and provides near to equal or better results when compared to the rare earth phosphors.

BRIEF DESCRIPTION OF THE FIGURES

The following drawings illustrate by way of example and not limitation. For the sake of brevity and clarity, every feature of a given structure is not always labeled in every figure in which that structure appears.

Figure 1A depicts the emission and excitation spectra for the as-prepared g-C_3N_4, and nitric acid treated g-C_3N_4. Line a1 is for the untreated, while a2 has been treated with 34.4% nitric acid, a3 with 47.6% nitric acid, and a4 with 60.7% nitric acid.

Figure 1B depicts the emission and excitation spectra for Cu-Cy at room temperature.

Figure 2 depicts the XRD patterns of the g-C_3N_4 synthesized at 500°C and g-C_3N_4 treated with nitric acids of different concentrations.

Figure 3A and Figure 3B show SEM images of g-C_3N_4 prior to acid treatment.

Figure 3C and FIG 3D show SEM images of g-C_3N_4 depicting delamination, which occurred after the treatment with 60.7% nitric acid.

Figure 3E shows a TEM image of g-C_3N_4 prior to acid treatment.

Figure 3F shows a TEM image of g-C_3N_4 depicting delamination, which occurred after treatment with 60.7% nitric acid.

Figure 4A depicts the absorption spectrum of Cu-Cy.

Figure 4B depicts the corresponding band gap of 3.11 eV due to the sharp absorption edge of Cu-Cy as depicted in Fig 4A.

Figure 5 and Figure 6 depict the emission spectra and CIE (Commission International de L'Eclairage) chromaticity positions of the phosphors made of different mass ratios of the 60.7% nitric acid treated g-C_3N_4 and Cu-Cy.

The inset in **Figure 6** shows a photo of the mixed phosphors excited by a 365 nm UV lamp.

Figure 7 shows a single-composition WLED lamp and the corresponding white-light emission driven under a forward bias current of 300 mA.

Figure 8A shows Zn:Ag,Mn under white room light.

Figure 8B shows Zn:Ag,Mn under a 360 nm UV lamp.

Figure 9 depicts the XRD pattern of the ZnS:Ag,Mn powder, showing both sphalerite and wurtzite structure.

Figure 10A and Figure 10B show SEM images of ZnS:Ag,Mn which display the co-existence of large (~3 μm) on **Figure 11A** and small (~100 nm) particles on **Figure 11B.**

Figure 11 depicts the emission (PL) and excitation (PLE) spectra of ZnS:Ag,Mn monitored by different wavelengths.

Figure 12 depicts the CIE chromaticity coordinates of ZnS:Ag,Mn under different excitations (310, 320, and 330 nm) displayed as those black dots (circled by the dash line) that are located in white color region.

DETAILED DESCRIPTION

The materials, compounds, compositions, articles, and methods described herein may be understood more readily by reference to the following detailed description of specific aspects of the disclosed subject matter and the Examples included therein.

Before present materials, compounds, compositions, and methods are disclosed and described, it is to be understood that the aspects described below are not limited to specific synthetic methods or specific reagents, as such may, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular aspects only and is not intended to be limiting.

All percentages, ratios and proportions herein are by weight, unless otherwise specified. All temperatures are in degrees Celsius (^{o} C) unless otherwise specified.

Also, throughout this specification, various publications are referenced. The disclosures of these publications in their entireties are hereby incorporated by reference into this application in order to more fully describe the state of the art to which the disclosed

matter pertains. The references disclosed are also individually and specifically incorporated by reference herein for the material contained in them that is discussed in the sentence in which the reference is relied upon.

The terms "comprise" (and any form of comprise, such as "comprises" and "comprising"), "have" (and any form of have, such as "has" and "having"), "include" (and any form of include, such as "includes" and "including") and "contain" (and any form of contain, such as "contains" and "containing") are open-ended linking verbs. As a result, an apparatus that "comprises," "has," "includes" or "contains" one or more elements possesses those one or more elements, but is not limited to possessing only those elements. Likewise, a method that "comprises," "has," "includes" or "contains" one or more steps possesses those one or more steps, but is not limited to possessing only those one or more steps.

Ranges can be expressed herein as from "about" one particular value, and/or to "about" another particular value. When such a range is expressed, another aspect includes from the one particular value and/or to the other particular value. Similarly, when values are expressed as approximations, by use of the antecedent "about," it will be understood that the particular value forms another aspect. It will be further understood that the endpoints of each of the ranges are significant both in relation to the other endpoint, and independently of the other endpoint. It is also understood that there are a number of values disclosed herein, and that each value is also herein disclosed as "about" that particular value in addition to the value itself. For example, if the value "10" is disclosed, then "about 10" is also disclosed. It is also understood that when a value is disclosed, then "less than or equal to" the value, "greater than or equal to the value," and possible ranges between values are also disclosed, as appropriately understood by the skilled artisan. For example, if the value "10" is disclosed, then "less than or equal to 10" as well as "greater than or equal to 10" is also disclosed. It is also understood that throughout the application data are provided in a number of different formats and that this data represent endpoints and starting points and ranges for any combination of the data points. For example, if a particular data point "10" and a particular data point "15" are disclosed, it is understood that greater than, greater than or equal to, less than, less than or equal to, and equal to 10 and 15 are considered disclosed as well as between 10 and 15. It is also understood that each unit between two particular units are also disclosed. For example, if 10 and 15 are disclosed, then 11, 12, 13, and 14 are also disclosed.

The terms "a" and "an" are defined as one or more unless this disclosure explicitly requires otherwise. Ranges may be expressed herein as from "about" one particular value,

and/or to "about" another particular value. When such a range is expressed, another aspect includes from the one particular value and/or to the other particular value. Similarly, when values are expressed as approximations, by use of the antecedent "about," it will be understood that the particular value forms another aspect. It will be further understood that the endpoints of each of the ranges are significant both in relation to the other endpoint, and independently of the other endpoint.

Values expressed as "greater than" do not include the lower value. For example, when the "variable x" is defined as "greater than zero" expressed as "0 < x" the value of x is any value, fractional or otherwise that is greater than zero. Similarly, values expressed as "less than" do not include the upper value. For example, when the "variable x" is defined as "less than 2" expressed as "x < 2" the value of x is any value, fractional or otherwise that is less than 2.

"Optional" or "optionally" means that the subsequently described event or circumstance can or cannot occur, and that the description includes instances where the event or circumstance occurs and instances where it does not

Any embodiment of any of the apparatuses, systems, and methods can consist of or consist essentially of – rather than comprise/include/contain/have – any of the described steps, elements, and/or features. Thus, in any of the claims, the term “consisting of” or “consisting essentially of” can be substituted for any of the open-ended linking verbs recited above, in order to change the scope of a given claim from what it would otherwise be using the open-ended linking verb.

The feature or features of one embodiment may be applied to other embodiments, even though not described or illustrated, unless expressly prohibited by this disclosure or the nature of the embodiments.

Any embodiment of any of the apparatuses, systems, and methods can consist of or consist essentially of - rather than comprise/include/contain/have - any of the described steps, elements, and/or features. Thus, in any of the claims, the term "consisting of or "consisting essentially of can be substituted for any of the open-ended linking verbs recited above, in order to change the scope of a given claim from what it would otherwise be using the open- ended linking verb. The feature or features of one embodiment may be applied to other embodiments, even though not described or illustrated, unless expressly prohibited by this disclosure or the nature of the embodiments.

As used herein, "electromagnetic radiation" refers to a form of energy containing both electric and magnetic wave components which includes ultraviolet (UV), visible and infrared (IR) radiation.

As used herein, “plant” or “plants” can be used interchangeably with the term “crops” which refers to grains, such as rice, wheat, barley, oats, soy beans, rye, spelt, corn, millet, sorghum, buckwheat, chia, quinoa, chickpeas, lentils, lima beans, peanuts, rapeseed, flax seed, and the like. Plant further refers to non-edible plants, for example, flowers, hay and the like.

The feature or features of one embodiment may be applied to other embodiments, even though not described or illustrated, unless expressly prohibited by this disclosure or the nature of the embodiments.

Details associated with the embodiments described above and others are described below.

Disclosed herein are composites, comprising:

a) one or more of the disclosed nanophosphors; and

b) a substrate;

wherein the nanophosphors are situated within the substrate.

In one aspect the disclosed composites, comprise:

a) a visible light enhancing composition, comprising:

i) a first phosphor that emits visible light in the range of from about 520 nm to about 700 nm when exposed to UV radiation; and

ii) a second phosphor that emits visible light in the range of from about 400 to about 520 nm when exposed to UV radiation; and

b) a substrate

The disclosed composite materials provide a source of strong white light that can be used for solid-state lighting, full color displays, and as a light source for plant growth, crop improvement and interior lighting. The disclosed materials can have any form chosen by the formulator, for example, films, transparent solid shapes, semi-transparent solid shapes, or a transparent shaped-solid that has one or more reflective surfaces on the inside of the material or on portions of the outside surface.

In one aspect the disclosed composite material is a film. In another aspect the composite material is in the form of a transparent solid. In a further aspect the disclosed composite material is in the form of a semi-transparent solid. Each of these aspects is capable of converting sources of electromagnetic radiation in the ultraviolet range, or above,

into electromagnetic radiation in the visible range (*i.e.*, visible light). This ability applies to either natural sources, *i.e.*, direct sunlight, or artificial ultraviolet sources.

Graphitic-phase nitrogen carbon is a stable allotrope under ambient conditions. g-C_3N_4 is abundant and can be readily obtained via a one-step polymerization of a variety of precursors, non-limiting examples include cyanamide, urea, thiourea, melamine, and dicyandiamide. The band gap of g-C_3N_4 is 2.7 eV as estimated from absorption spectrum and it decreases as the condensation temperature increases.

For the purposes of the present disclosure, visible light is divided into an upper visible light range (400-520nm) range and a lower visible light range (520-700 nm). One aspect of the disclosure comprises at least two compounds that when excited by X-ray or UV light produces visible light in both the upper range and lower range. In certain aspects, however, the composite is only be required to emit light in either the upper of lower range.

In one aspect disclosed are visible light enhancing compositions, comprising:

i) a first phosphor that emits visible light in the range of from about 520 nm to about 700 nm when exposed to UV radiation; and

ii) a second phosphor that emits visible light in the range of from about 400 to about 520 nm when exposed to UV radiation;

thereby providing an enhancement in the amount of visible light.

In a further aspect disclosed herein are compositions, comprising a phosphor that emits visible light in the range of from about 520 nm to about 700 nm when exposed to UV radiation.

In another aspect disclosed herein are compositions, comprising a phosphor that emits visible light in the range of from about 400 nm to about 520 nm when exposed to UV radiation.

The disclosed compositions comprise phosphors that are in the form of nanoparticles. As used herein, the term "phosphor" means a substance that exhibits the phenomenon of luminescence. The disclosed phosphors emit electromagnetic radiation in specific ranges of visible light. Combinations of phosphors as disclosed herein, typically do not have emission peaks at the same wavelength, but can have some overlapping wavelengths. The disclosed phosphor nanoparticles can optionally comprise one or more rare earth elements.

In one aspect, the disclosed phosphor is delaminated graphitic-phase nitrogen carbon (g-C_3N_4).

In another aspect, the disclosed phosphor is copper-cysteamine having the formula $(Cu_3Cl(SCH_2CH_2NH_2)_2$.

In a further aspect the disclosed a visible light enhancing composition, comprise:

a) delaminated graphitic-phase nitrogen carbon (g-C_3N_4); and

b) one or more phosphors chosen from copper-cysteamine ($Cu_3Cl(SR)_2$, R is – $CH_2CH_2NH_2$, zinc sulfide (ZnS), silver-and manganese doped zinc sulfide (ZnS:Ag, Mn), or activated zinc sulfide (ZnS(Mn)).

In a still further aspect the visible light enhancing compositions, comprise:

a) delaminated graphitic-phase nitrogen carbon (g-C_3N_4); and

b) copper-cysteamine ($Cu_3Cl(SR)_2$,R=$SCH_2CH_2NH_2$;

wherein the ratio of g-C_3N_4 to $Cu_3Cl(SCH_2CH_2NH_2)_2$ is from about 1:1 to about 1:5.

In yet further aspect the visible light enhancing compositions, comprise:

a) delaminated graphitic-phase nitrogen carbon (g-C_3N_4); and

b) zinc sulfide (ZnS);

wherein the ratio of g-C_3N_4 to ZnS is from about 1:0.5 to about 1:10.

In a yet another aspect the visible light enhancing compositions, comprise:

a) delaminated graphitic-phase nitrogen carbon (g-C_3N_4); and

b) silver-and manganese doped zinc sulfide (ZnS:Ag, Mn);

wherein the ratio of g-C_3N_4 to ZnS:Ag, Mn is from about 1:0.5 to about 1:10.

In a still yet further aspect the visible light enhancing compositions, comprise:

a) delaminated graphitic-phase nitrogen carbon (g-C_3N_4); and

b) activated zinc sulfide (ZnS(Mn));

wherein the ratio of g-C_3N_4 to ZnS(Mn) is from about 1:0.5 to about 1:10.

The disclosed delaminated graphitic-phase nitrogen carbon (g-C_3N_4) can be delaminated by treatment with a strong mineral acid, for example, nitric acid. By varying the concentration of the acid, the formulator can affect the properties of the final phosphor.

Each of the composites described herein above, can further comprise other non-rare earth nanoparticles. One non-limiting example includes which CuS can be added to the composites to reduce heat and protect from infrared radiation damage.

EXAMPLE 1

1. Preparation of the disclosed phosphors

Delaminated graphitic-phase nitrogen carbon (g-C3N4) powder was obtained through a low temperature thermal condensation of melamine.[12] Briefly, melamine (2 g) was heated at 500 °C in air for 2 hours with a heating rate of 3 °C/min to obtain the desired

g-C3N4 as a yellow powder. g-C3N4 (1.5 g) was dispersed in nitric acid solutions (25 mL) having different concentrations of nitric acid; 34.4 wt%, 47.6 wt% and 60.7 wt% respectively. Once combined the solutions were heated at 90°C while stirring for 2 hours. Then, the solutions were cooled to room temperature and centrifuged to obtain the acid-treated g-C3N4. The solids were washed with deionized water until all trace of acid was removed, then the samples were dried at 70 °C in an air to obtain the desired materials as a white powder.

EXAMPLE 2

Delaminated g-C_3N_4 (30 mg) and Cu-Cy (40 mg) are charged to a 2 mL centrifuge tube and the tube shaken until a complete admixture results. The resulting composition has a ratio of g-C_3N_4:Cu-Cy of 1.1.33.

Figure 1A demonstrates the effect of nitric acid concentration on the hypsochromic shift in the spectrum of various delaminated g-C_3N_4 samples versus control as described in Example 1. **Spectra a1** are the excitation and emission spectra of the control (non-treated g-C_3N_4), **Spectra b1** are the excitation and emission spectra of g-C_3N_4 treated with a 34.4 wt% solution of HNO_3, **Spectra c1** are the excitation and emission spectra of g-C_3N_4 treated with a 47.6 wt% solution of HNO_3,and **Spectra d1** are the excitation and emission spectra of g-C_3N_4 treated with a 60.7 wt% solution of HNO_3. As seen in **Figure 1A**, the intensity of the excitation and emissions increases with increasing acid concentration. The emission wavelength is also shifted from 461 nm (a1), to 441 nm (b 1), to 438 nm (c 1) and finally to 435 nm (d 1). All samples where excited at 365 nm.

Figure 1B depicts the emission and excitation spectra for Cu-Cy at room temperature. The sample is irradiated at 365 nm, the same as the samples in Figure 1A, however, the emission occurs at 610 nm. Cu-Cy has a structure in which both the thio and amine group form cysteamine bonded with the copper ions. The Cu–Cy particles include two different Cu atoms–Cu (1) and Cu (2), which bind to 4 and 3 other atoms respectively. The valence analyses from single crystal X-ray diffraction and solid-state nuclear magnetic spectroscopy indicate that they are both Cu^+ ions.[11] g-C_3N_4 and Cu-Cy have similar excitation spectra, *i.e.*, both have broad excitation band ranging from 250 to 420 nm with a maximum at about 365 nm. This indicates that the two luminescent materials can be activated using a single wavelength excitation. The absorption spectrum of Cu-Cy has a sharp absorption edge at 399 nm that corresponds to a band gap of 3.11 eV (as shown in **Figure 4A and 4B**). g-C_3N_4 shows almost no emission below 400 nm as shown in **Figure 1A**, *i.e.*, the blue emission of g-C_3N_4 is not obviously overlapped with the absorption of Cu-

Cy, therefore, no reabsorption or energy transfer occurs between the two materials. Therefore, a composite comprising the g-C_3N_4 phosphors and Cu-Cy would produce two separate emission peaks.

Figure 2 depicts the change in crystal structure of the samples depicted in **Figure 1A**. The XRD pattern of g-C_3N_4 synthesized at 500°C exhibits two peaks. The intense peak at 27.4° is associated with an interlayer distance d = 0.326 nm and is indexed for graphitic-phase nitrogen carbon as the (002) plane. This peak represents the characteristic interplanar stacking of aromatic systems.[5] The weak diffraction peak at 13.1° corresponds to the in-plane structural packing motif indexed as the (100) plane.[6] Treatment with nitric acid afffects the peak at 13° which is gradually reduced and finally disappears in spectrum (d), while the peak at 27.4°shifts to 27.9°.

The bulk of the disclosed untreated g-C_3N_4 are composed of small particles having a size of about 200 nm as shown by the SEM images in **Figure 3A** and **Figure 3B,** as well as the TEM image in **Figure 3E**. After nitric acid treatment, some g-C_3N_4 was delaminated as shown by the SEM image in **Figure 3C.** The layer-like powders contain smaller particles, and some are as small as 15 nm as seen in **Figure 3D** and **Figure 3F**.

Without wishing to be limited by theory, the decrease in the particle size accounts for the gradual weakening and the disappearance of the low-angle reflection peak at 13° as a consequence of the destruction in the long-range order of the in-plane structural packing.[7, 8, 9] The delamination of the bulk materials causes the shift of the peak at 27° because of the shrinking of the distance between the sheets. The single layers in bulk g-C_3N_4 are potentially undulated, but can be planarized by heating using nitric acid, resulting in a denser stacking.[7, 9] The calculated density of states (DOS) of single-layered g-C_3N_4 nanosheets shows an increase of DOS at the conduction band edge with respect to the bulk counterpart, indicating that the g-C_3N_4 nanosheets possess more charge carriers.[10] Delamination coupled with the formation of nano-sized particles causes the blue shift of the absorption edge and emission peak due to quantum size effect. As the nitric acid concentration is increasing, there are more delaminations and formed nanoparticles, therefore, the emission spectrum indicates a continuous blue-shift and the emission intensity is gradually enhanced.

Figure 5 displays the emission spectra and CIE (Commission Internationale de L'Eclairage) chromaticity positions of the disclosed phosphors, *i.e.*, delaminated g-C_3N_4 treated with the 60.7% nitric acid treatment, Cu-Cy, and phosphors comprising g-C_3N_4 and Cu-Cy having the g-C_3N_4 to Cu-Cy weight ratios listed in Table I below. Under excitation

at 365 nm, the emission extends through the whole visible light region from 400 to 700 nm. The two strong emission peaks at 435 nm (blue) and 610 nm (orange) are from the emissions of g-C_3N_4 and Cu-Cy, respectively. The emission spectrum of the composites is a mechanical mixture of their respective emission spectrum, and the luminescent intensity of the component material increases with its ratio in the mixture. **Figure 6** shows the CIE chromaticity positions of the emission-tunable phosphors excited at 365 nm. The inset is a digital photo of the mixed phosphors excited by a 365 nm UV lamp. As shown in Table I is the fact that the color coordinates can be gradually tuned from blue (0.156, 0.083) through white-light (0.365, 0.265) toward orange (0.533, 0.409) in the visible spectral region via a systematic changing of the weight ratio of g-C_3N_4 and Cu-Cy. When the weight ratio of g-C_3N_4 and Cu-Cy is 1:1.67, the quantum yield (QY) is 20%.

TABLE I

Composition	mass ratio	CIE x	CIE y
g-C_3N_4		0.156	0.083
g-C_3N_4:Cu-Cy	1:1.33	0.336	0.238
g-C_3N_4: Cu-Cy	1:1.67	0.365	0.265
g-C3N_4: Cu-Cy	1:2.67	0.393	0.287
Cu-Cy		0.533	0.409

Other materials can be combined with delaminated g-C_3N_4 to form the disclosed nanophosphors, non-limiting examples of which include cysteamine ($HSCH_2CH_2NH_2$), zinc oxide (ZnO), zinc sulfide (ZnS), silver-activated zinc sulfide (ZnS(Ag)), and manganese-activated zinc sulfide (ZnS:Mn) either in conjunction with Cu-Cy or separately.

An example of a silver and manganese-activated zinc sulfide (ZnS:Ag,Mn) is shown in **Figure 8A** and **8B.** In **Figure 8A** the composite is shown under white light and **Figure 8B** shows the composite under a 360 nm UV lamp. The emissions of this composite by 360 nm UV light can be seen in **Figure 11**, ~450 nm (blue) and ~600 nm (orange) wavelengths.

2. Preparation of Composites

As disclosed herein above, the composites which comprise the disclosed phosphors can convert UV radiation from an artificial or natural source into electromagnetic radiation in the visible range. Light efficiency for photosynthesis and interior light can be boosted by the use of a transparent or semi-transparent film wherein the disclosed phosphors are embedded therein. The film can comprise any polymer or polymer-like material, non-limiting examples of which include polyethylene, polyester, polyvinyl chloride,

polystyrene, poly(methyl methacrylate), etc. The film can be placed on or sandwiched between other transparent materials. In addition to loading transparent polymer films the composites may be directly embedded into transparent materials for use in sunlight conversion.

EXAMPLE 3

The nanoparticle phosphors are synthesized in water using 3-mercaptopropanoic acid (MPA) as a surfactant (0.5 mm cadmium chloride is dissolved in water (50 mL) followed by the addition of 100 μL 3-MPA). The pH of the solution is adjusted to 10 by NaOH. Thiourea (0.5 mmol) in water (10 mL) was added and the solution refluxed at 90°C for 4 hours. The solvent was reduced by evaporation and the precipitated material are washed with a water-acetone mixture and re-dispersed in 20 mL water. Transfer of the highly water dispersible nanoparticles into chloroform is accomplished by replacing 3-MPA with hexadecyl-p-vinylbenzyldimethylammonium chloride (HVDAC). The required amount of HVDAC is dissolved in chloroform (10 mL) followed by addition of the aqueous solution of the nanoparticles (20 mL). After 10 minutes of incubation, the chloroform phase is separated from the aqueous phase using a separating funnel, and nanoparticles are isolated by evaporation of the chloroform.

The nanoparticles are combined with styrene in the desired amount after which an organic peroxide is added. The resulting admixture is sintered at 70°C for 72 hours to provide a transparent film comprising the disclosed nanophosphors. The resulting polymeric film can be further processed by any conventional means.

For example, the nanophosphor/styrene admixture was heated and homogenized in an extruder screw until molten and evenly mixed. The admixture melt is forced through a flat extrusion die that presses the melt into the desired film shape. The thickness and strength of the film can further be affected by elongation rollers while the materials are still hot and pliable. The extruded film is then cooled, cut and packaged. The film transparency and luminescence properties as well as mechanical strength can be optimized by adjusting the particle loading concentration, size and surface coating.

Any monomer which results in a polymeric substrate that is capable of retaining the disclosed nanophosphors and allowing transmission of the emitted electromagnetic radiation is suitable for use. In addition to polystyrene, the following are non-limiting examples of suitable polymer for us as substrates: polystyrene, polyethylene, polyester, polyvinyl chloride, polystyrene, poly(methyl methacrylate), and the like.

In one aspect the composites are transparent. In one embodiment the nanophosphors are aligned along a first surface of a transparent substrate. In another embodiment the nanophosphors are aligned along a second transparent surface, and the first surface comprises a semi-transparent surface. In a further embodiment the nanophosphors are in the interior of the substrate. In one embodiment the first surface is transparent and captures natural or artificial UV radiation and the composite is configured such that the emitted enhanced visible light passes through the second semi-transparent surface to produce a muted glow.

In addition to the formation of a single transparent film comprising the disclosed nanophosphors, the nanophosphors can be embedded or supported by other transparent or semi-transparent substrates. Alternatively the nanophosphor embedded composites can be formed into geometric shapes. As such, all of the final polymeric composites can have a greater or lesser degree of flexibility depending upon the choice of the type of polymer, the amount of polymer, the configuration of the composite, as well as the concentration of nanophosphor. Non-limiting matrices that can substitute for polymers includes glass, transparent ceramic and transparent aluminum.

In one embodiment, the composites can comprise other electromagnetic property modulating materials. For example, CuS can be added to the nanophosphor/polymer admixture as a protectant against infrared damage.

In one aspect the disclosed composites can be used to form white light-emitting diodes. **Figure 7** shows the electroluminescence spectrum of a WLED (white light-emitting Diode) lamp, fabricated by deposition of g-C3N4 and Cu-Cy (weight ratio 1:1.67) on a 365 nm NUV (near ultraviolet) LED chip. The WLED has a broad blue emission at 435 nm from g-C_3N_4 and a broad red emission at 610 nm attributed to Cu-Cy (**Figure 7**). The inset of **Figure 7** shows a single-composition WLED lamp and its white-light emission driven under a forward bias current of 300 mA. The detailed CIE color coordinates, CCT (correlated color temperature) and CRI (color rendering index) of the WLED lamp under forward bias of 300 mA are: x = 0.352, y = 0.320, 4523 K and 94.3, respectively. The luminescence intensity of the WLED increases when the bias current is from 100 mA to 150 mA.

In another aspect the disclosed composites can be fabricated into devices, including lamps, sheets, coverings and the like which can be configured with crops to provided enhance visible light. The enhanced visible light serves as a means for enhancing the photosynthesis of the treated crops.

Disclosed herein is a method for preparing delaminated graphitic-phase nitrogen carbon (g-C_3N_4), comprising:

(a) dispersing from about 2% to about 10% weight/volume of g-C_3N_4 into a nitric acid solution;

(b) heating the dispersion; and

(c) isolating the delaminated g-C_3N_4.

In one aspect the nitric acid solution contains from about 30% to about 70% by weight nitric acid. Therefore, the nitric acid solution can contain 30%, 31%, 32%, 33%, 34%, 35%, 36%, 37%, 38%, 39%, 40%, 41%, 42 %, 43%, 44%, 45%, 46%, 47%, 48%, 49%, 50%, 51%, 52%, 53%, 54%, 55%, 56%, 57%, 58%, 59%, 60%, 61%, 62%, 63%, 64%, 65%, 66%, 67%, 68%, 69% or 70% by weight nitric acid.

In another aspect the amount of g-C_3N_4 dispersed into the nitric acid solution in step (a) is from about 2% to about 5% w/v.

In a further aspect the amount of g-C_3N_4 dispersed into the nitric acid solution in step (a) is from about 5% to about 10% w/v.

In a still further aspect the amount of g-C_3N_4 dispersed into the nitric acid solution in step (a) is from about 3% to about 8% w/v.

In another aspect the amount of g-C_3N_4 dispersed into the nitric acid solution in step (a) is from about 4% to about 6% w/v. The amount of g-C_3N_4 dispersed into the nitric acid solution can be 2% w/v, 3% w/v, 4% w/v, 5% w/v, 6% w/v, 7% w/v, 8% w/v, 9% w/v, or 10% w/v.

In a still further aspect the dispersion is heat at temperature from about 80 °C to about 100 °C. The dispersion can be heated to 80 °C, 81 °C, 82 °C, 83 °C, 84 °C, 85 °C, 86 °C, 87 °C, 88 °C, 89 °C, 90 °C, 91 °C, 92 °C, 93 °C, 94 °C, 95 °C, 96 °C, 97 °C, 98 °C, 99 °C, or 100 °C.

The delaminated g-C_3N_4 can be isolated before cooling or after cooling. The delaminated g-C_3N_4 can be isolated by any means chosen by the formulator. In one embodiment the cooled dispersion is centrifuged to concentrate the g-C_3N_4 followed by washing with water until the nitric acid is removed followed by air drying.

The claims are not intended to include, and should not be interpreted to include, means-plus- or step-plus-function limitations, unless such a limitation is explicitly recited in a given claim using the phrase(s) "means for" or "step for," respectively.

METHODS

Disclosed herein are methods for utilizing the disclosed composites. In one aspect the composites provide methods for increasing the amount of visible light present when a natural or artificial source of electromagnetic radiation impinges upon the composite. In one embodiment the composite can comprise a visible light enhancing composition comprising one or more of the disclosed phosphors and a substrate. In one iteration the phosphors are deposited are deposited within a transparent substrate. In one example, the transparent substrate is the window of a structure receiving natural light from outside. In another example, the window is an opening between rooms wherein natural light and/or artificial light impinges upon the substrate thereby providing increased visible light.

In another embodiment the composite can comprise a visible light enhancing composition comprising one or more of the disclosed phosphors and a substrate wherein one surface is a reflecting surface that reflects electromagnetic radiation inward. In this embodiment radiation travels through the substrate and is reflected outward toward the source. This provides a means for enhancing the incoming, as well as the reflected radiation.

Disclosed herein is a method for providing solid state lighting having enhanced visible light, comprising:

A) exposing a composite, comprising:

a) a visible light enhancing composition, comprising:

i) a first phosphor that emits visible light in the range of from about 520 nm to about 700 nm when exposed to UV radiation; and

ii) a second phosphor that emits visible light in the range of from about 400 to about 520 nm when exposed to UV radiation; and

b) a substrate;

B) to a source of electromagnetic radiation;

wherein the electromagnetic radiation impinges upon the composite thereby increasing the amount of electromagnetic radiation in the visible range.

Also disclosed are methods for enhancing the growth of one or more plants. In a manner like the method disclosed above, the composite can be a large sheet of plastic, transparent, translucent, or otherwise allowing the transmission of visible light, which is place over growing plants. One use is to provide a covering over plants that would get

reduced lighting due to the natural climate conditions or due to the reduced light due to seasonal lighting change.

In another aspect disclose herein is a method for detecting radiation, comprising:

A) exposing an article of manufacture, comprising:

a) a composite, comprising:

i) a first phosphor that emits visible light in the range of from about 520 nm to about 700 nm when exposed to UV radiation; and

ii) a second phosphor that emits visible light in the range of from about 400 to about 520 nm when exposed to UV radiation; and

b) a substrate;

B) to a source of radiation; and

C) detecting the increased amount of visible light present.

Radiation from a high energy source can be converted to radiation at longer wavelengths depending upon the selection and the concentration of phosphors. For example, the composite can have several layers of nanophophers that capture and re-emit the electromagnetic radiation to be captured again and re-emitted at an even longer wavelength. Embodiments can be used to capture and detect X-rays and gamma-ray emissions. In a further embodiment a plurality of composites can be spaced apart wherein each composite comprises different nanophosphors. In one example, a vacuum is created between the layers to facilitate transmission of the re-emitted radiation onto the next layer.

Further disclosed herein are methods for the preparation of delaminated graphitic-phase nitrogen carbon (g-C_3N_4), comprising:

(a) dispersing from about 2% to about 10% weight/volume of g-C_3N_4 into a nitric acid solution;

(b) heating the dispersion; and

(c) isolating the delaminated g-C_3N_4.

The amount of g-C_3N_4 utilized in step (a) can range from about 2% to about 10% w/v. The formulator, however, can utilize any amounts in this range, for example, 2%, 3%, 4%, 5%, 6%, 7%, 8%, 9% or 10%.

In addition, the dispersion can be heated to any temperature from about 80 °C to about 100 °C. The formulator, however, can utilize any temperature in this range, for

example, 80 °C, 81 °C, 82 °C, 83 °C, 84 °C, 85 °C, 86 °C, 87 °C, 88 °C, 89 °C, 90 °C, 91 °C, 92 °C, 93 °C, 94 °C, 94 °C, 96 °C, 97 °C, 98 °C, 99 °C, or 100 °C.

In addition, the formulator can use any concentration of nitric acid in step (a) about 30% to about 70% by weight. The formulator, however, can use any concentration in this range, for example, 30%, 31%, 32 m, 33%, 34%, 35%, 36%, 37%, 38%, 39%, 40%, 41%, 42 m, 43%, 44%, 45%, 46%, 47%, 48%, 49%, 50%, 51%, 52%, 53%, 54%, 55%, 56%, 57%, 58%, 59%, 60%, 61%, 62%, 63%, 64%, 65%, 66%, 67%, 68%, 69%, or 70%.

The delaminated g-C_3N_4 can be isolated by any means convenient to the formulator, for example, filtration, extraction, centrifugation and the like.

The present disclosure provides a description of the structure and use of non-limiting illustrative embodiments. Although certain embodiments have been described with a certain degree of particularity, or with reference to one or more individual embodiments, those skilled in the art could make numerous alterations to the disclosed embodiments without departing from the scope of this invention. As such, the various illustrative embodiments of the devices are not intended to be limited to the particular forms disclosed. Rather, they include all modifications and alternatives falling within the scope of the claims, and embodiments other than the one shown may include some or all of the features of the depicted embodiment. For example, components may be omitted or combined as a unitary structure, and/or connections may be substituted. Further, where appropriate, aspects of any of the examples described above may be combined with aspects of any of the other examples described to form further examples having comparable or different properties and addressing the same or different problems. Similarly, it will be understood that the benefits and advantages described above may relate to one embodiment or may relate to several embodiments.

References

The following references, to the extent that they provide exemplary procedural or other details supplementary to those set forth above, are specifically incorporated by reference.

[1] Zhu X-G, Long SP, Ort DR. Annu Revi Plant Biol 2010;61:235-261.

[2] Zhu X-G, Long SP, Ort DR. Current Opinion in Biotechnology 2008; 19:153-159.

[3] Peng SB, Tang Q, Zou Y. Plant Prod Sci 2009;12:3-8.

[4] Wiebe K, editor. The State of Food and Agriculture 2008. Biofuels: Prospects, Risks and Opportunities; 2008.

[5] J. Xu, Y. Li, S. Peng, G. Lu, S. Li, Phys. Chem. Chem. Phys. 2013, 15, 7657.

[6] J. Zhou, Y. Yang, C.Y. Zhang, Chem. Commun. 2013, 49, 8605.

[7] M. Groenewolt, M. Antonietti, Adv. Mater. 2005, 17, 1789.

[8] P Niu, G Liu, HM Cheng, J. Phys. Chem. C 2012, 116, 11013

[9] P Niu, L. L. Zhang, G. Liu, H. M. Cheng, Adv. Funct. Mater. 2012, 22, 476

[10] X. D. Zhang, X. X, H. Wang, J. J. Zhang, B. C. Pan, Y. Xie, J. Am. Chem. Soc. 2013, 135, 18.

[11] L. Ma, W. Chen, G. Schatte, W. Wang, A.G. Joly, Y. Huang, R. Sammynaiken, M. Hossu, J. Mat. Chem. C. 2014, 2, 4239.

[12] Y. Zhang, Q. Pan, G. Chai, M. Liang, G. Dong, Q. Zhang, J. Qiu, *Sci. Rep.* 2013, *3*,1943.

[13] E. Fred Schubert, J. K. Kim, Science 2005,308, 1274

[14] S. B. Kim, B. G. Kum, H. M. Jang, A. Lakshmanan, B. K. Kang, J. Lumin. 2011, 131, 1625.

[15] Y.L. Huang, Y. M. Yu, T. Tsebin, H. J. See, Opt. Express 2012, 20, 4360

[16] J. K. Kim, H. Luo, E. F. Schubert, J. Cho, C. Sone, Y. Park, Jon. J. Appl. Phys. 2005, 44, L649.

[17] S. E. Brinkley, N. Pfaff, K. A. Default, Z. J. Zhang, H. T. Hint Zen, R. Sephardi, S. Nakamura, S.P. Debars, Appl. Phys. Lett. 2011, 99, 241106.

WHAT IS CLAIMED IS:

1. A method for preparing delaminated graphitic-phase nitrogen carbon (g-C_3N_4), comprising:
   (a) dispersing from about 2% to about 10% weight/volume of g-C_3N_4 into a nitric acid solution;
   (b) heating the dispersion; and
   (c) isolating the delaminated g-C_3N_4.

2. The method according to Claim 1, wherein the nitric acid solution contains from about 30% to about 70% by weight nitric acid.

3. The method according to either Claim 1 or 2, wherein the dispersion is heated at temperature from about 80 °C to about 100 °C.

4. The method according to any one of Claims 1 to 3, wherein the g-C_3N_4 is isolated by centrifuging the dispersion after cooling to room temperature.

5. A composite, comprising:
   a) a visible light enhancing composition, comprising:
      i) a first phosphor that emits visible light in the range of from about 520 nm to about 700 nm when exposed to UV radiation; and
      ii) a second phosphor that emits visible light in the range of from about 400 to about 520 nm when exposed to UV radiation; and
   b) a substrate.

6. The composite according to Claim 5, wherein the composition comprises delaminated graphitic-phase nitrogen carbon (g-C_3N_4) and a phosphor chosen from copper-cysteamine (Cu-Cy), zinc sulfide (ZnS), silver-and manganese doped zinc sulfide (ZnS:Ag, Mn), or activated zinc sulfide (ZnS(Mn)).

7. The composite according to either Claim 5 or 6, wherein the composition comprises g-C_3N_4 and Cu-Cy.

8. The composite according to either Claim 5 or 6, wherein the composition comprises g-C_3N_4 and ZnS.

9. The composite according to either Claim 5 or 6, wherein the composition comprises g-C_3N_4 and ZnS:Ag, Mn.

10. The composite according to either Claim 5 or 6, wherein the composition comprises g-C_3N_4 and ZnS(Mn).

11. The composite according to any one of Claims 5 to 10, wherein at least one phosphor is a nanophosphor.

12. The composite according to any one of Claims 5 to 11, wherein at both phosphors are a nanophosphore.

13. The composite according to any one of Claims 5 to 12, wherein the substrate is a polymer.

14. The composite according to any one of Claims 5 to 13, wherein the substrate is a polymer chosen from polystyrene, polyethylene, polyester, polyvinyl chloride, polystyrene, or poly(methyl methacrylate).

15. The composite according to any one of Claims 5 to14, wherein the substrate is transparent.

16. The composite according to any one of Claims 5 to14, wherein the substrate is semi-transparent.

17. The composite according to any one of Claims 5 to14, wherein the substrate has a first transparent surface and a second semi-transparent surface.

18. The composite according to any one of Claims 5 to 17, wherein the substrate is in the form of a film.

19. The composite according to any one of Claims 5 to 17, wherein the substrate is in the form of a geometric shape.

20. A method for providing solid state lighting having enhanced visible light, comprising;

A) exposing a composite, comprising:

a) a visible light enhancing composition, comprising:

i) a first phosphor that emits visible light in the range of from about 520 nm to about 700 nm when exposed to UV radiation; and

ii) a second phosphor that emits visible light in the range of from about 400 to about 520 nm when exposed to UV radiation; and

b) a substrate;

B) to a source of electromagnetic radiation;

wherein the electromagnetic radiation impinges upon the composite thereby increasing the amount of electromagnetic radiation in the visible range.

21. The method according to Claim 20 wherein the composite is a transparent opening in a structure.

22. The method according to either Claim 20 or 22, wherein the transparent opening comprises a polymeric material.

23. The method according to either Claim 20 or 22, wherein the transparent opening comprises glass.

24. A method for enhancing the growth rate of one or more plants, comprising covering the plant with:

A) exposing an article of manufacture, comprising:

a) a composite, comprising:

i) a first phosphor that emits visible light in the range of from about 520 nm to about 700 nm when exposed to UV radiation; and

ii) a second phosphor that emits visible light in the range of from about 400 to about 520 nm when exposed to UV radiation; and

b) a substrate;

B) to a source of electromagnetic radiation;

wherein the electromagnetic radiation impinges upon the article of manufacture wherein the composite increases the amount of electromagnetic radiation emitted in the visible range and thereby provides for increased growth rate to the one or more plants.

25. The method according to Claim 24, wherein the article of manufacture is a polymeric sheet.

26. The method according to Claim 24, wherein the one or more plants is a field of crops.

27. A method for detecting radiation, comprising:

A) exposing an article of manufacture, comprising:

a) a composite, comprising:

i) a first phosphor that emits visible light in the range of from about 520 nm to about 700 nm when exposed to UV radiation; and

ii) a second phosphor that emits visible light in the range of from about 400 to about 520 nm when exposed to UV radiation; and

b) a substrate;

B) to a source of radiation; and

C) detecting the increased amount of visible light present.

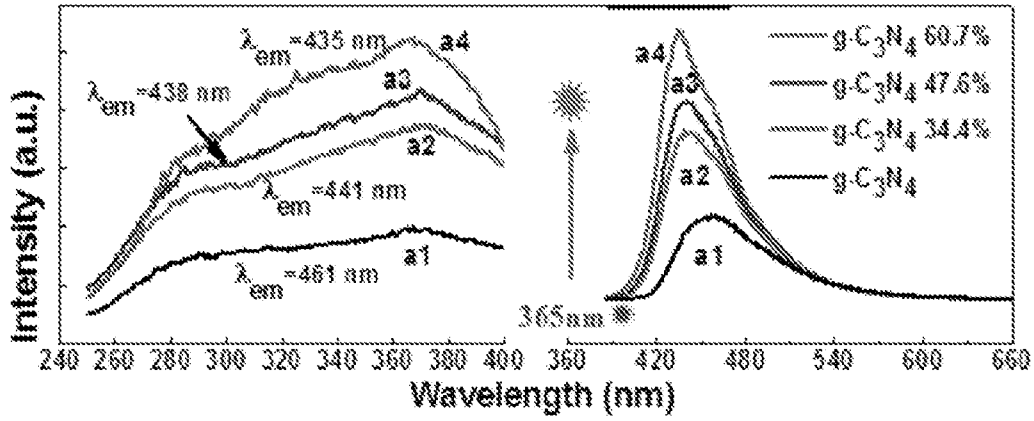
Intensity (a.u.)
λem=435 nm
λem=438 nm
λem=441 nm
λem=461 nm
a4
a3
a2
a1
365nm
g-C3N4 60.7%
g-C3N4 47.6%
g-C3N4 34.4%
g-C3N4
240 260 280 300 320 340 360 380 400
360 420 480 540 600 660
Wavelength (nm)

FIG. 1A

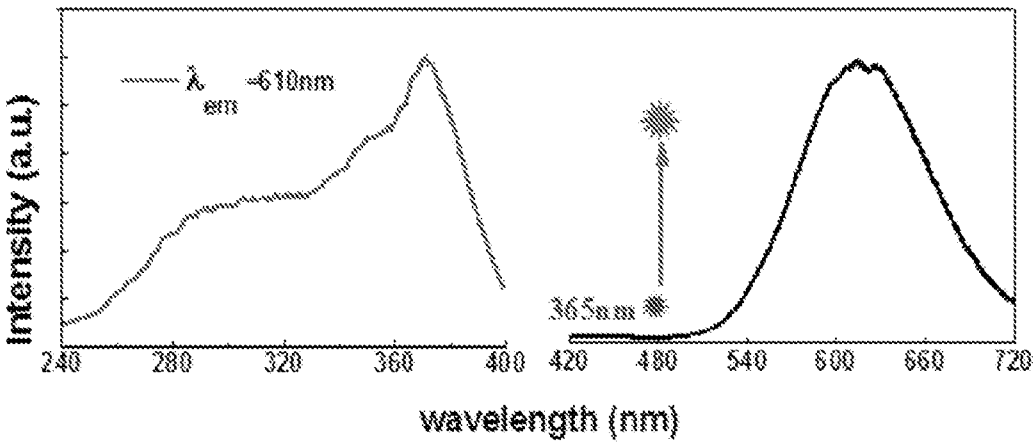
Intensity (a.u.)
λem=610nm
365nm
240 280 320 360 400
420 480 540 600 660 720
wavelength (nm)

FIG. 1B

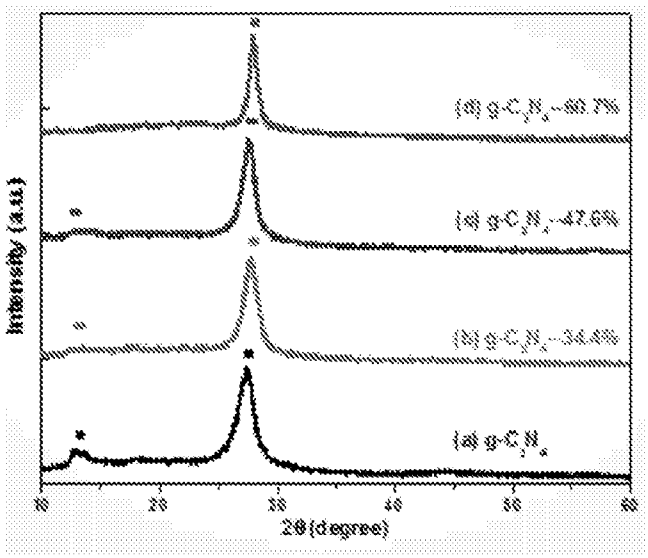

FIG. 2

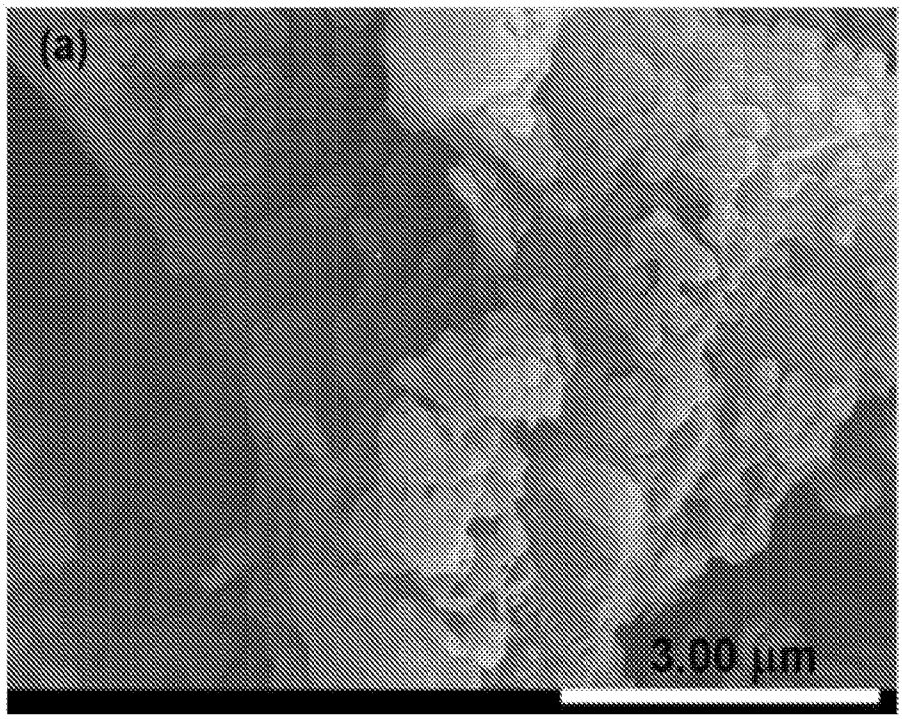

FIG. 3A

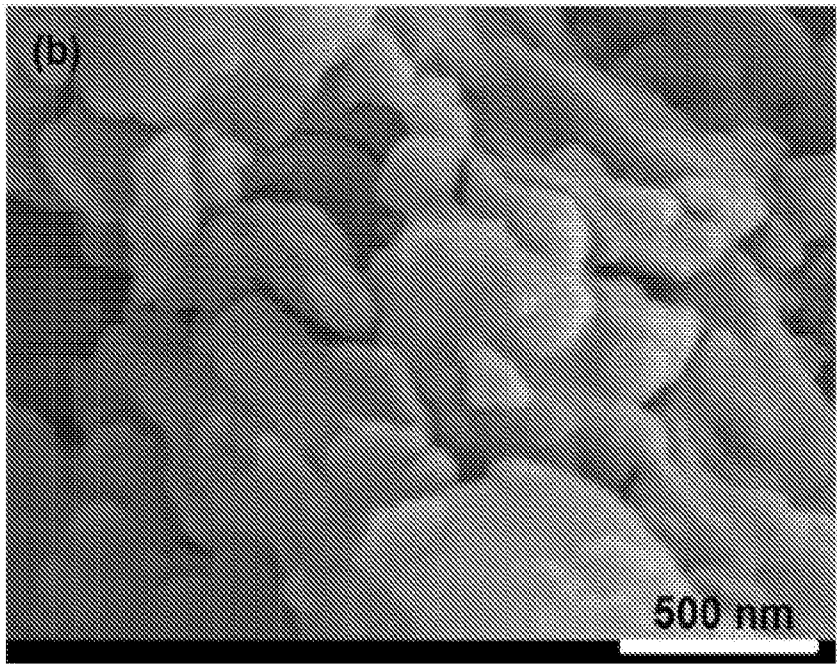

FIG. 3B

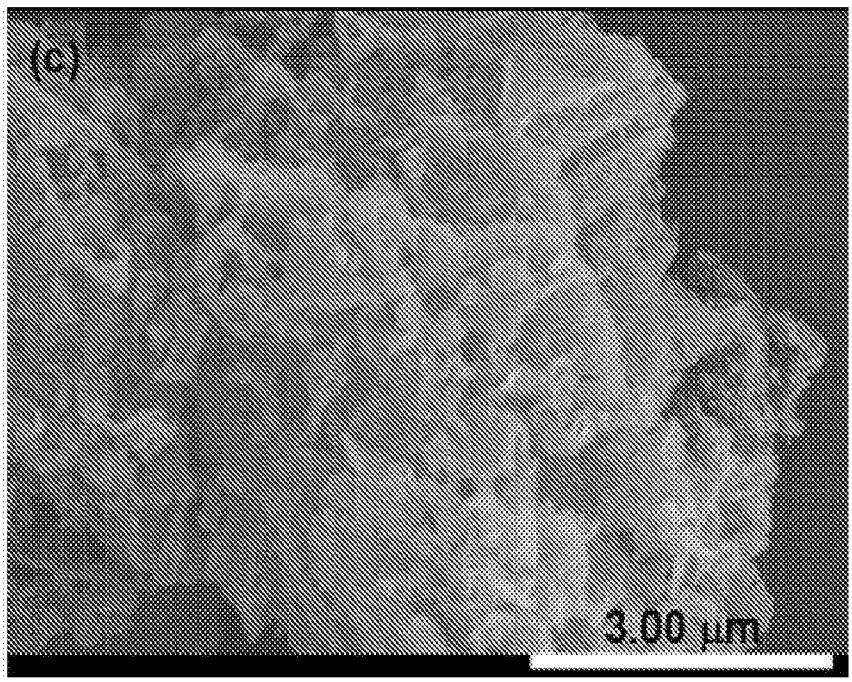

FIG. 3C

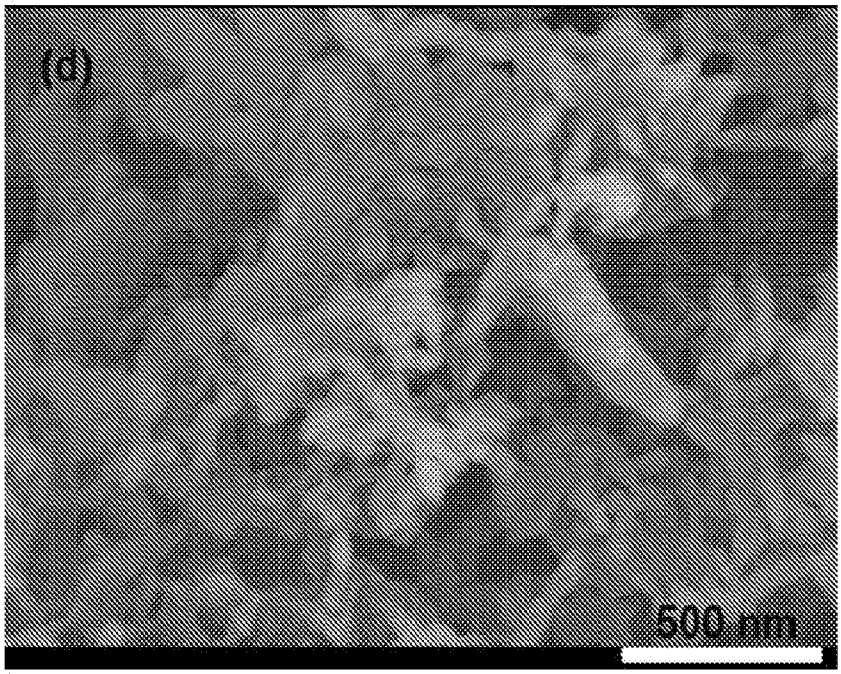

FIG. 3D

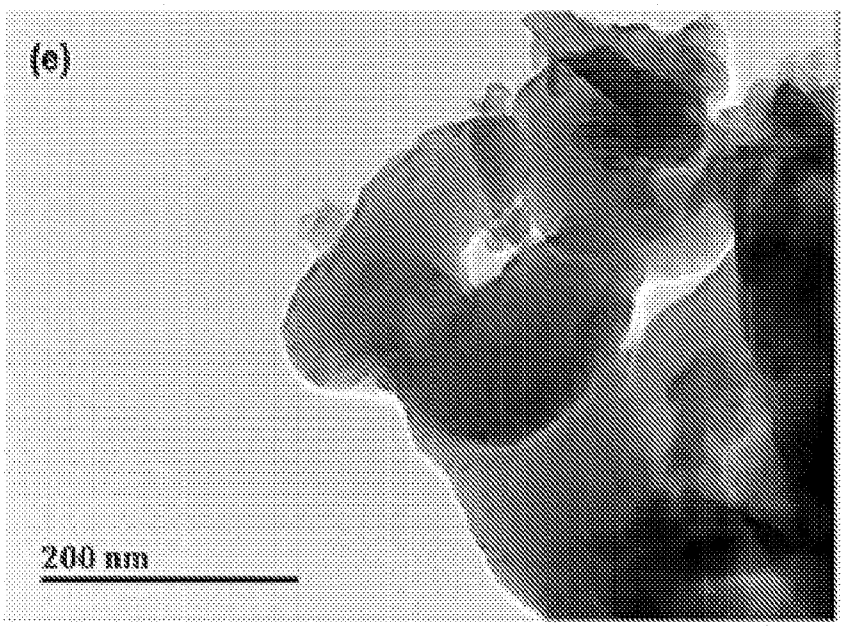

FIG. 3E

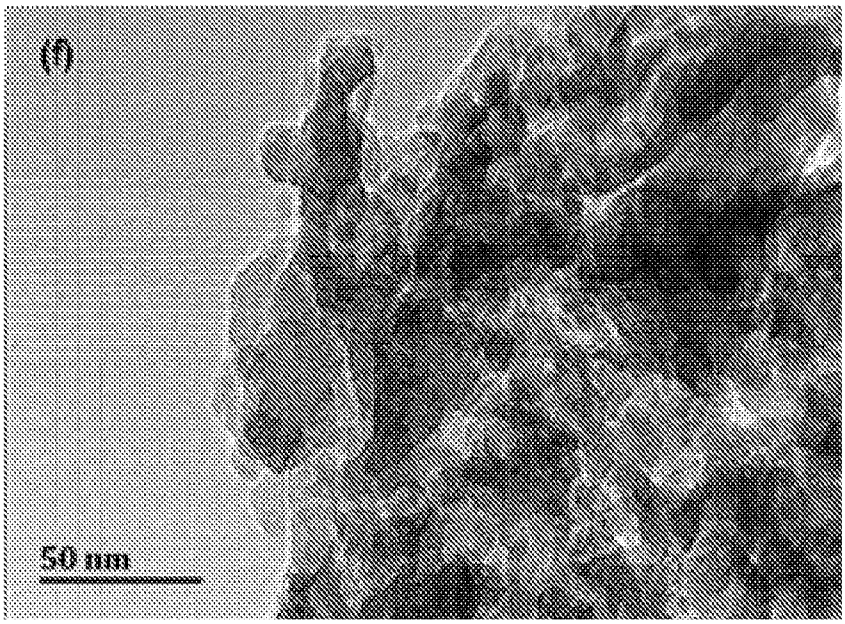

FIG. 3F

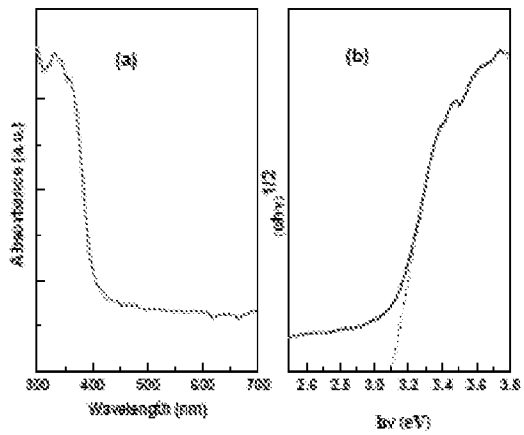

FIG. 4A FIG. 4B

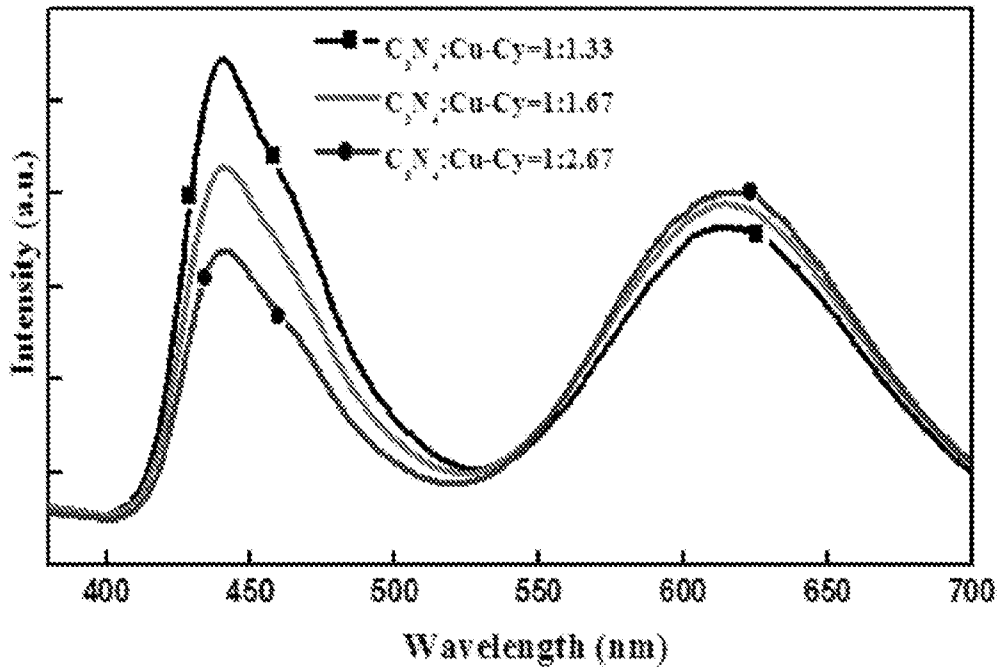
C3N4:Cu-Cy=1:1.33
C3N4:Cu-Cy=1:1.67
C3N4:Cu-Cy=1:2.67
Intensity (a.u.)
400
450
500
550
600
650
700
Wavelength (nm)

FIG. 5

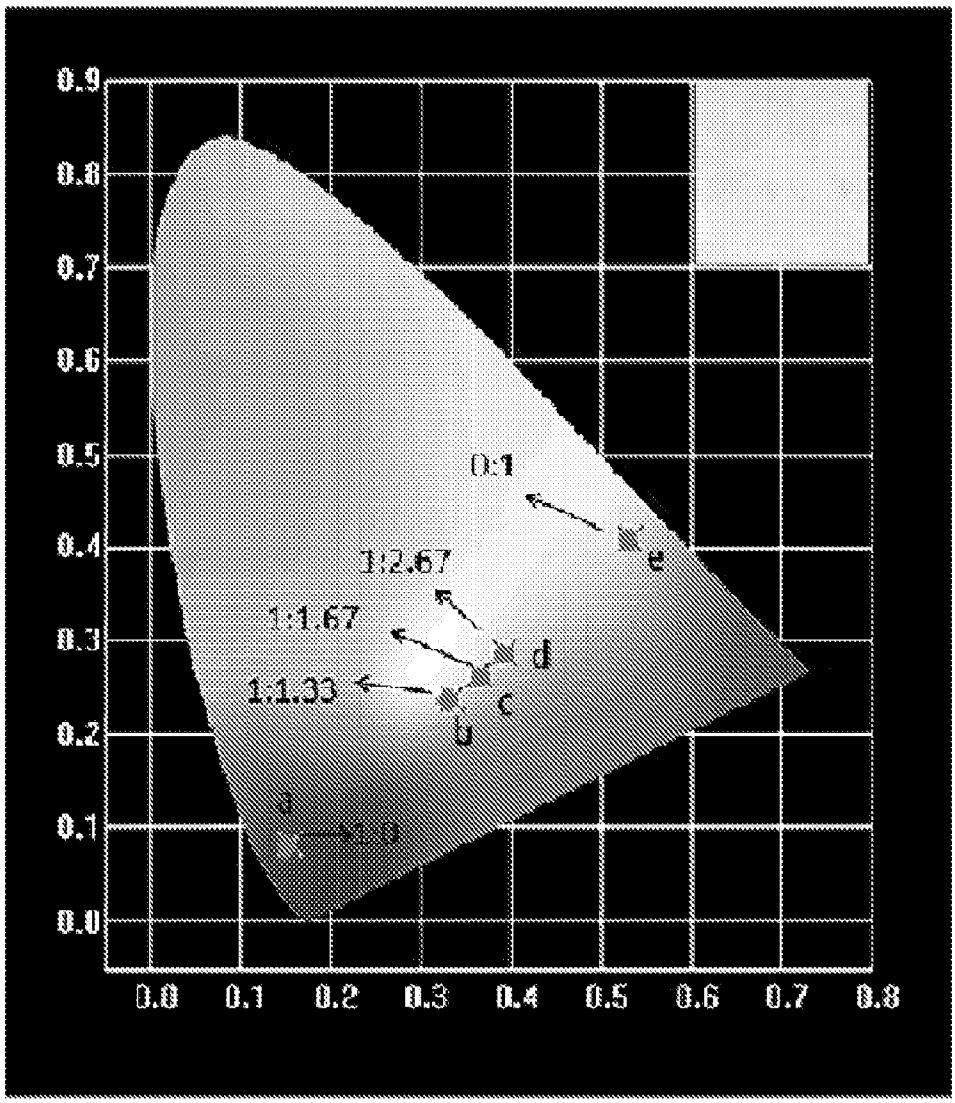
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0.0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8
0:1
1:2.67
1:1.67
1:1.33
e
d
c
b

FIG. 6

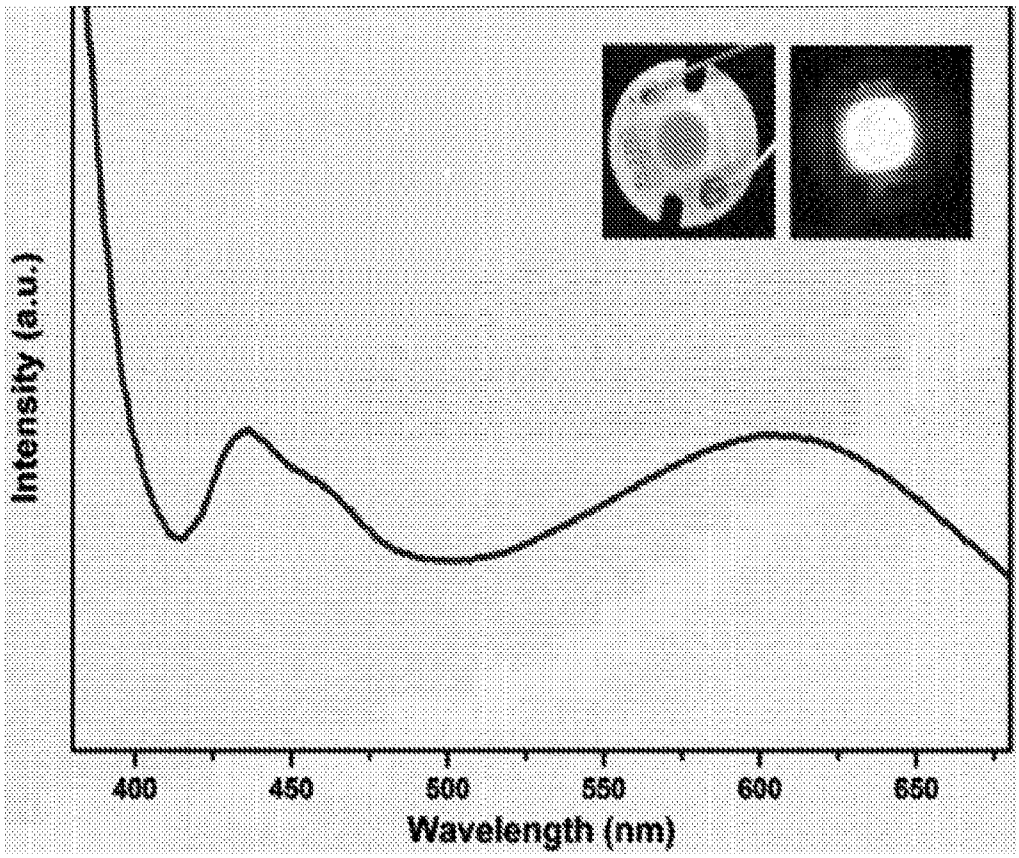

FIG. 7

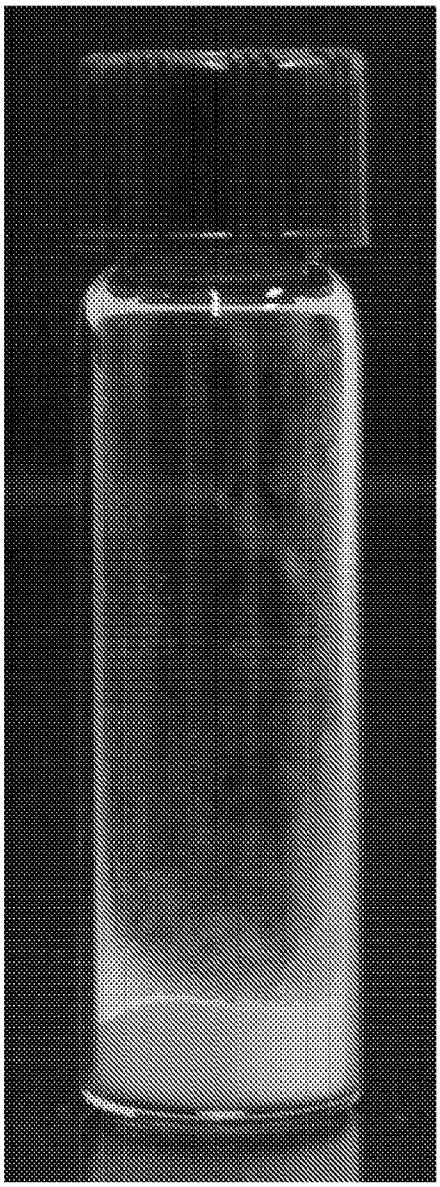

FIG. 8A

FIG. 8B

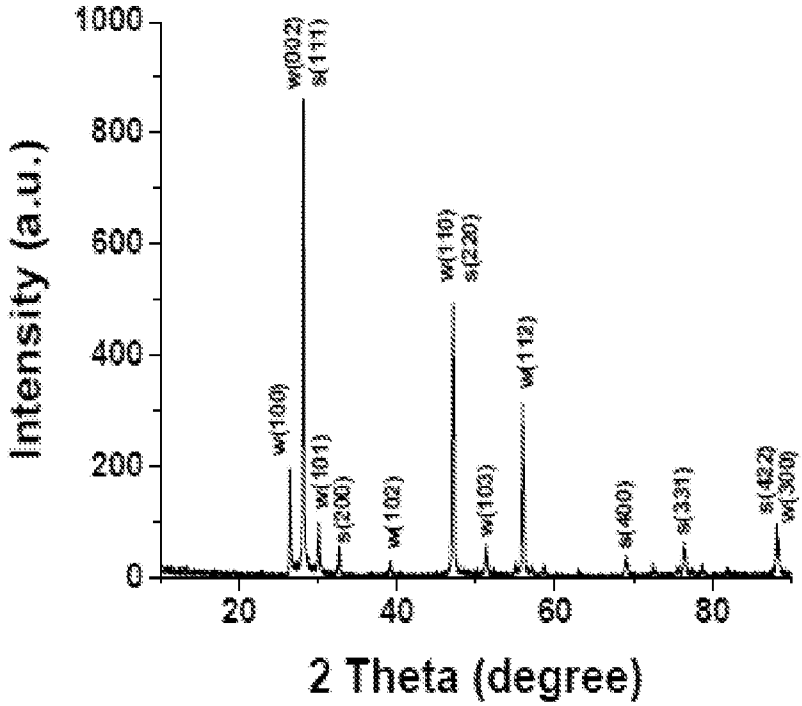
Intensity (a.u.)
2 Theta (degree)
1000
800
600
400
200
0
20
40
60
80
w(002)
s(111)
w(100)
w(101)
s(200)
w(102)
w(110)
s(220)
w(103)
w(112)
s(400)
s(331)
s(422)
w(300)

FIG. 9

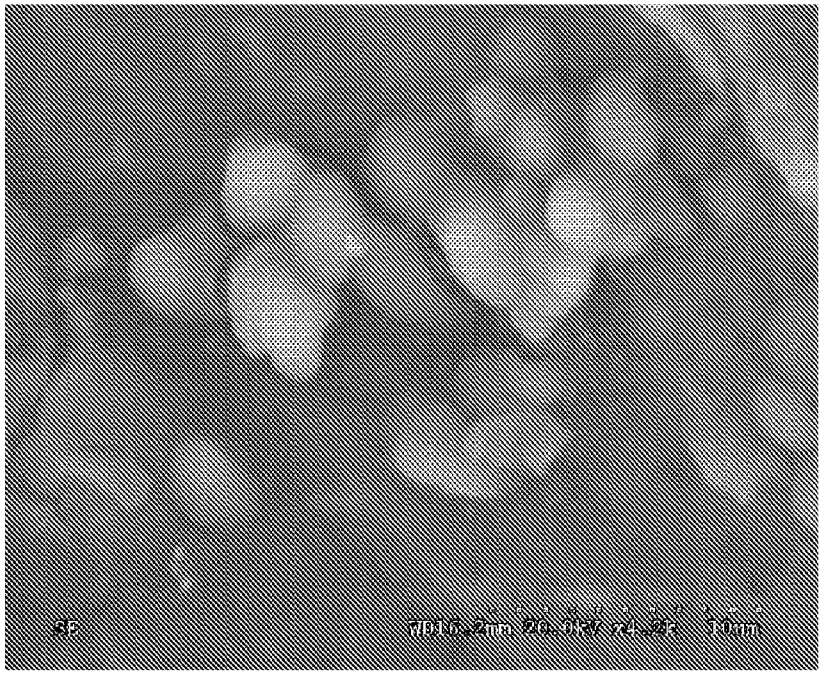

FIG. 10A

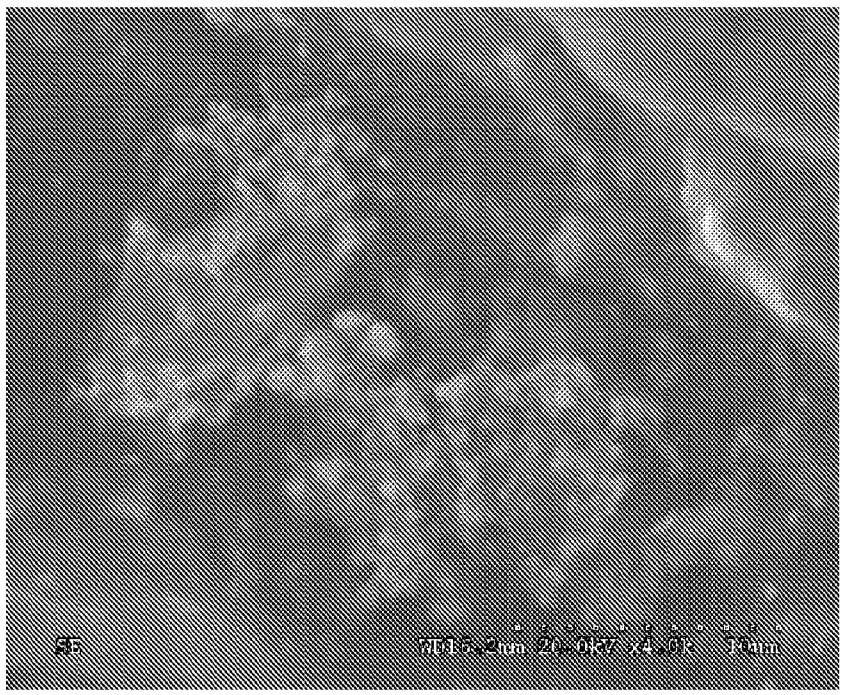

FIG. 10B

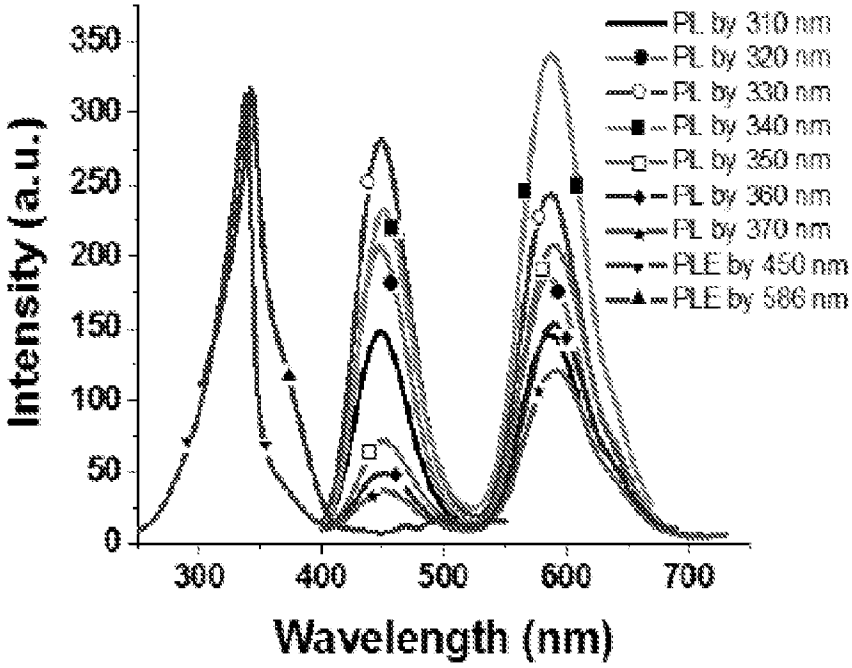
Intensity (a.u.)
Wavelength (nm)
PL by 310 nm
PL by 320 nm
PL by 330 nm
PL by 340 nm
PL by 350 nm
PL by 360 nm
PL by 370 nm
PLE by 450 nm
PLE by 586 nm
0
50
100
150
200
250
300
350
300
400
500
600
700

FIG. 11

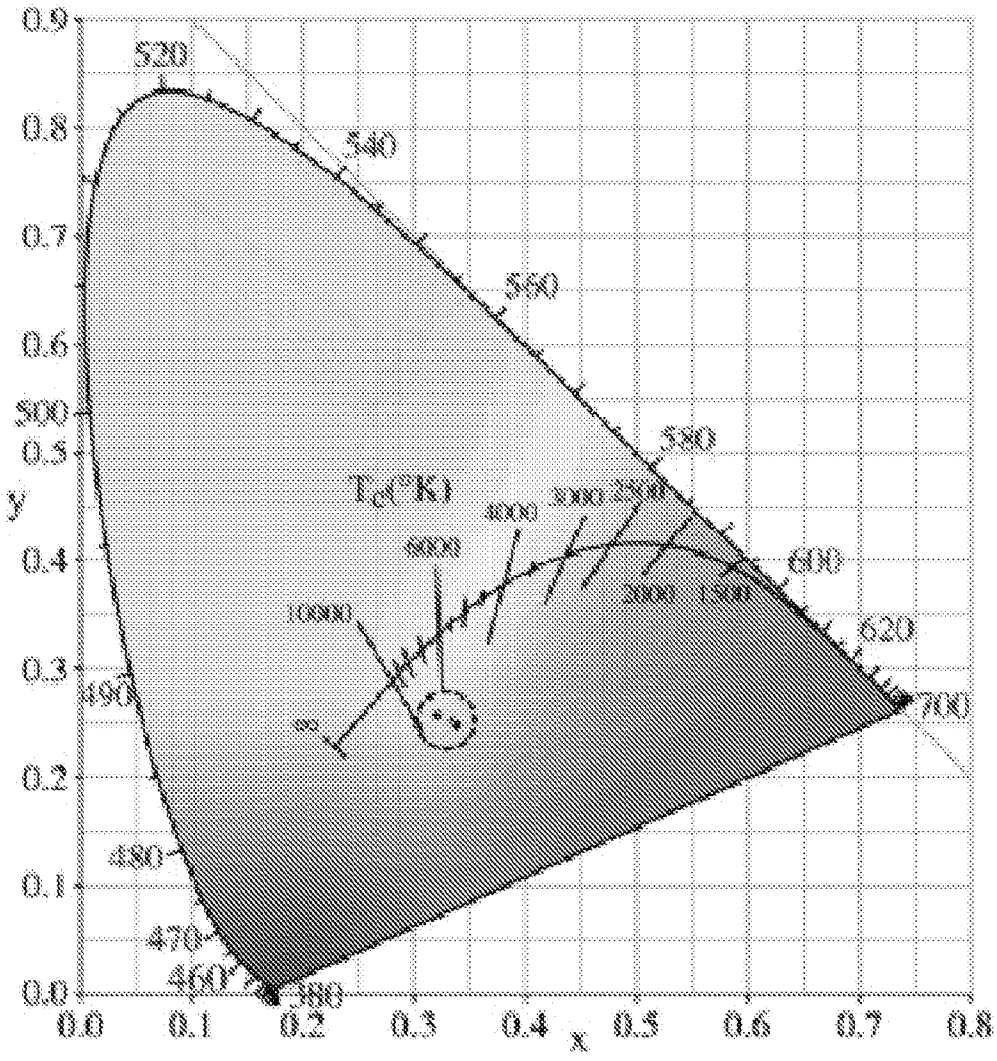
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
y
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
x
520
540
560
580
600
620
700
500
490
480
470
460
380
T_c(°K)
4000
3000
2500
2000
1500
10000
9000
∞

FIG. 12

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US17/13210

A. CLASSIFICATION OF SUBJECT MATTER

IPC - B01D 53/86; B01J 37/08; C01B 31/04; B82Y 30/00, 40/00 (2017.01)
CPC - B01D 53/8687; B01J 37/08, 35/004; C01B 31/04; B82Y 30/00

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)
See Search History document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
See Search History document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	CN 103848405 A (NORTHWESTERN UNIVERSITY) June 11, 2014; see machine translation, entire document	1-3
Y	Ma, T et al. "Proton-Functionalized Two-Dimensional Graphitic Carbon Nitride Nanosheet: An Excellent Metal-/Label-Free Biosensing Platform"; Small, Vol. 10, No. 12; Publication [online]. 1 June 2014 [retrieved 24 April 2017]. Retrieved from the Internet: <URL: http://onlinelibrary.wiley.com/doi/10.1002/smll.201303827/full>; pp 2382-2389	1-3
Y	Chen, F et al."The amphoteric properties of g-C3N4 nanosheets and fabrication of their relevant heterostructure photocatalysts by an electrostatic re-assembly route"; Chemical Communications, Vol. 51, No. 33; Publication [online]. 09 April 2015 [retrieved 24 April 2017]. Retrieved from the Internet: <URL: http://pubs.rsc.org/is/content/articlelanding/2015/cc/c5cc01035g#!divAbstract>; pp 7176-7179.	1-3
Y	CN 104888832 A (WUHAN UNIVERSITY OF TECHNOLOGY) September 09, 2015; see machine translation, entire document	1-3

☐ 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
25 April 2017 (25.04.2017)	22 MAY 2017
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 Shane Thomas PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

Form PCT/ISA/210 (second sheet) (January 2015)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US17/13210

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 4 & 11-19
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:
Group I: Claims 1-3; Group II: Claims 5-10 & 20-27

-Continued from extra sheet.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-3

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

-Continued from Box III:

Claim 22 is objected to under PCT Rule 66.2(a)(v) as lacking clarity under PCT Article 6 because claim 2 is indefinite for the following reason: Claim 22 depends on itself which is indefinite. Claim 22 has been interpreted to depend on either claim 20 or claim 21 instead of claim 20 or 22 based on the applicant's specification.

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fee must be paid.

Group I: Claims 1-3 appear to be directed towards dispersing from about 2% to about 10% weight/volume of g-C3N4 into a nitric acid solution.

Group II: Claims 5-10 & 20-27 appear to be directed towards a first phosphor that emits visible light in the range of from about 520 nm to about 700 nm when exposed to UV radiation.

The inventions listed as Groups I & II do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features.

The special technical features of Group I appear to be at least A method for preparing delaminated graphitic-phase nitrogen carbon (g-C3N4), compnsmg: (a) dispersing from about 2% to about 10% weight/volume of g-C3N4 into a nitric acid solution; (b) heating the dispersion; and (c) isolating the delaminated g-C3N4, which are not present in Group II.

The special technical features of Group II appear to be at least a method for providing solid state lighting having enhanced visible light, compnsmg; A) exposing a composite, comprising: a) a visible light enhancing composition, comprising: i) a first phosphor that emits visible light in the range of from about 520 nm to about 700 nm when exposed to UV radiation; and ii) a second phosphor that emits visible light in the range of from about 400 to about 520 nm when exposed to UV radiation; and b) a substrate; B) to a source of electromagnetic radiation; detecting the increased amount of visible light present, wherein the electromagnetic radiation impinges upon the composite thereby increasing the amount of electromagnetic radiation in the visible range, which are not present in Group I.

There are no common features between Groups I & II and so Groups I & II lack unity.