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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
28 December 2017 (28.12.2017)

WIPO | PCT

(10) International Publication Number
WO 2017/219722 A1

(51) International Patent Classification:
H01L 21/44 (2006.01)

(21) International Application Number: PCT/CN2017/077451

(22) International Filing Date: 21 March 2017 (21.03.2017)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
15/188,181 21 June 2016 (21.06.2016) US

(71) Applicant: CITY UNIVERSITY OF HONG KONG [CN/CN]; 83 Tat Chee Avenue, Kowloon, Hong Kong (CN).

(72) Inventors: WANG, Aiwu; c/o Department of Physics and Materials Science, City University of Hong Kong, 83 Tat Chee Avenue, Kowloon, Hong Kong (CN). **LI, Yang Yang**; c/o Department of Physics and Materials Science, City University of Hong Kong, 83 Tat Chee Avenue, Kowloon, Hong Kong (CN). **LU, Jian**; c/o Department of Mechanical and Biomedical Engineering, City University of Hong Kong, 83 Tat Chee Avenue, Kowloon, Hong Kong (CN).

(74) Agent: RUNPING & PARTNERS; Suite 515,Yingu Mansion, No. 9 Beisihuanxilu, Haidian District, Beijing 100190 (CN).

(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,

(54) Title: A MATERIAL FOR AN ELECTRONIC DEVICE

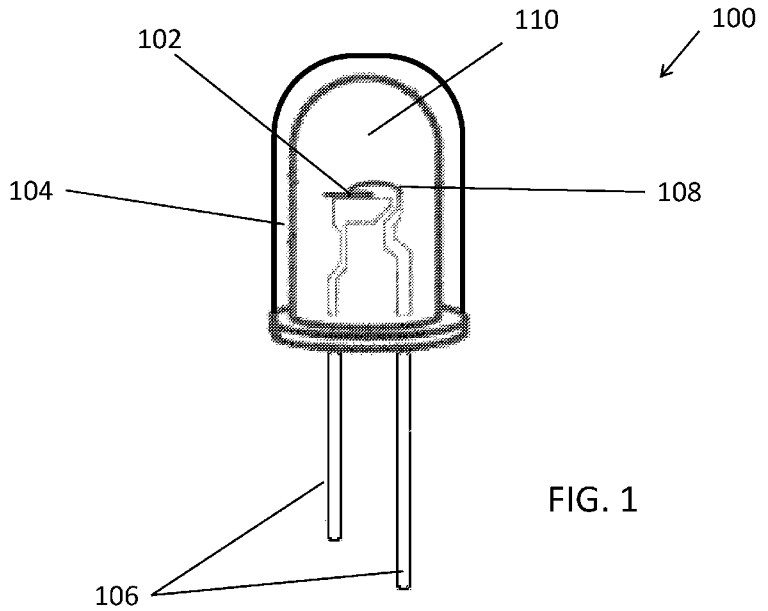


FIG. 1

(57) Abstract: A material for an electronic device includes a substance arranged to emit light in a predetermined range of wavelength upon receiving an excitation energy, wherein the substance includes a plurality of carbon nitride particles and a siloxane material. A method of producing the material and a light emitting device including the material are also described.

[Continued on next page]

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))*

A MATERIAL FOR AN ELECTRONIC DEVICE

TECHNICAL FIELD

The present invention relates to a material for an electronic device and a method for fabricating the material, although not exclusively, to a bio-compatible material for a light emitting device.

BACKGROUND

Electronic or electrical lighting devices such as light emitting diodes may be used in various applications. According to different applications, lighting devices with different colors may be used.

Some light emitting diodes may emit white light which may be used for illumination purposes. For example, a lighting device including multiple white LEDs may be used as illumination sources in premises which facilitate human activities. In some other examples, light sources in white color may be also required in other applications or appliances such as microscopic imaging, endoscopes, video capturing in low light condition, etc.

SUMMARY OF THE INVENTION

In accordance with a first aspect of the present invention, there is provided a material for an electronic device, comprising: a substance arranged to emit light in a predetermined range of wavelength upon receiving an excitation energy, wherein the substance includes a plurality of carbon nitride particles and a siloxane material.

In an embodiment of the first aspect, the predetermined range of wavelength includes a range of wavelength visible to human eye.

In an embodiment of the first aspect, the light emitted by the substance is in white color visible to human eye.

In an embodiment of the first aspect, the excitation energy includes a photon excitation.

In an embodiment of the first aspect, the excitation energy includes ultra-violet light.

In an embodiment of the first aspect, the photon excitation has a range of excitation wavelength of 345 nm to 365 nm.

In an embodiment of the first aspect, the photon excitation is at least partially absorbed by the plurality of carbon nitride particles and/or the siloxane material.

In an embodiment of the first aspect, the plurality of carbon nitride particles includes C3N4 particles.

In an embodiment of the first aspect, each of the plurality of carbon nitride particles is of a size in a range of 1 nm to 1000 nm.

In an embodiment of the first aspect, the siloxane material includes N-(β-aminoethyl)-g-aminopropylmethyldimethoxysilane.

In an embodiment of the first aspect, the each of the carbon nitride particles and the siloxane material is arranged to at least partially contribute the light emitted by the substance.

In an embodiment of the first aspect, the plurality of carbon nitride particles is arranged to contribute a first emission spectrum of blue color within the predetermined range of wavelength of the light emitted by the substance.

In an embodiment of the first aspect, the siloxane material is arranged to contribute a second emission spectrum within the predetermined range of wavelength of the light emitted by the substance such that the light emitted by the substance is in white color visible to human eye.

In an embodiment of the first aspect, at least one of the plurality of carbon nitride particles is functionalized by the siloxane material.

In an embodiment of the first aspect, the substance is a solid.

In an embodiment of the first aspect, the substance is flexible.

In an embodiment of the first aspect, the substance is adhesive.

In an embodiment of the first aspect, the substance is bio-compatible.

In an embodiment of the first aspect, the electronic device is a light-emitting device or a sensor.

In an embodiment of the first aspect, the plurality of carbon nitride particles is further arrange to operate as a photocatalyst.

In an embodiment of the first aspect, the photocatalyst is arranged to degrade an organic substance when upon the substance receives the excitation energy.

In accordance with a second aspect of the present invention, there is provided a method of producing a material for an electronic device, comprising the steps of: synthesizing a plurality of carbon nitride particles; and mixing a siloxane material to the plurality of carbon nitride particles to form a substance; and wherein the substance is arranged to emit light in a predetermined range of wavelength upon receiving an excitation energy.

In an embodiment of the second aspect, the step of synthesizing the plurality of carbon nitride particles comprises the step of mixing citric acid with thiourea to form a precursor of the plurality of carbon nitride particles.

In an embodiment of the second aspect, the method further comprises the step of heating the precursor at 120 °C to 300 °C.

In an embodiment of the second aspect, the method further comprises the step of filtering out the plurality of carbon nitride particles from the precursor.

In an embodiment of the second aspect, the method further comprising the step of heating the substance at 120 °C to 300 °C.

In an embodiment of the second aspect, the method further comprises the step of solidifying the substance to form a thin film.

In accordance with a third aspect of the present invention, there is provided a light emitting device, comprising a light emitting element arranged to emit an excitation energy; and a material having a substance arranged to emit light in a predetermined range of wavelength upon receiving the excitation energy, wherein the substance includes a plurality of carbon nitride particles and a siloxane material.

In an embodiment of the third aspect, the light emitting element includes a light emitting diode.

In an embodiment of the third aspect, the substance is a thin film at least partially covering the light emitting element.

BRIEF DESCRIPTION OF THE DRAWINGS

Embodiments of the present invention will now be described, by way of example, with reference to the accompanying drawings in which:

Figure 1 is a perspective view of a light emitting device in accordance with one embodiment of the present invention;

Figure 2 is a schematic drawing of an AEATMS-capped C_3N_4 particle with multiaminosilane-functionalized surface in the substance of material of the light emitting device of Figure 1;

Figure 3A is a plot showing a photoluminance spectrum of pure C_3N_4 material being excited at 365 nm, 430 nm, 480 nm and 580 nm respectively, and the AEATMS material being excited at 365 nm;

Figure 3B is plot showing a photoluminance spectrum of the substance of material of the light emitting device of Figure 1 excited at 365 nm;

Figure 4 is a CIE-1931 chromaticity diagram showing the position of the exemplary emission from substance of material of the light emitting device of Figure 1 excited at 365 nm;

Figure 5 is a plot showing Fourier transform infrared (FTIR) spectra of AEATMS, the C_3N_4 silica gel (Si-g-CNDs) and the C_3N_4 particles (g-CNDs);

Figure 6 is a plot showing a comparison between the photoluminescence responses of the substance of material of the light emitting device of Figure 1 under excitation of light in 360 nm and 440 nm;

Figures 7A to 7D are plots respectively showing (a) Full , (b) C 1s, (c) N 1s and (d) Si 2p spectra in an XPS characterization of g-C_3N_4-silica-gels;

Figures 8A to 8B are plots respectively showing (a) Si 2p and (b) S 2p spectra in an XPS characterization of g-C_3N_4-silica-gels;

Figures 9A and 9B are plots respectively showing DLS particle size distributions of the g-C_3N_4 nanoparticles after and before dialysis;

Figure 10 is a TEM image of the as-synthesized g-C_3N_4 nanoparticles;

Figure 11 is a photographic image showing a thin film of the material for an electronic device in accordance with an embodiment of the present invention;

Figure 12 is a photographic image illustrating a flexibility of the thin film of the material in Figure 11;

Figure 13 is a photographic image showing a light emitting device in accordance with an embodiment of the present invention, wherein the light emitting device is attached to a fabric material;

Figure 14 is a photographic image showing the light emitting device of Figure 13 wherein the light emitting device is lighted up;

Figures 15A to 15D are photographic images of a blue LED (a) without the silica gel coated and is off, (b) without the silica gel coated and is on, (c) with the silica gel coated and is off, and with the silica gel coated and is on respectively;

Figure 15E is a photographic image of a calligraphy written using the freshly prepared g-C_3N_4-silica-gels as ink on a piece of filter paper;

Figure 15F and 15G are photographic images of the calligraphy of Figure 15E when illuminated with a hand-held UV lamp (365 nm) and after dipped in water for five times, respectively;

Figures 16A to 16B are photographic images of a calligraphy written using the freshly prepared g-C_3N_4-silica-gel (letter “A”) and pure g-C_3N_4 nanodots (letter “P”) as ink on a piece of filter paper;

Figures 16C is a photographic image of a thin film of partially aged g-C3N4-silica-gels (aged for 40 min); and

Figure 16D is a photographic image of a comparison of g-C_3N_4-silica-gels of the left and g-C_3N_4 nanodots on the right.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

The inventors have, through their own research, trials and experiments, devised that white LED coatings for use in blue or ultra-violet LEDs may be made by mixing fluorescent powders (such as phosphor) with a polymer matrix. The coatings may include heavy metals and toxic organic species. Some of the conventional white LED techniques may suffer from low-efficiency, high toxicity and pollution, imposes potential risks to the health of manufacturing workers (e.g., possible airway inhalation of toxins), and its development is largely limited by the low abundance of the raw materials. Furthermore, due to the toxicity of these components, disposal of the used conventional LED products is not environmental-friendly.

White light-emitting diodes (WLEDs) have advantages over conventional lighting devices such as long lifetime, low power consumption, fast response, and high luminous efficiency. As one example, WLED materials may be based on a In-GaN blue-emitting chip mixed with Ce^{3+}:$Y_3Al_5O_{12}$ (Ce:YAG) yellow phosphor dispersed in epoxy resin or silicone. Alternatively, transition metal ion-doped semiconductor quantum dots include optical properties suitable for WLED applications. However, these WLED materials generally contain hazardous substances such as CdTe, CdSe, CuInS, PbS and CdS, raising toxicity and pollution concerns.

In some alternative examples, WLED materials may be based on carbon species by combining several carbon-based light-emitting materials of different emission wavelength. For example, LED materials may be synthesized by combining carbon and zinc copper indium sulfide quantum dots, or by blending silica/carbon dots (blue emission) with CdS nanocrystals (yellow emission). Alternatively, transparent polysiloxane-functionalized carbon dots (yellow emission) may be coated on the GaN bulb (blue emitting) to enable white light emission. However, some of these mixing strategies may be complex and time-consumable. Furthermore, some of these carbon-based WLED materials may contain toxic metal components.

With reference to Figure 1, there is shown an embodiment of a light emitting device 100, comprising a light emitting device 102 arranged to emit an excitation energy; and a material 104 having a substance arranged to emit light in a predetermined range of wavelength upon receiving the excitation energy, wherein the substance includes a plurality of carbon nitride particles and a siloxane material.

In this embodiment, the light emitting device 100 is an electronic device, such as light emitting diode (LED) comprising a conventional LED structures such as the anode and cathode electrodes 106, a light emitting device 102 such as an LED chip, internal wiring 108 arranged to connects the LED chip 102 to the electrodes 106 and an encapsulation 110 arranged to encapsulate the LED chip 102, the internal wiring and at least a portion of the electrodes 106 and to fix their positions. During normal operation, electrical voltage bias may be applied to the light emitting device 100 to power up the light emitting device 102 via the electrodes 106 and the wiring provided, the light emitting device 102 emits an excitation energy such as photons or an electromagnetic radiation, which may be observed by a human eye as light if the wavelength of the emitting energy is within a range visible to a human eye.

Alternatively, the light emitting device 102 may include other types of light sources, such as but not limited to a LASER diode, a light filament, a fluorescent tube, etc.

The light emitting device 100 further comprises a material or coating 104 having a substance for converting the electromagnetic radiation to light. The emitted light may include one or more electromagnetic wave at different wavelengths, such that the light emitted by the material 104 or the substance appears to be in different color to a human eye.

For example, the material 104 or the included substance may absorb all of the excitation energy in form of a photon excitation having a range of excitation wavelength of 345 to 365 nm generated by the LED chip 102, which corresponds to ultra-violet light in the electromagnetic wave spectrum, and then emit light covering at least a range of wavelengths in the spectrum visible to human eyes (typically 400 – 700 nm) and appearing to be in white color visible to an human eye.

Alternatively, the emitted light may appear to be in different color which includes at least one of the red, blue and green components in different intensities. Alternatively, the emitted light may be invisible to a human eye.

Preferably, the substance may be provided in a thin film 104 partially or entirely covering the light emitting device 102 or travelling paths of the excitation energy generated by the light emitting device 102. The thin film 104 may be of different thickness or coverage based on different requirements. For example, a thicker film 104 including more of the material or the substance to covert more photon excitations to light in the desire spectrum within the predetermined range of wavelength of light emitted by the substance. Alternatively, a thinner film of material 104 may be included to allow certain amount of the photon excitations generated by the light emitting device 102 to pass through and escape to the external environment, thus a part of the generated photon excitations also contribute the light emitted by the electronic device 100. Alternatively, at least a part of the light emitting device

100 is not covered by the thin film 104 so as to allow the transmission of the generated photon excitations to external environment.

During the conversion, the substance in the thin film 104 may be excited by the excitation energy (such as photon energy) and is in an excited state, subsequently, the substance then emit an output energy matching one or more energy band gaps of the substance and return back to a metastable state. The output energy may be in a form of a photon or an electromagnetic wave having a wavelength according to the energy band gap of the material 104 or the substance. Therefore, when the substance is excited continuously, continuous wave of electromagnetic energy is emitted by the substance.

Preferably, the substance includes carbon nitride particles and a siloxane material that may be used to absorb photons and emit lights or radiations with different wavelengths, and the combination of the carbon nitride particles and the siloxane material may form a silica gel which may be coated on a surface of a structure.

With reference to the example structure as shown in Figure 2, the carbon nitrides particles may include C_3N_4 particles for converting at least part of the excitation energy generated by the light emitting device 102 to a part or all of the light output of the electronic device 100. Preferably, such output may include a first emission spectrum of blue color within the predetermined range of wavelength of the light emitted by the substance.

In addition, the substance further includes a siloxane material such as N-(β-aminoethyl)-g-aminopropylmethyldimethoxysilane (AEATMS). The siloxane material may functionalize the carbon nitride particles, and may also absorb excitation energy and emit light which may be in different wavelengths compared to that of the excitation energy. For example, the siloxane material may contribute a second emission spectrum (which may include color of green and red) within the predetermined range of wavelength of the light emitted, such that the light emitted by the substance is in white color visible to human eye when the light includes the red and green light contributed by the siloxane material and the blue light contributed by the carbon nitride particles.

With reference to Figures 3A and 3B, there is shown a measurement result of an operation of the electronic device 100 or the light emitting device in accordance with the embodiments of the present invention. In this example, the material 104 or the substance is illumination by a UV-LED chip (365 nm excitation). The light emitted by the substance includes four peaks (430, 480, 580, and 627 nm) across the spectrum, which contributes to a white light emission. It is also observed that the emission spectrum of C_3N_4 silica gels have red-shift peaks compared to pure C3N4 dots due to self-absorption and spontaneous emission of silica gels (high concentration).

White light emission normally features multiple peaks in the visible region. The obtained g-C_3N_4-silica-gels exhibited 4 peaks (430 nm, 480 nm, 580 nm and 627 nm) as shown in Figure 3B. Considering that the pure g-C_3N_4 nanodots possess a single peak at 430 nm as shown in Figure 3A, the peaks at 480 nm and 580 nm can be attributed to the silica-functionalization of g-C_3N_4.

Referring to Figure 4, the chromaticity coordinates are (0.295, 0.293), as shown in the white gamut, falling within the white gamut of the CIE-1931 color space chromaticity diagram.

The light emitting mechanism of the thin film 104 or the g-C_3N_4-silica-gels were investigated. The g-C_3N_4-silica-gels turned from dark brown to orange under room light upon aging to form the thin film 104, with its emission simultaneously shifted from green to white under the UV illumination (365 nm) with reference to Figures 16A to 16D.

With reference also to Figures 3A and 3B, pure silica gel synthesized by heating AEATMS has no photoluminescence under UV light. The intense blue fluorescent peak (430 nm) of the g-C_3N_4-silica-gels arises from the nitrogen-rich g-C_3N_4, as indicated from the photoluminescence spectrum of the pure g-C_3N_4. The blue emission of g-C_3N_4 persists after the surface functionalization of silica gel. In addition, the synthesized g-C_3N_4-silica-gel has a higher quantum yield (27%) than the synthesized pure g-C_3N_4 (18%) due to surface passivation.

The emergence of the emission at 480, 580, and 630 nm of the aged g-C_3N_4-silica-gels can be ascribed to the self-excitation effect, i.e., the blue emission at 430 nm upon UV excitation is partially absorbed by the gel itself, exciting photoluminance peak at 490 nm, which is further partially absorbed exciting photoluminance peak at 580 nm, which is again further partially absorbed exciting photoluminance peak at 630 nm. This emission mechanism is supported by the photoluminescence spectra of the pure g-C3N4 excited at 430 nm, 480 nm, and 580 nm.

With reference to Figure 5, there is shown an exemplary Fourier transform infrared (FTIR) spectra of AEATMS, the C_3N_4 silica gel (Si-g-CNDs) and the C_3N_4 particles (g-CNDs). It is indicated in the FTIR that the existence of AEATMS-capped C_3N_4 particles in the C_3N_4 silica gel, which shows a characteristic peak at 1655 cm^{-1} assigned to the stretching vibration of C=O groups from the C=ONH units and two signals at 1035 and 1123 cm^{-1} assigned to the Si−O−C and Si−O−Si vibrations respectively.

In an alternative example, the material 104 or the substance may be excited by light of different color. With reference to Figure 6, different color can be obtained from the C_3N_4 silica gel 104 by different excitation wavelengths. For example, when the material is excited by light with a wavelength of 440 nm, yellowish orange light with an emission peak at 570 nm is emitted by the substance. It is observed by the inventor that as the ratio of C/N increased, the peak is red shifted. Therefore, desire color of the light emitted by the substance may be accurately and flexibly obtained by tuning the C/N ratio and or the composition of the silica gel. Other parameters may also affect the emission color/temperature. For example, the surface state of the substance may also affect luminescence of the light emit by the substance.

Due to their special semiconductor properties, such as having an energy band gap of 2.7 eV, visible light absorption and high stability, the C_3N_4 particles may operate as a photocatalyst. For example, the material 104 or the substance may combine with other photocatalysts or substances such as titania to achieve further improved photocatalytic performance. In this example, the photocatalyst may degrade an organic substance (such as a volatile organic compound) when upon the substance receives an excitation energy.

Besides, C_3N_4 is also an electron acceptor material with high luminescence that may be used in sensors. In an example embodiment, the electronic device is a sensor where different metal ions may show different impact on the emission spectrum of the C_3N_4 particles, thus C_3N_4 particles may be used in electronic devices for detecting metal ions.

With reference to Figures 7A to 8B, there is shown an example analysis of the g-C_3N_4-silica-gels using X-ray photo-electron spectroscopy (XPS). The full scan spectra of the samples showed five peaks at ~102 eV, 161 eV, 288 eV, 399 eV, and 531.5 eV, which can be assigned to S 2p, Si 2p, C1s, N1s, and O1s, respectively. The detailed C 1s scan revealed a peak located at 284.8 eV which was assigned to the sp2 C-C bonds of 286.4 eV corresponding to the sp2 C-N bond (each carbon atom bonded to 3 nitrogen atoms in the g-C_3N_4 lattice), and peaks located at 285.7 eV and 289.2 eV which respectively were assigned to the C-OH bond and C-O bond, indicating the existence of oxygen-rich groups. Four features at 398.2 eV (pyridinic), 399.7 eV (amino), 400.8 eV (pyrrolic), and 401.3 eV (graphitic) were observed in the N 1s spectrum, convincing of g-C3N4 particles feature heptazine heterocyclic rings. Two peaks at 103.1 eV (assigned to the Si-O bond) and 101.7 eV (assigned to the Si-C bond) were present in the Si 2p spectrum, in good agreement with the O 1s scan which exhibited a peak at 534 eV corresponding to the Si-O-Si bonds. Together with the FTIR results discussed earlier and illustrated in Figure 5, the XPS analysis confirms that the presence of the silica functionalized g-C_3N_4 in the g-C_3N_4-silica-gels.

Preferably, the method of producing such material for an electronic device 100 or a light emitting device 100 may comprise the steps of: synthesizing a plurality of carbon nitride particles; and mixing a siloxane material to the plurality of carbon nitride particles to form a substance.

For example, C_3N_4 nanodots or particles may be synthesized by mixing citric acid with thiourea to form a precursor of the carbon nitride particles. The precursor may include a mixture of 0.41 g of anhydrous citric acid and 0.42 g thiourea. The precursor may then be heated at 120 – 300 °C, preferably at 180°C, for a predetermined period such as 2 hours to produce the C_3N_4 particles. The C_3N_4 particles may be filtered out from the precursor. Preferably, the synthesized carbon nitride particles are of a size in a range of 1 nm to 1000 nm.

Alternatively, to collect the nanodots from the precursor, the mixture may be dissolved in water, sonicated for 30 minutes, and then stirred for an hour. The g-C_3N_4 particles may then be collected by centrifugation at 12,000 rpm for 10 minutes followed by water rinsing (and optionally repeated for 3 times). The solid precipitation was then filtered through a 14,000 Da dialysis bag washed with deionized water to collect only the g-C3N4 nanodots.

Yet alternatively, pure g-C3N4 nanodots may also be produced using a similar synthesis method but without adding the silica species, i.e. it is investigated in a DLS analysis that the thus-obtained g-C_3N_4 nanodots possessed an average diameter of ~ 5 nm as shown in Figures 9A and 9B.

A siloxane material such as 10 mL of N-(b-aminoethyl)-g-aminopropylmethyldimethoxysilane (AEAPMS) may be added to the C_3N_4 particles to form a mixture of carbon nitride particles and siloxane material, and the carbon nitride particles are functionalized by the siloxane when curing in another baking process at 120 – 300 °C. The precursor or the mixture of the particles and the siloxane material may be placed in a Teflon-lined autoclave for the thermal treatment, in which the autoclave lid is tightly closed during the thermal treatment.

Alternatively, the process may be simplified in which the siloxane material may be added to the precursor followed by baking the mixture at 120 – 300 °C to obtained the functionalized carbon nitride particles.

For example, 0.4 g of citric acid monohydrate and 0.4 g thiourea may be added to 10 ml of N-(b-aminoethyl)-g-aminopropylmethyldimethoxysilane (AEATMS) under vigorous stirring. The mixture may then be transferred to a Teflon-lined autoclave (volume of 50 ml) to undergo the solvothermal reaction at 180 °C for 2 hours, followed by naturally cooling down to room temperature.

After cooling, the mixture may form a substance or silica gel which may be further solidified to form a thin film 104. For example, the substance may be adhesive to another material such as glass and polymer, and the substance may be coated on the surface of the encapsulation 110 of a UV-LED. After the substance or the material is fully solidify (such as aged for 3 hours or any predetermined period of time), the substance is a solid covering the UV-LED and the substance may be used to convert the UV light to white light during operation. The thin film 104 is transparent and flexible.

With reference to Figures 15A to 15D, the freshly-prepared gel may be coated onto the encapsulation of a UV (365 nm) LED using dip coating techniques. It was tested by the inventors that the bright white light emission under the UV excitation has a quantum yield of 27%.

Alternatively, referring to Figures 15E to 16D, the freshly prepared gel can also be used as water-washable ink of high fluorescence. With reference to Figures 15E to 15G, a calligraphy of letters “CityU” was written on a filter paper using the gel ink, the gel appears to be brown in daylight, while glowing intensive white light under a hand-held UV lamp (365 nm). The filter paper was dipped in water for 5 times immediately after the writing, and the letters remained a sharp fluorescent print afterwards. After the gel becomes completely solidified, the blurring of the fluorescence ink in water may be completely eliminated.

With reference to Figures 16A to 16D, the g-C_3N_4 nanodots were also applicable as fluorescent ink to enable calligraphy invisible under daylight and blue under UV light (365 nm). However, the ink based on pure g-C3N4 nanodots is not as water-resistant as that based on g-C_3N_4-silica-gels.

With reference to Figures 11 to 12, a solid form of a thin film 104 of the substance or material is illustrated. Alternatively, additional gluing adhesive or polymer matrix may be used in fixing the carbon nitride particles to the electronic device 100. The substance or the thin film 104 produced is transparent and flexible such that it may be applied to different flexible surfaces such as clothing or a flexible substrate. Advantageously, the flexible thin film 104 may be used in a wide range of applications, such as flexible displays and wearable devices. For example, the g-C_3N_4-silica-gels based white LEDs can be used in wearable devices, due to their excellent biocompatibility and good color rendering index.

With reference to Figures 13 to 14, a white LED may be implemented with the aged g-C_3N_4-silica-gels knitted in a sweater which emitted bright white light. It may be advantageous that the wearable white LED devices 100 may be manufactured in large-scale production, in which the LEDs have the benefits of no toxicity, low cost, great fabrication convenience, environmental friendliness and high efficiency.

With reference to the table below, there is shown a comparison of the g-C_3N_4-silica-gels with other possible WLED materials.

Materials	Biocompa-tibility	Fabrication convenience	Quantum Yield	CIE coordinates
g-C_3N_4-silica-gels	excellent	easy	27%	(0.295, 0.293)
Silicon and carbon dots	good	complex	relatively low	(0.34, 0.32)
MOF	poor	medium	5%	(0.27, 0.30)
Carbon dots and $AgInS_2$	poor	medium	15%	(0.3385, 0.3062)
Carbon nanorings	good	easy	-	(0.28, 0.27)
Copper indium sulfide	poor	complex	62%	(0.33, 0.27)
(YAG:Ce) phosphor and silicone resin	poor	complex	34.7%	(0.3360, 0.3355)

These embodiments may be advantageous also in that, the material may be applied in various applications due to its superior properties. The material is non-toxic, bio-compatible and bio-degradable such that it is suitable for applications such as wearable electronics and light sources in endoscopes, and it is environmental-friendly in both the production and the disposal the material.

According to the experiments carried out by the inventors, the thin film materials is non-metal and biocompatible graphite-carbon nitride (g-C3N4) silica gels (g-C3N4-silica-gels), which have the advantages of low cost, high quantum yield, high transparency, mechanical flexibility. Carbon nitride, may be viewed as graphite whose carbon lattice is partially substituted with N atoms in a regular fashion, is an appealing material for a variety of applications, such as but not limited to catalysts, bioimaging, drug delivery and sensing.

Advantageously, the material has a good color rendering index (70 as determined by the inventors) and the color may be fine-tuned within a range to suit different applications or requirements. In addition, the material has a high fluorescence output. Therefore, the material may replace the use of phosphor coating which includes metals and toxins.

The production of the material is also simple and cost-effective. The fabrication process is carried out in ambient pressure, which eliminates the risks and complexity associated with the application of high pressure in some other hydrothermal methods.

It will be appreciated by persons skilled in the art that numerous variations and/or modifications may be made to the invention as shown in the specific embodiments without departing from the spirit or scope of the invention as broadly described. The present embodiments are, therefore, to be considered in all respects as illustrative and not restrictive.

Any reference to prior art contained herein is not to be taken as an admission that the information is common general knowledge, unless otherwise indicated.

CLAIMS

1. A material for an electronic device, comprising: a substance arranged to emit light in a predetermined range of wavelength upon receiving an excitation energy, wherein the substance includes a plurality of carbon nitride particles and a siloxane material.

2. A material in accordance with claim 1, wherein the predetermined range of wavelength includes a range of wavelength visible to human eye.

3. A material in accordance with claim 2, wherein the light emitted by the substance is in white color visible to human eye.

4. A material in accordance with claim 1, wherein the excitation energy includes a photon excitation.

5. A material in accordance with claim 4, wherein the excitation energy includes ultra-violet light.

6. A material in accordance with claim 5, wherein the photon excitation has a range of excitation wavelength of 345 nm to 365 nm.

7. A material in accordance with claim 4, wherein the photon excitation is at least partially absorbed by the plurality of carbon nitride particles and/or the siloxane material.

8. A material in accordance with claim 1, wherein the plurality of carbon nitride particles includes C_3N_4 particles.

9. A material in accordance with claim 8, wherein each of the plurality of carbon nitride particles is of a size in a range of 1 nm to 1000 nm.

10. A material in accordance with claim 1, wherein the siloxane material includes N-(β-aminoethyl)-g-aminopropylmethyldimethoxysilane.

11. A material in accordance with claim 1, wherein each of the plurality of carbon nitride particles and a siloxane material is arranged to at least partially contribute the light emitted by the substance.

12. A material in accordance with claim 10, wherein the plurality of carbon nitride particles is arranged to contribute a first emission spectrum of blue color within the predetermined range of wavelength of the light emitted by the substance.

13. A material in accordance with claim 12, wherein the siloxane material is arranged to contribute a second emission spectrum within the predetermined range of wavelength of the light emitted by the substance such that the light emitted by the substance is in white color visible to human eye.

14. A material in accordance with claim 1, wherein at least one of the plurality of carbon nitride particles is functionalized by the siloxane material.

15. A material in accordance with claim 1, wherein the substance is a solid.

16. A material in accordance with claim 1, wherein the substance is flexible.

17. A material in accordance with claim 1, wherein the substance is adhesive.

18. A material in accordance with claim 1, wherein the substance is bio-compatible.

19. A material in accordance with claim 1, wherein the electronic device is a light-emitting device or a sensor.

20. A material in accordance with claim 1, wherein the plurality of carbon nitride particles is further arrange to operate as a photocatalyst.

21. A material in accordance with claim 20, wherein the photocatalyst is arranged to degrade an organic substance when upon the substance receives the excitation energy.

22. A method of producing a material for an electronic device, comprising the steps of:
    - synthesizing a plurality of carbon nitride particles; and
    - mixing a siloxane material to the plurality of carbon nitride particles to form a substance; and

    wherein the substance is arranged to emit light in a predetermined range of wavelength upon receiving an excitation energy.

23. A method of producing a material in accordance with claim 22, wherein the step of synthesizing the plurality of carbon nitride particles comprises the step of mixing citric acid with thiourea to form a precursor of the plurality of carbon nitride particles.

24. A method of producing a material in accordance with claim 23, further comprises the step of heating the precursor at 120 °C to 300 °C.

25. A method of producing a material in accordance with claim 23, further comprises the step of filtering out the plurality of carbon nitride particles from the precursor.

26. A method of producing a material in accordance with claim 22, further comprising the step of heating the substance at 120 °C to 300 °C.

27. A method of producing a material in accordance with claim 22, further comprises the step of solidifying the substance to form a thin film.

28. A light emitting device, comprising a light emitting element arranged to emit an excitation energy; and a material having a substance arranged to emit light in a predetermined range of wavelength upon receiving the excitation energy, wherein the substance includes a plurality of carbon nitride particles and a siloxane material.

29. A light emitting device in accordance with claim 28, wherein the light emitting element includes a light emitting diode.

30. A light emitting device in accordance with claim 28, wherein the substance is a thin film at least partially covering the light emitting element.

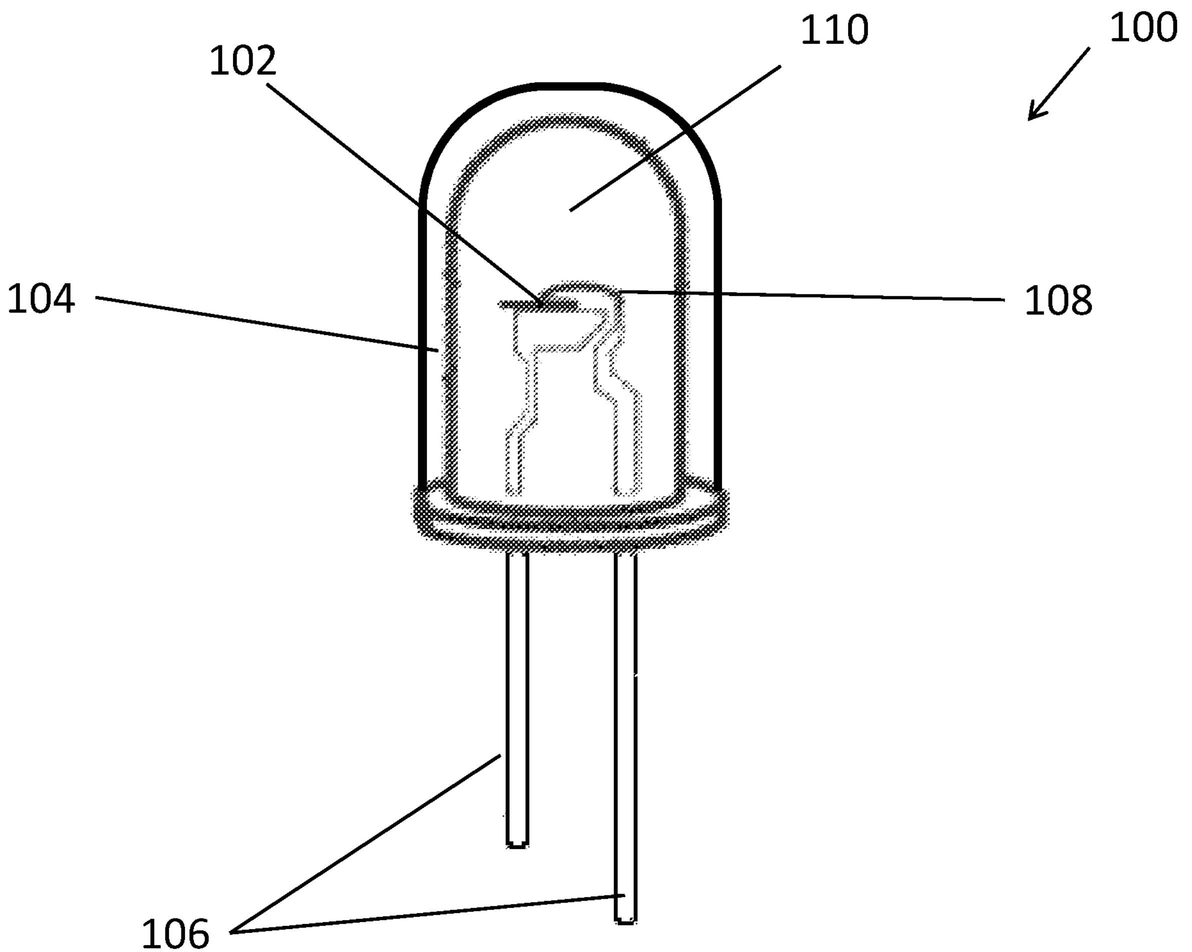


FIG. 1

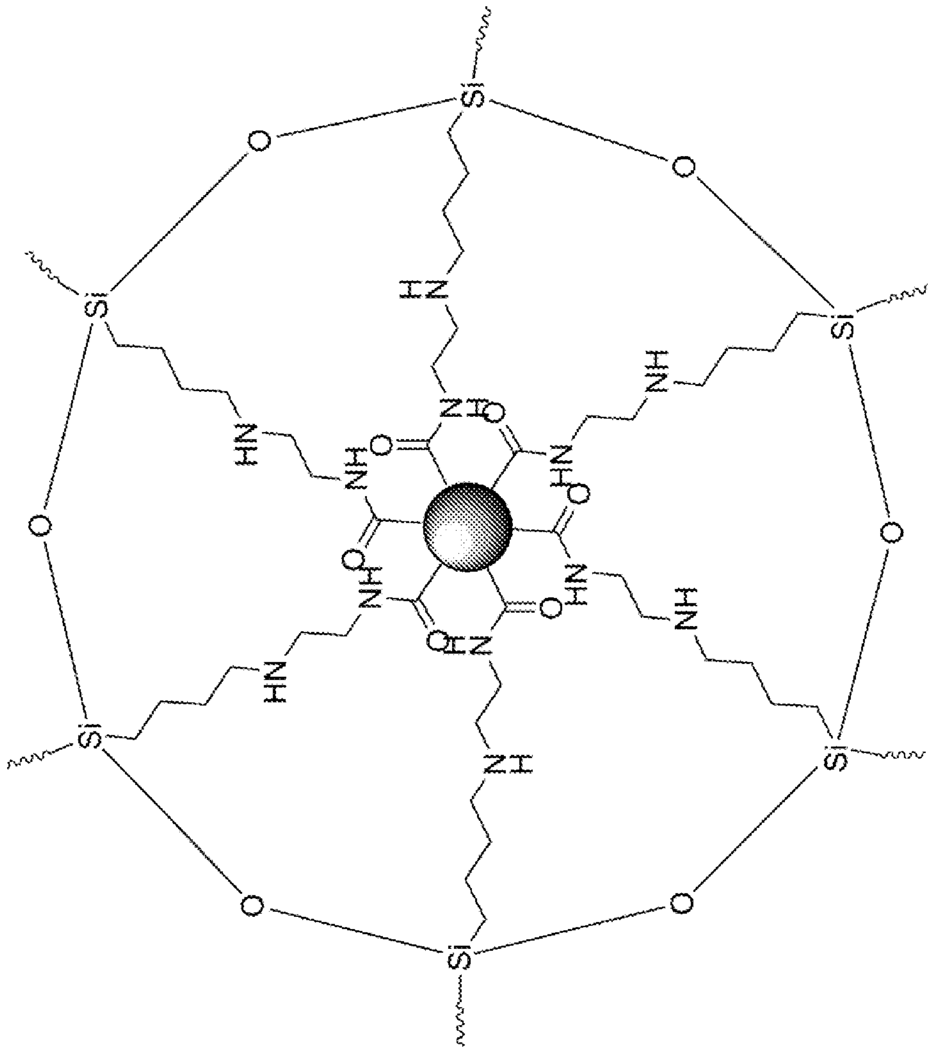


FIG. 2

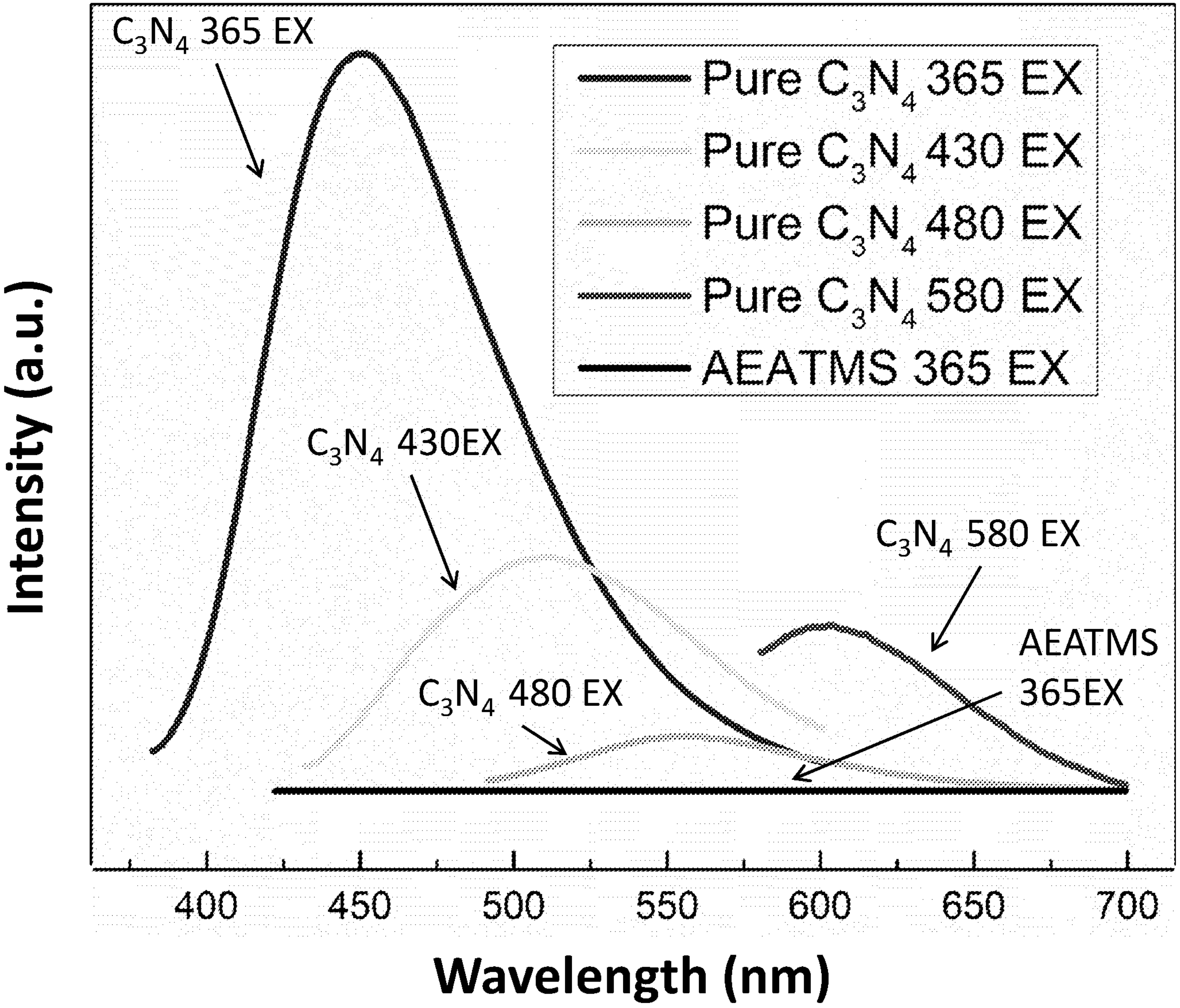

C_3N_4 365 EX
Pure C_3N_4 365 EX
Pure C_3N_4 430 EX
Pure C_3N_4 480 EX
Pure C_3N_4 580 EX
AEATMS 365 EX
C_3N_4 430EX
C_3N_4 580 EX
AEATMS
365EX
C_3N_4 480 EX
Intensity (a.u.)
400
450
500
550
600
650
700
Wavelength (nm)

FIG. 3A

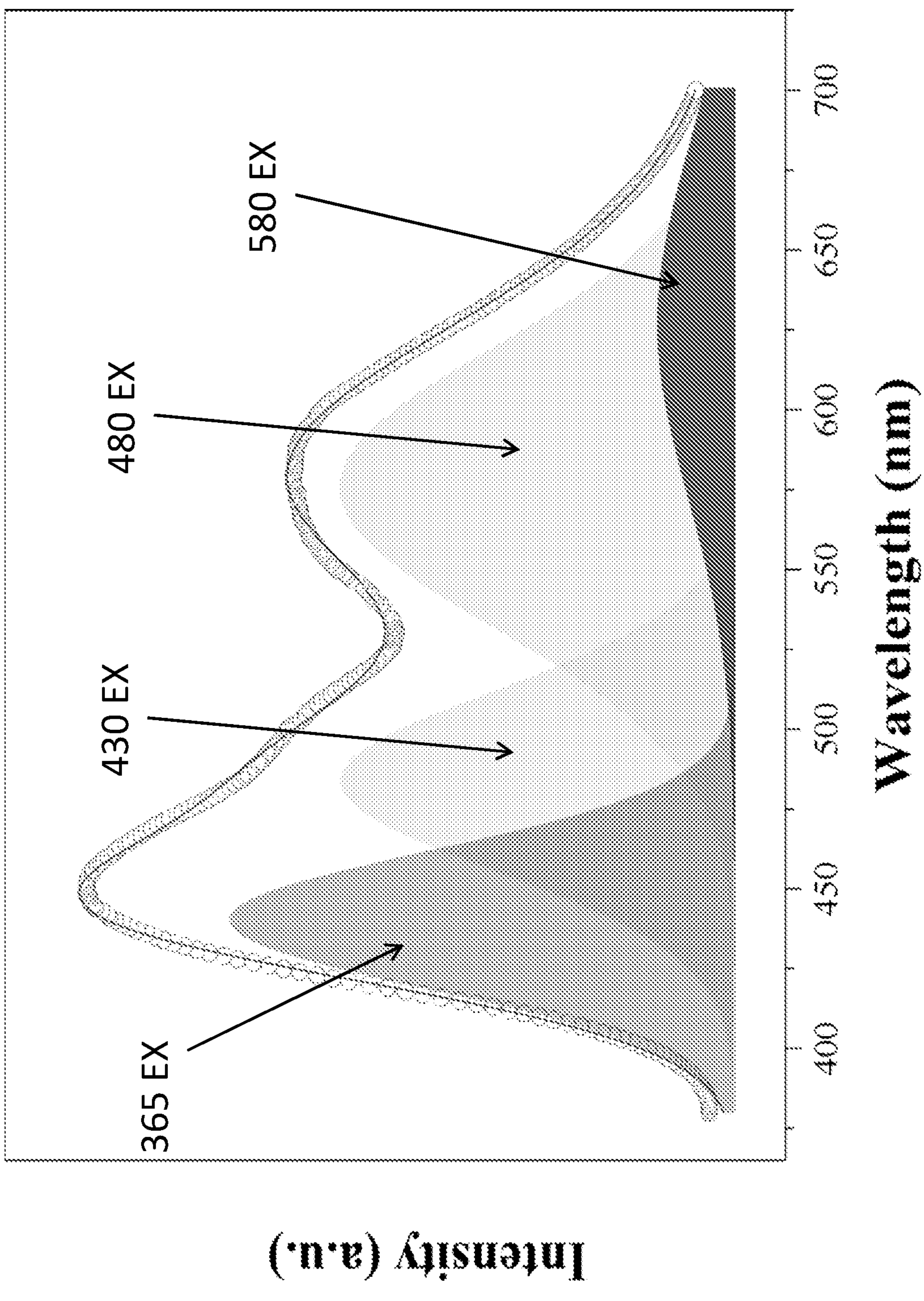
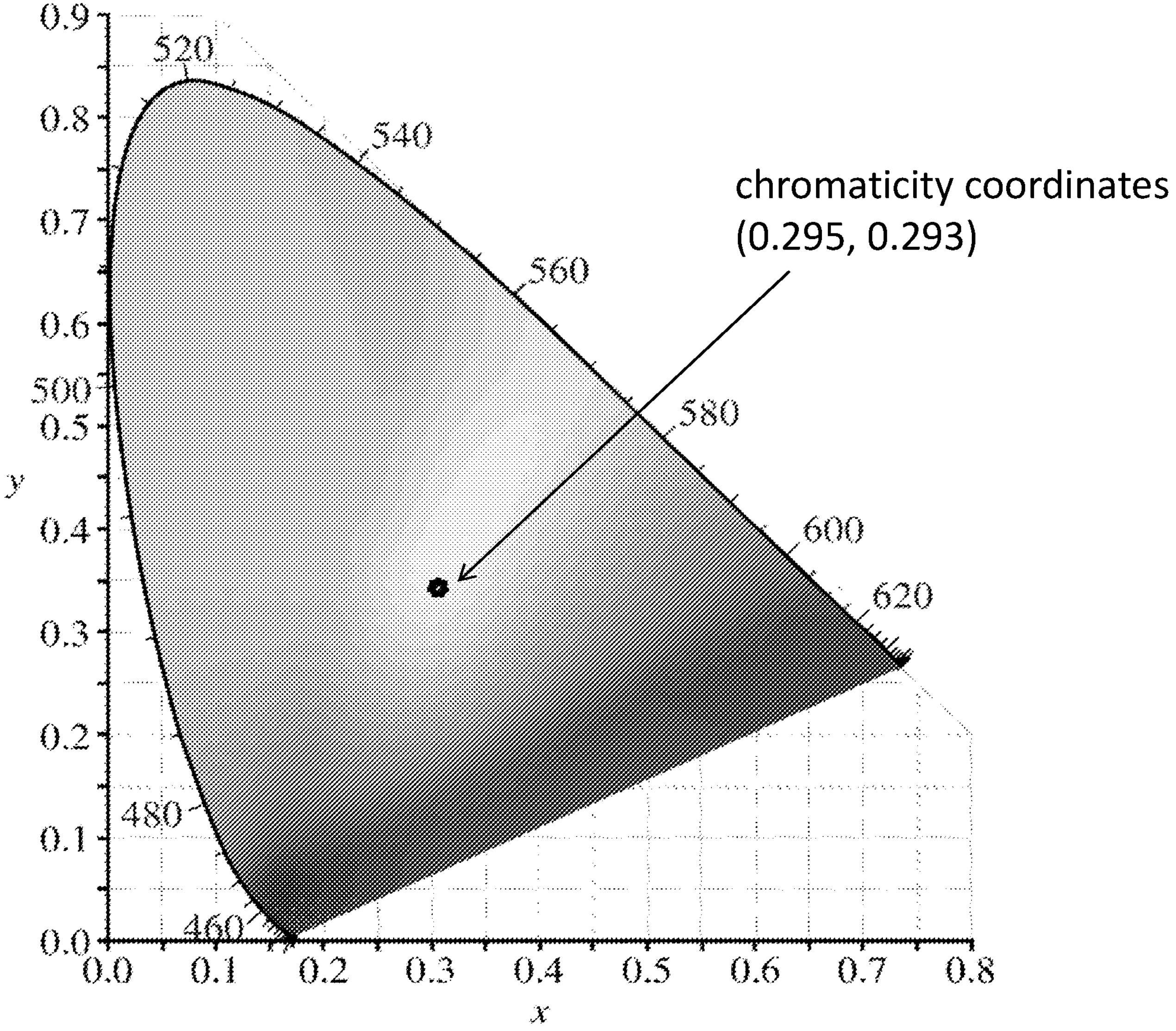

365 EX
430 EX
480 EX
580 EX
400
450
500
550
600
650
700
Wavelength (nm)
Intensity (a.u.)

FIG. 3B



chromaticity coordinates
(0.295, 0.293)

FIG. 4

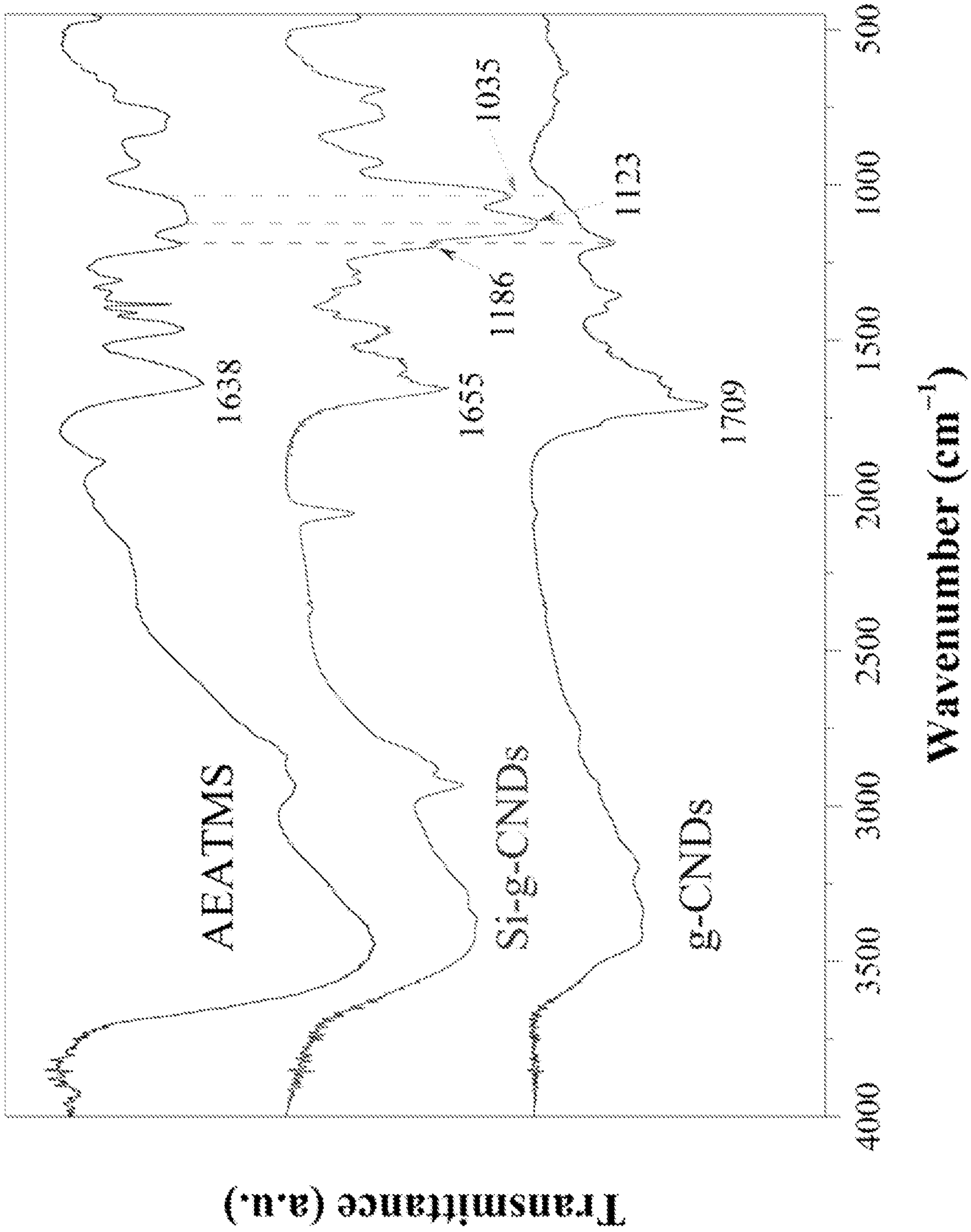

AEATMS
Si-g-CNDs
g-CNDs
1638
1655
1709
1186
1123
1035
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm^{-1})
Transmittance (a.u.)

FIG. 5

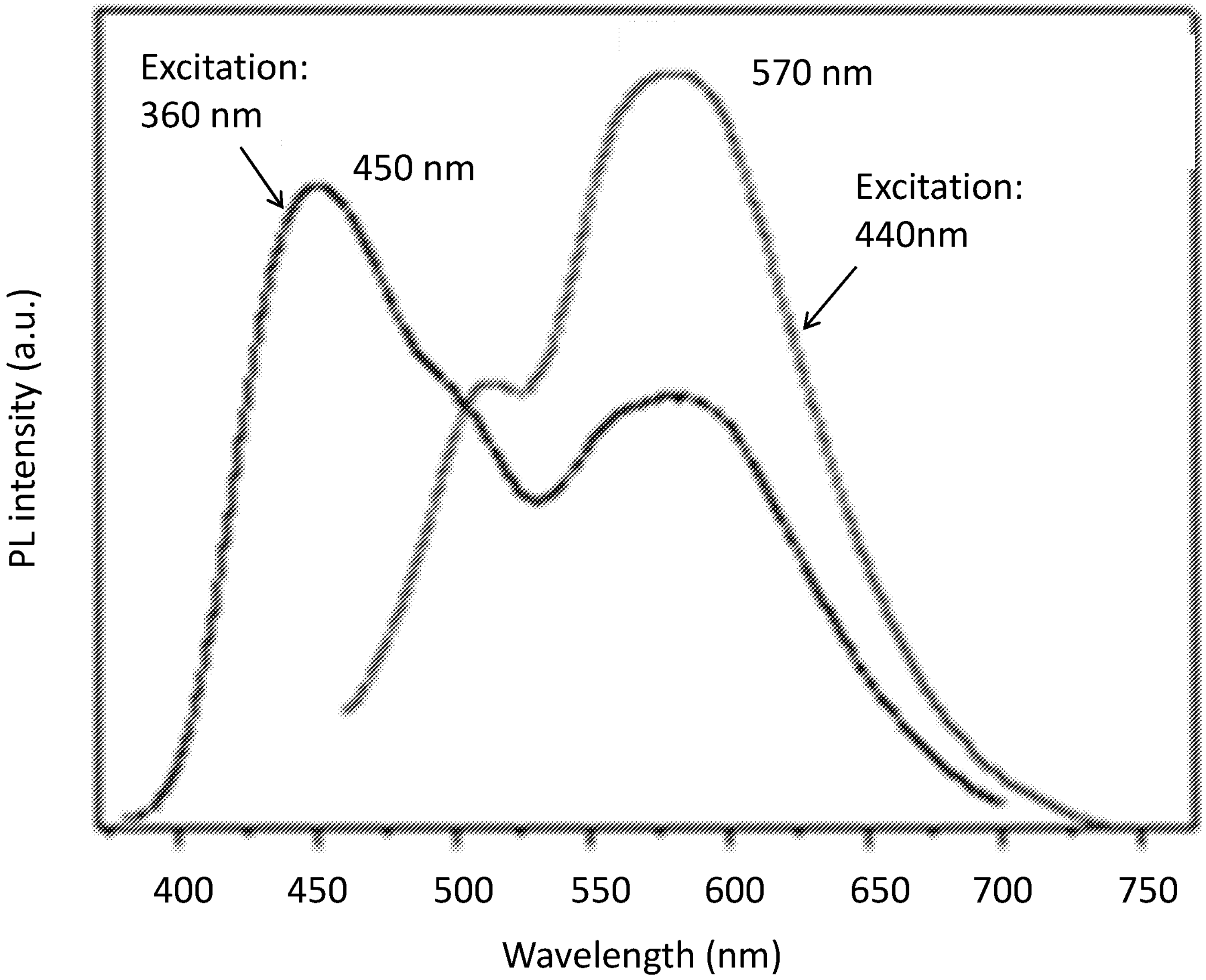

Excitation:
360 nm
450 nm
570 nm
Excitation:
440nm
PL intensity (a.u.)
400
450
500
550
600
650
700
750
Wavelength (nm)

FIG. 6

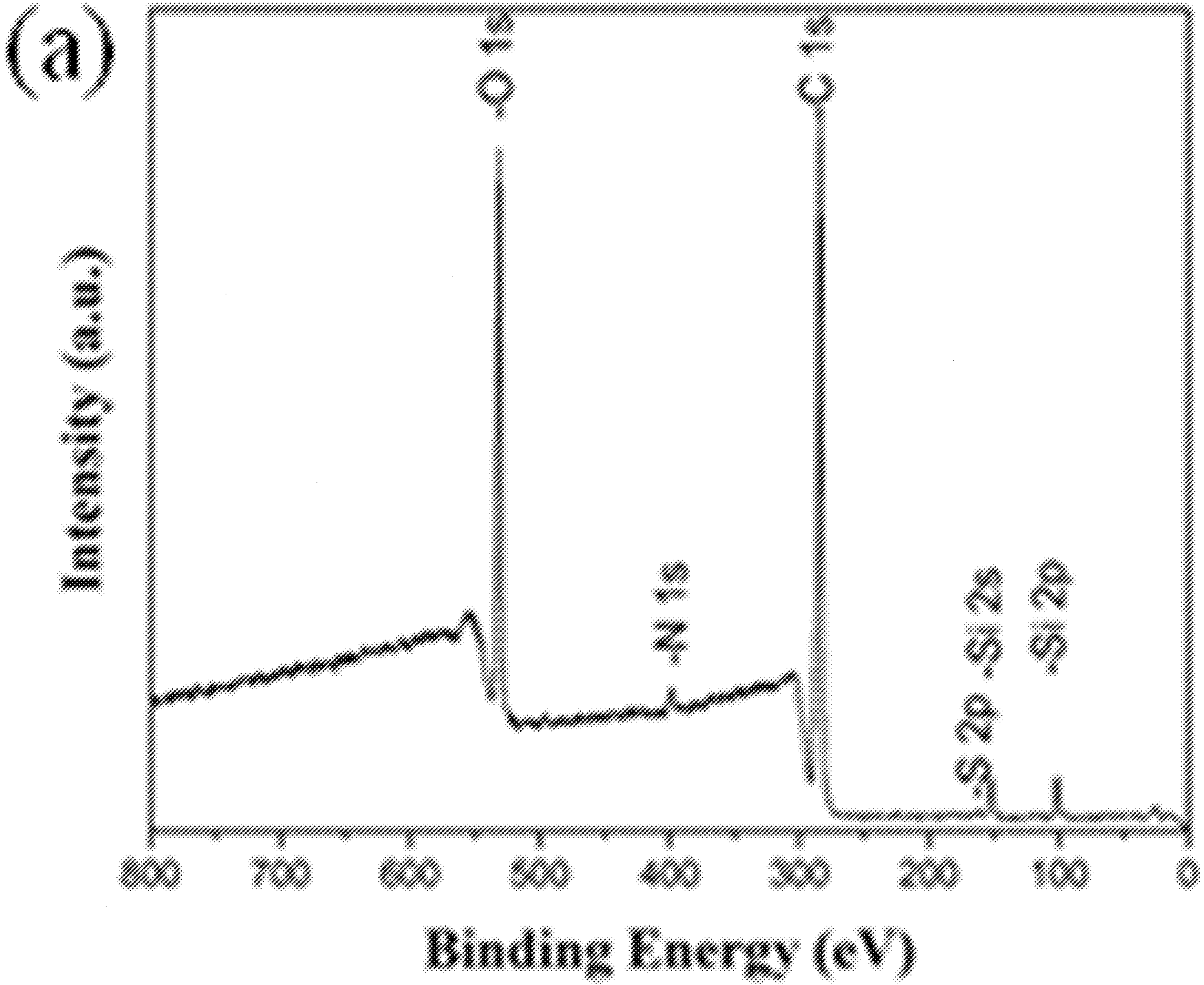

(a)
O 1s
C 1s
N 1s
S 2p
Si 2s
Si 2p
Intensity (a.u.)
800
700
600
500
400
300
200
100
0
Binding Energy (eV)

FIG. 7A

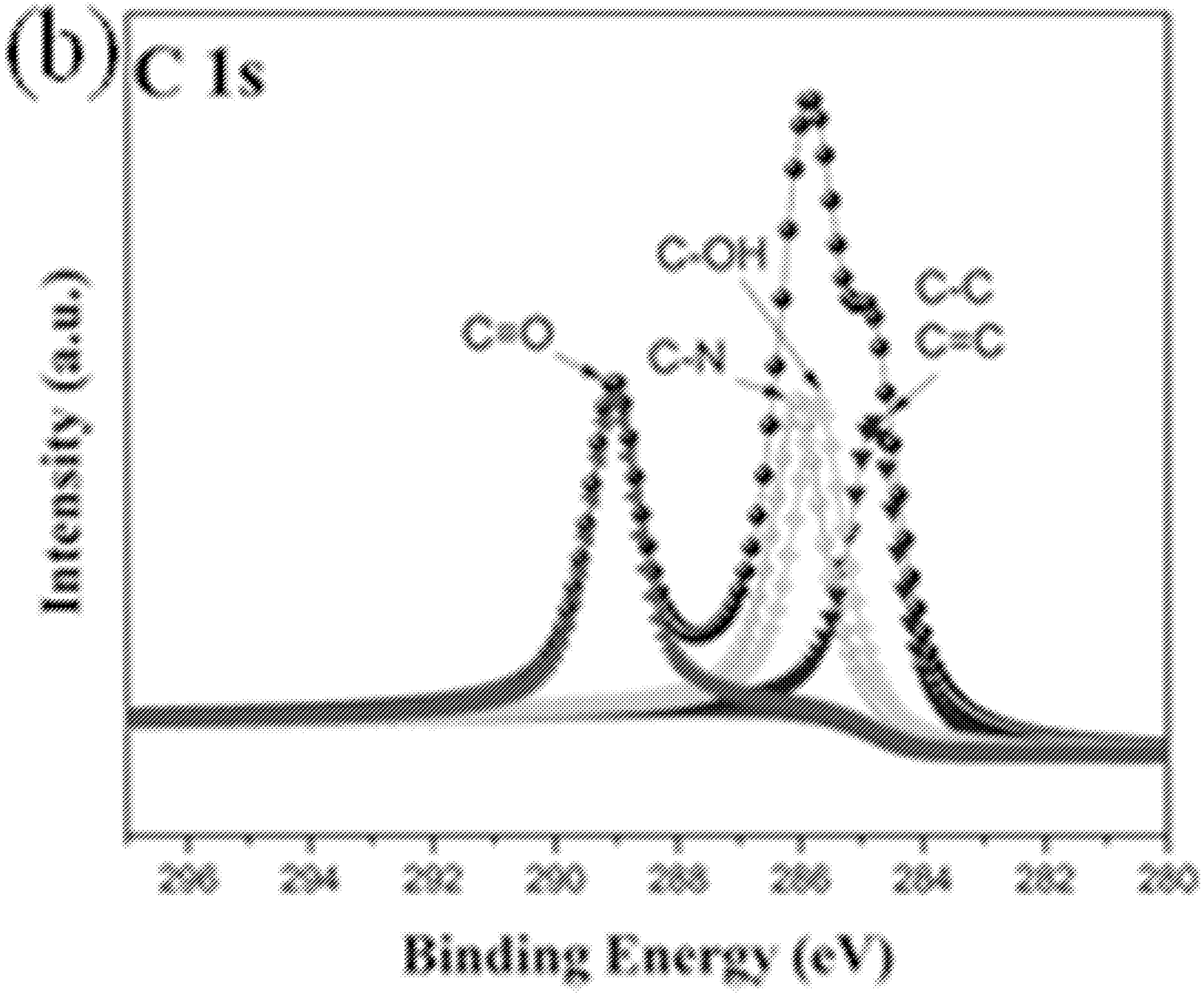

(b) C 1s
Intensity (a.u.)
C=O
C-OH
C-N
C-C
C=C
296
294
292
290
288
286
284
282
280
Binding Energy (eV)

FIG. 7B

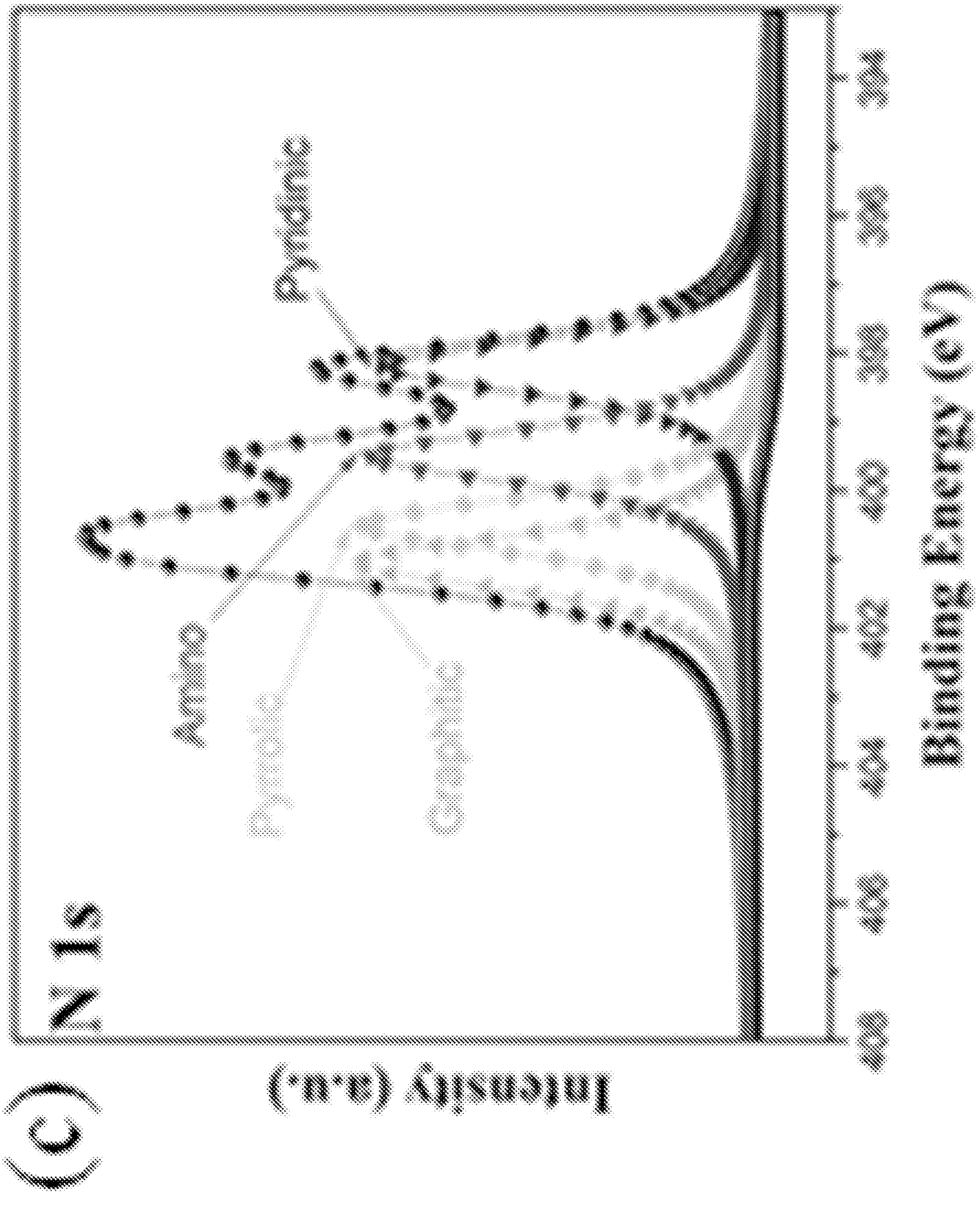

(c)
N 1s
Amino
Pyrrolic
Graphitic
Pyridinic
Intensity (a.u.)
Binding Energy (eV)
408
406
404
402
400
398
396
394

FIG. 7C

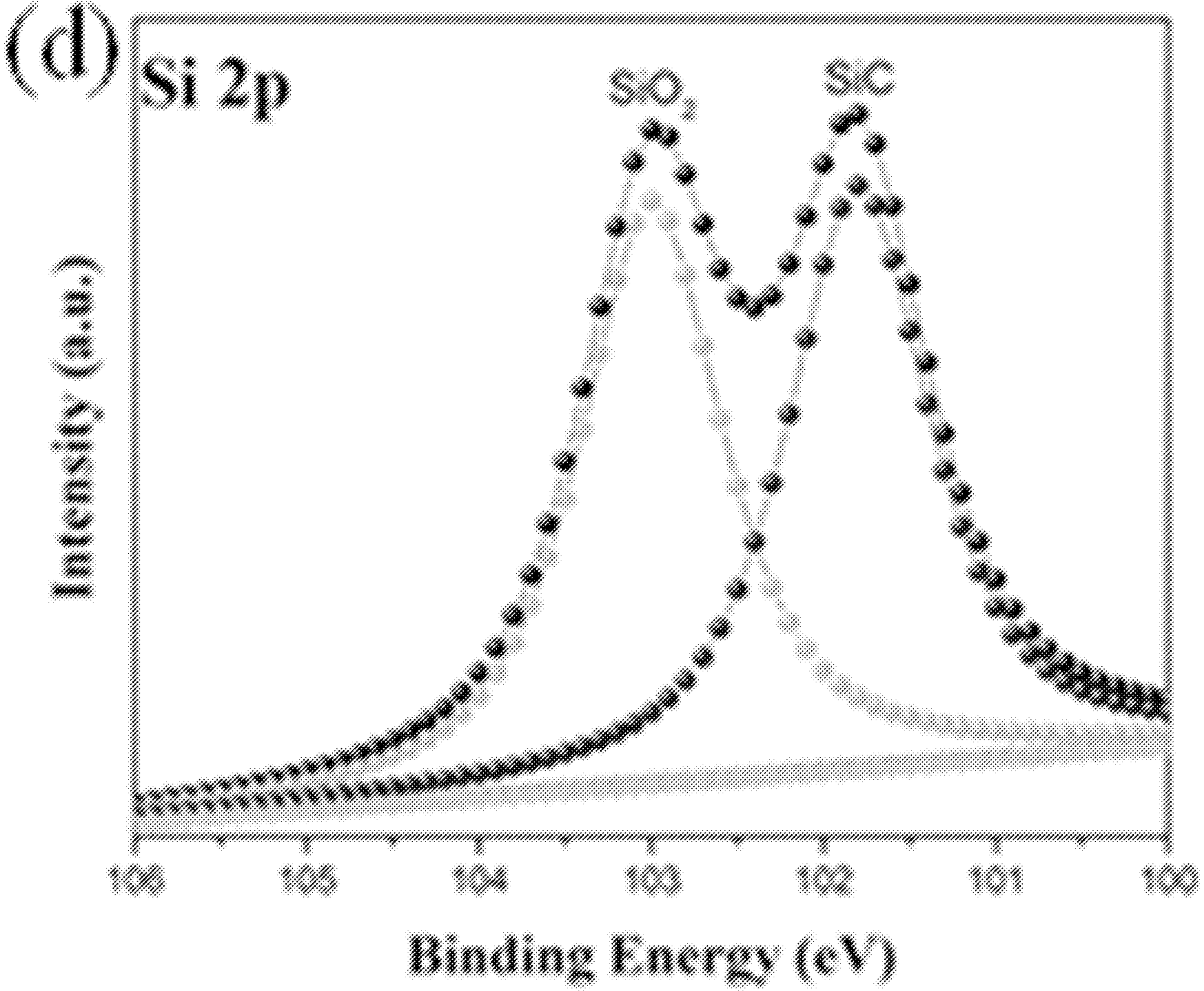

(d)
Si 2p
SiO$_2$
SiC
Intensity (a.u.)
106
105
104
103
102
101
100
Binding Energy (eV)

FIG. 7D

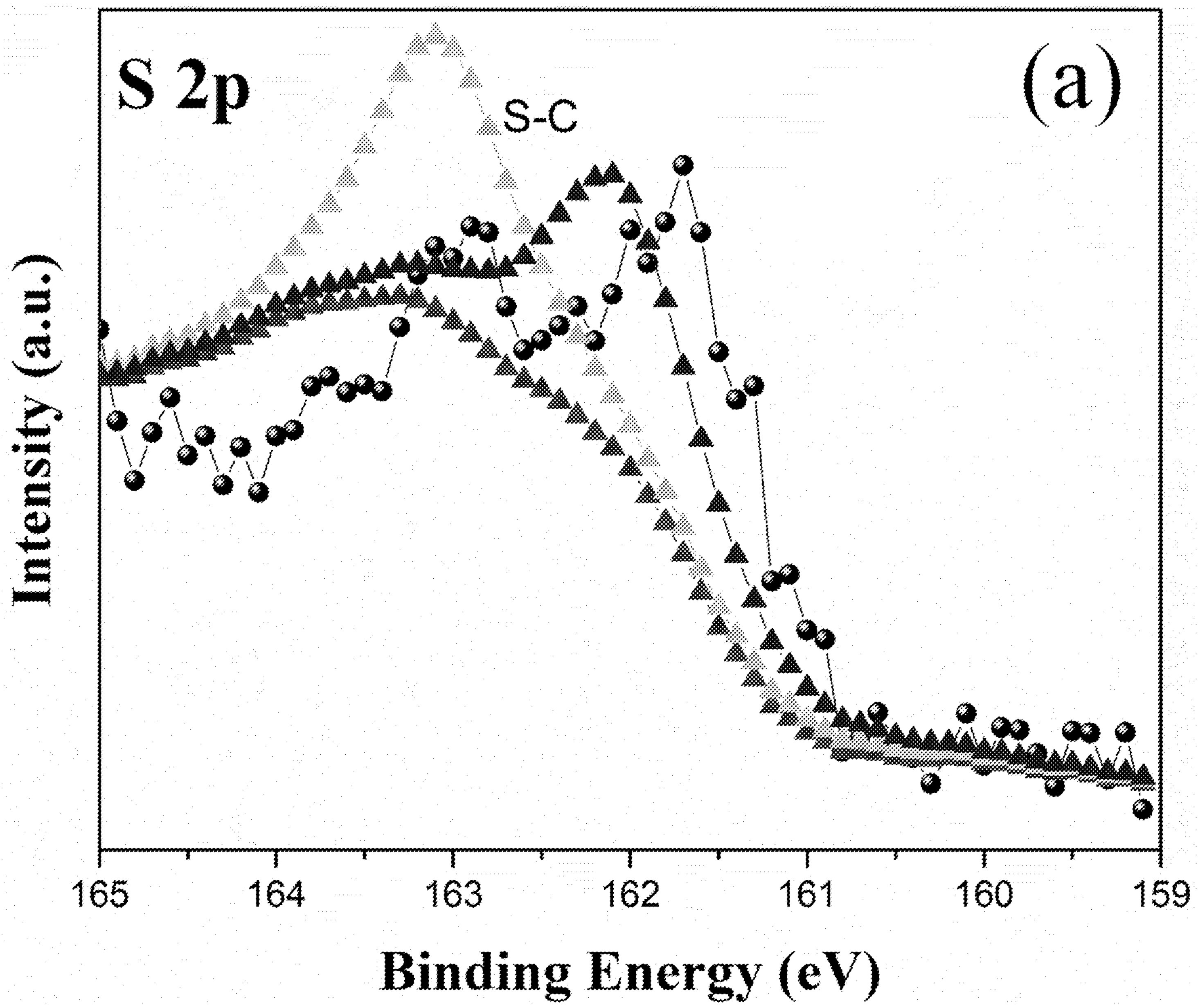

S 2p
(a)
S-C
Intensity (a.u.)
165
164
163
162
161
160
159
Binding Energy (eV)

FIG. 8A

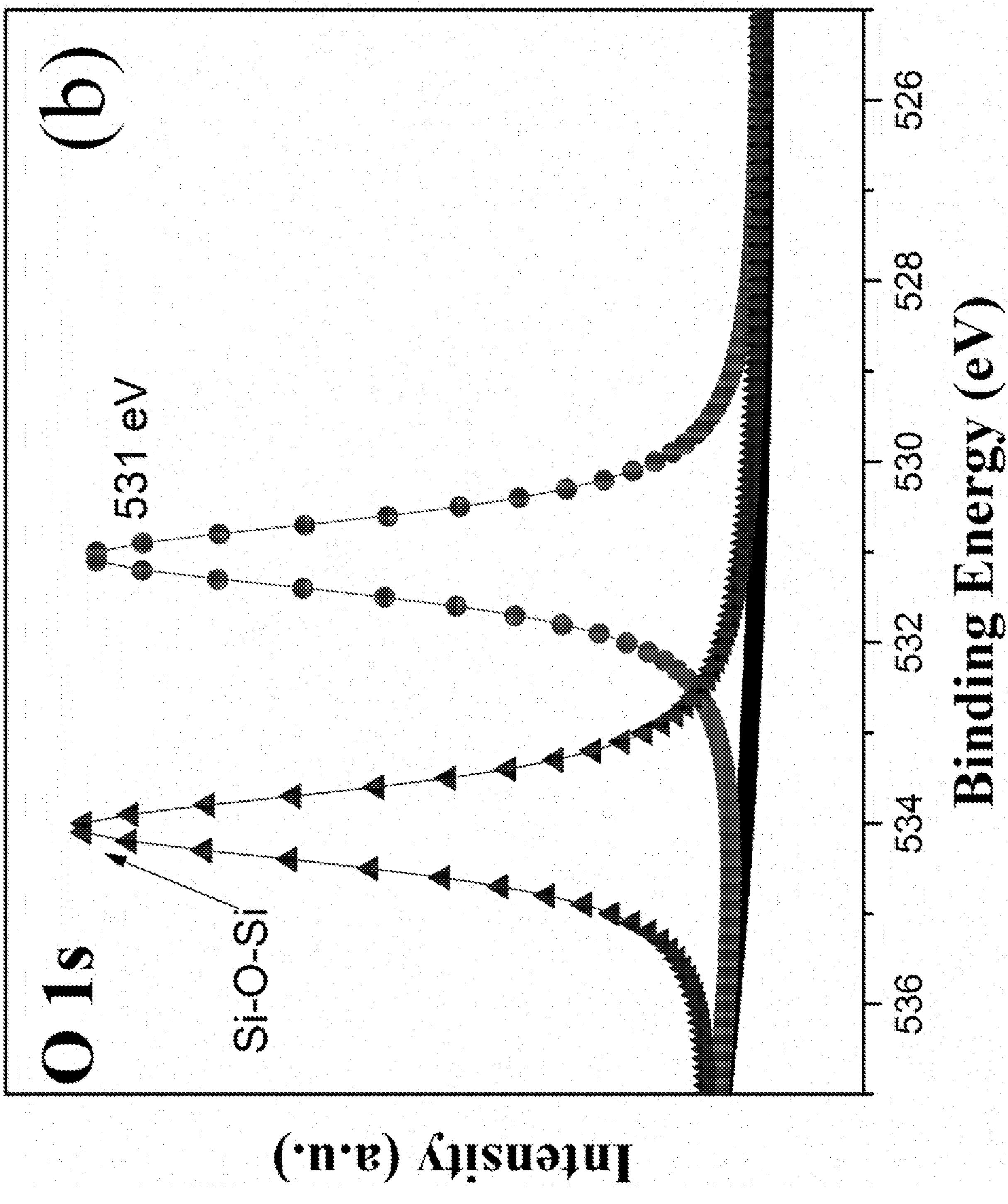

O 1s
(b)
Si-O-Si
531 eV
536
534
532
530
528
526
Binding Energy (eV)
Intensity (a.u.)

FIG. 8B

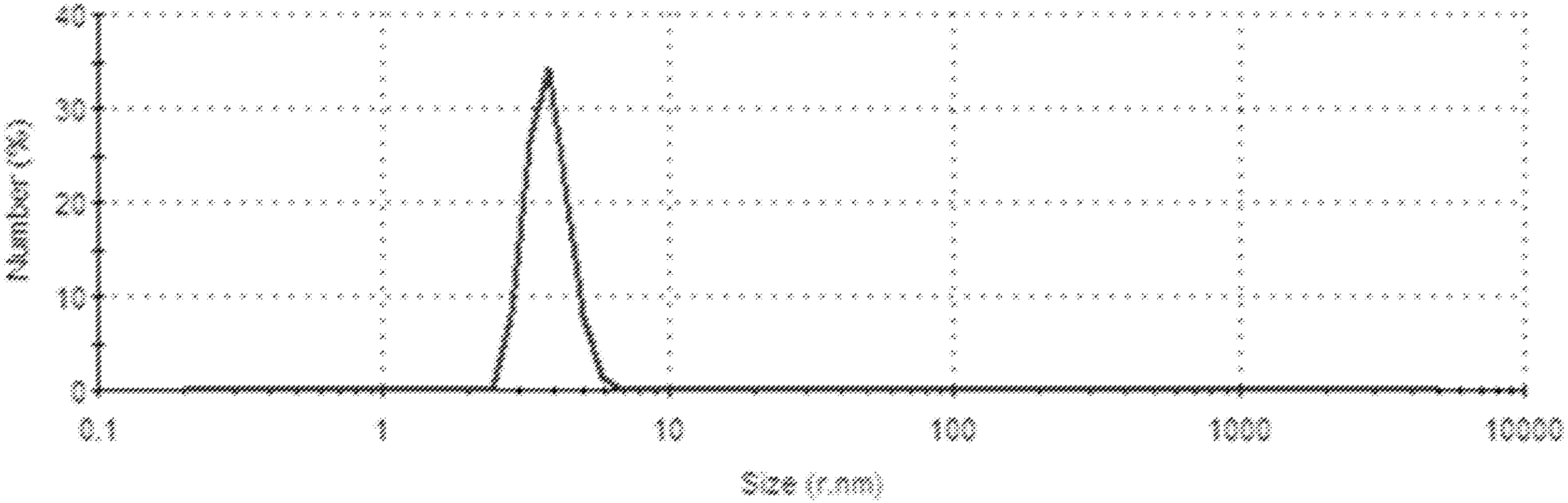

Number (%)
40
30
20
10
0
0.1
1
10
100
1000
10000
Size (r.nm)

FIG. 9A

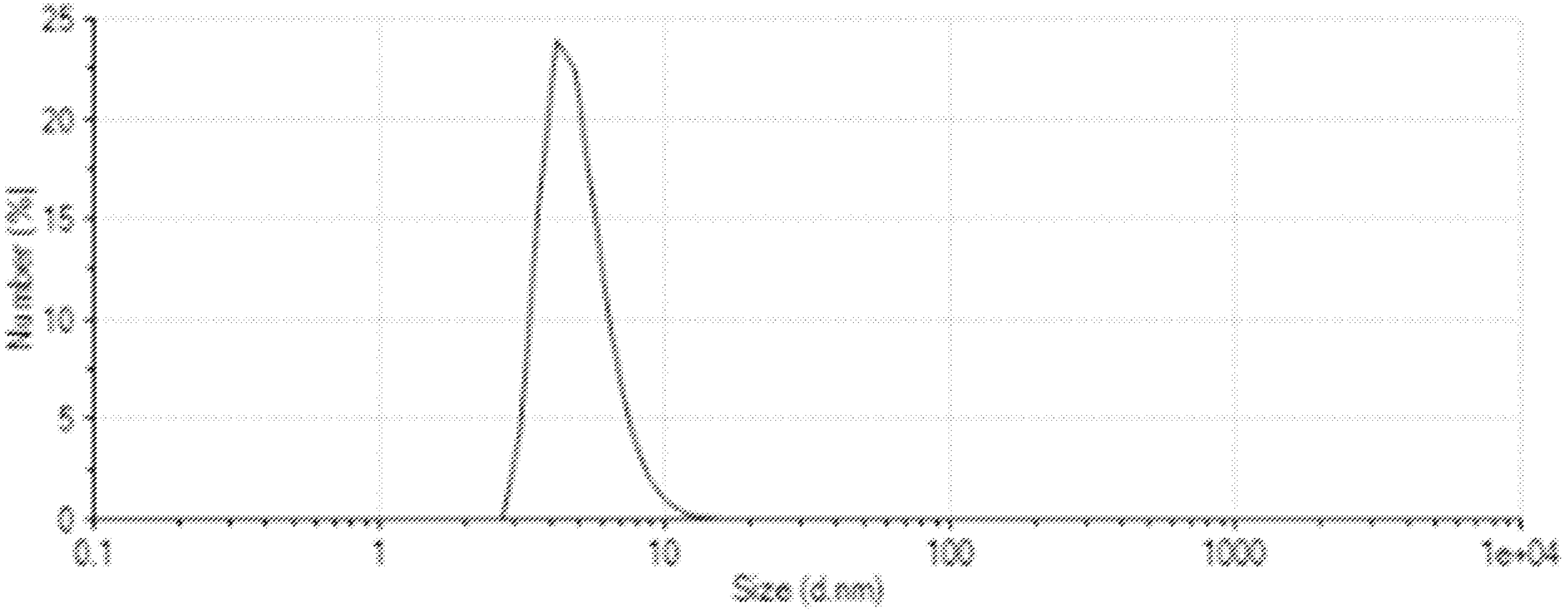

Number (%)
25
20
15
10
5
0
0.1
1
10
100
1000
1e+04
Size (d.nm)

FIG. 9B

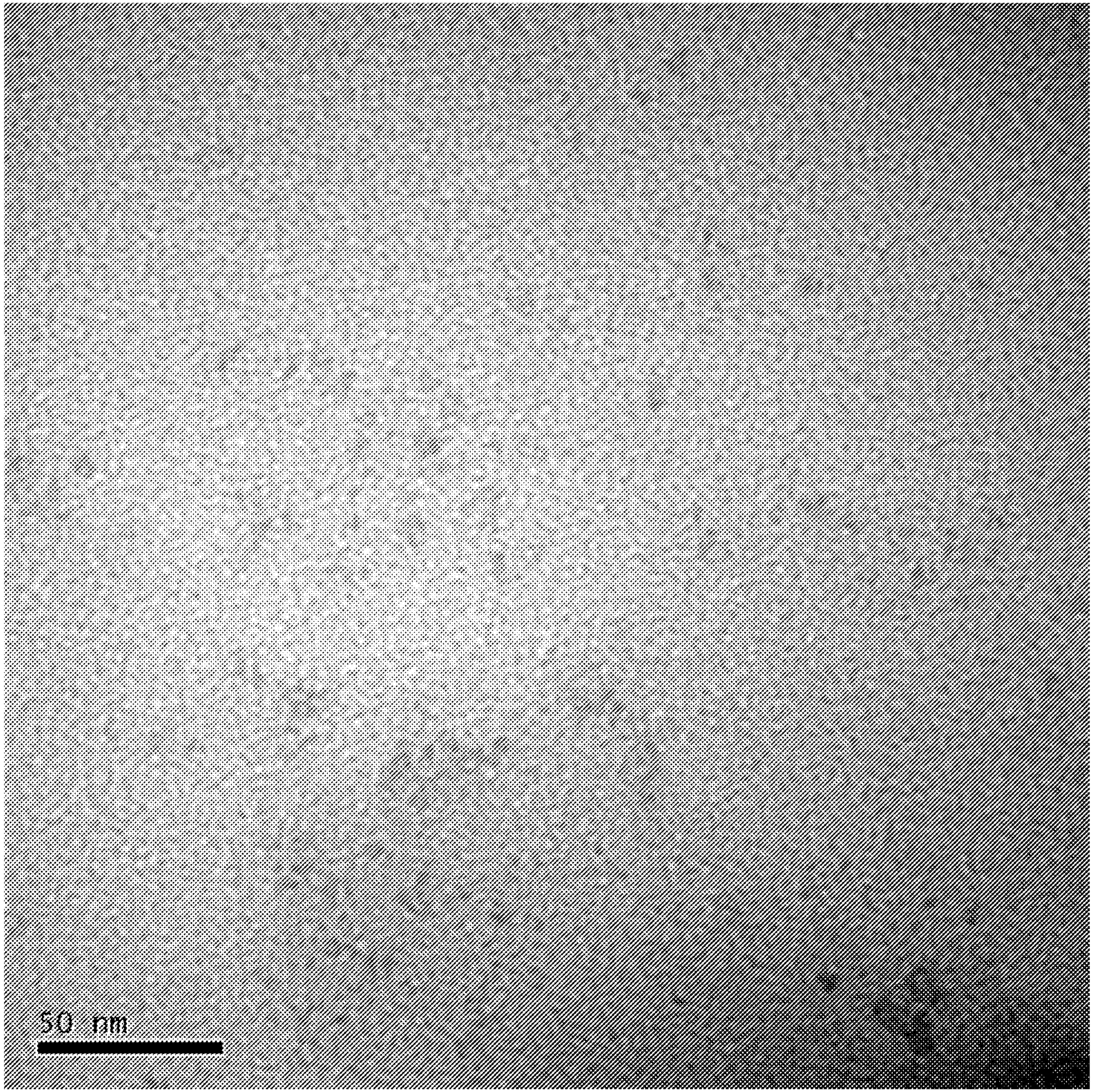


FIG. 10

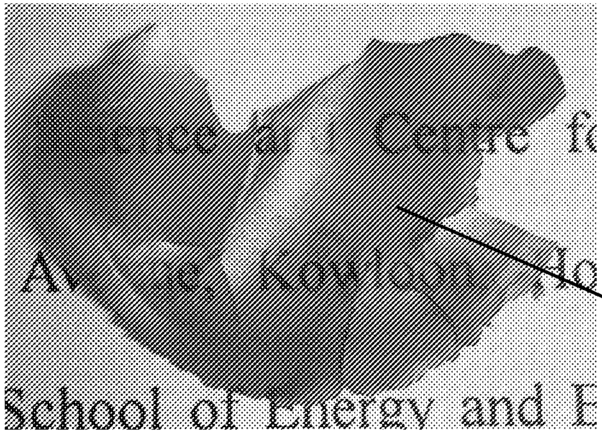


FIG. 11

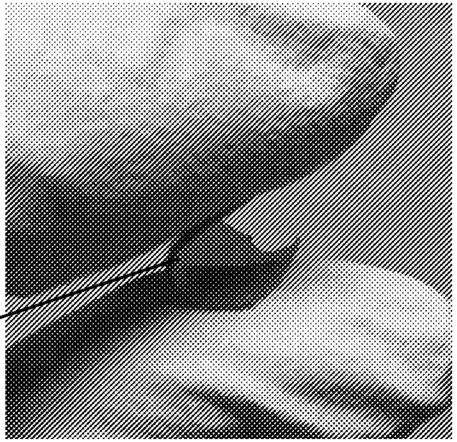


FIG. 12

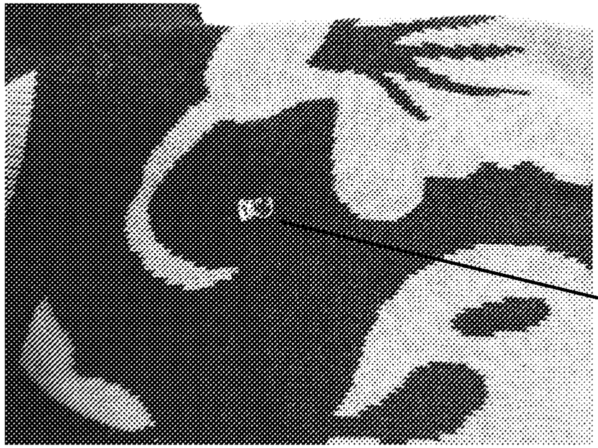


FIG. 13

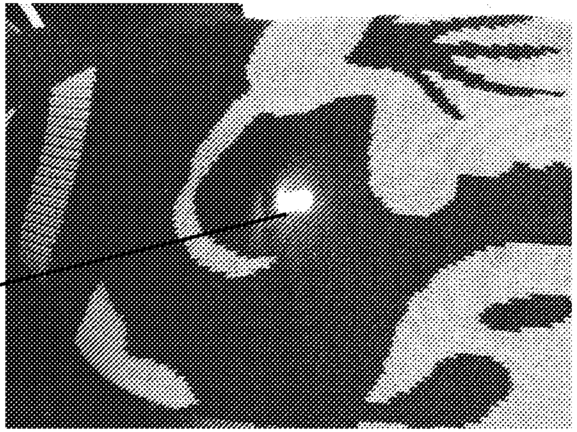


FIG. 14

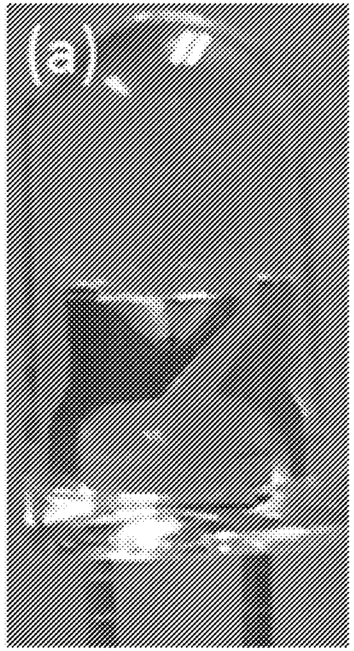


FIG. 15A

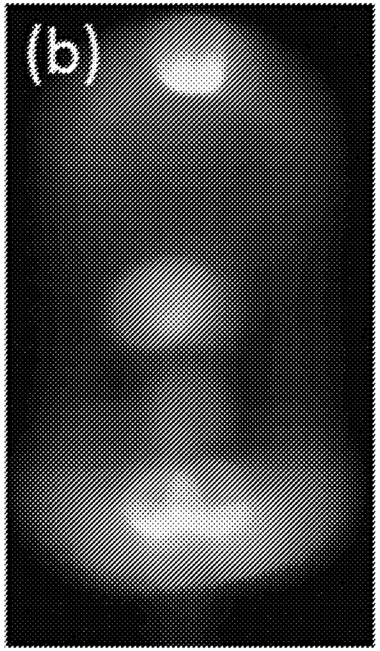


FIG. 15B

FIG. 15C

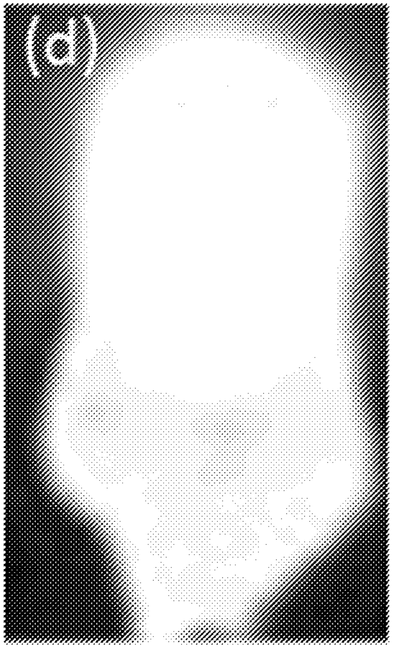


FIG. 15D

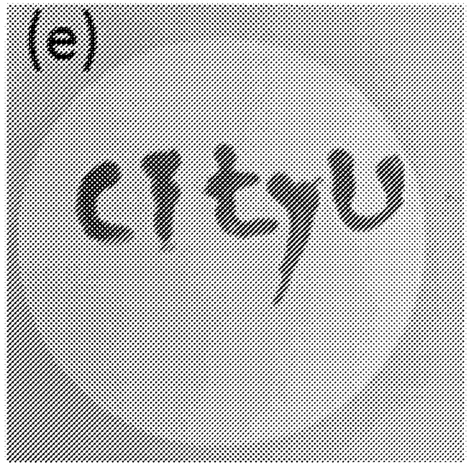


FIG. 15E

FIG. 15F

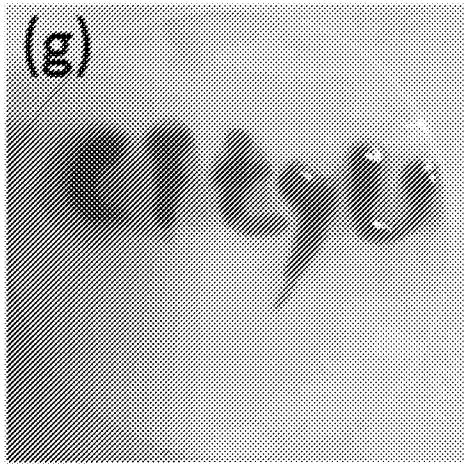


FIG. 15G

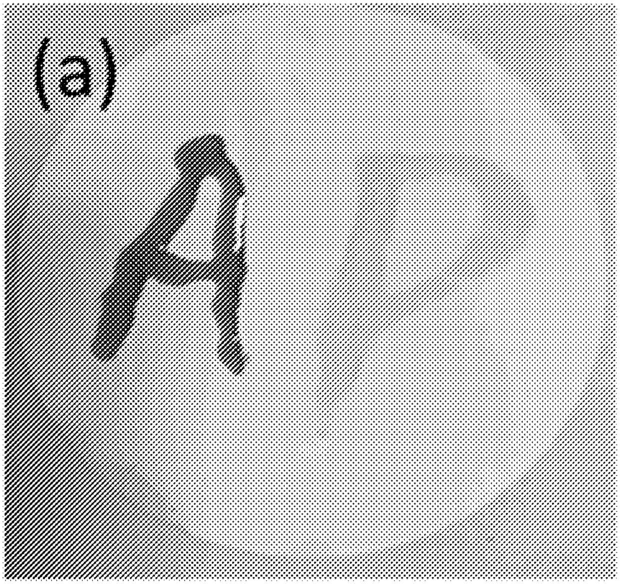


FIG. 16A

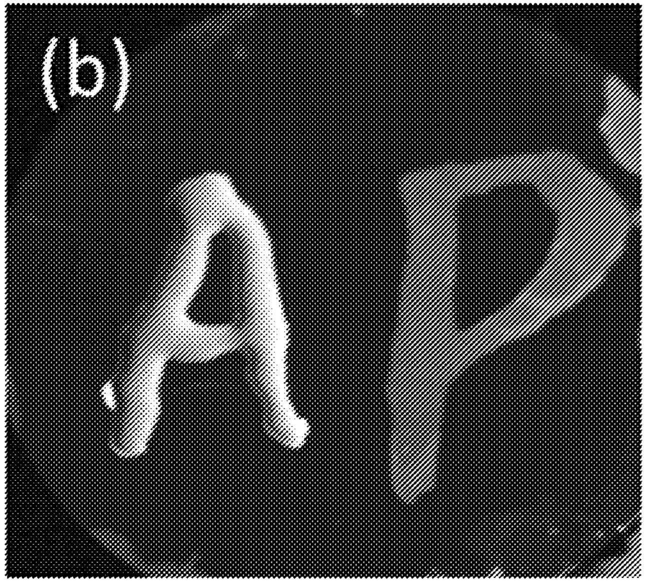


FIG. 16B

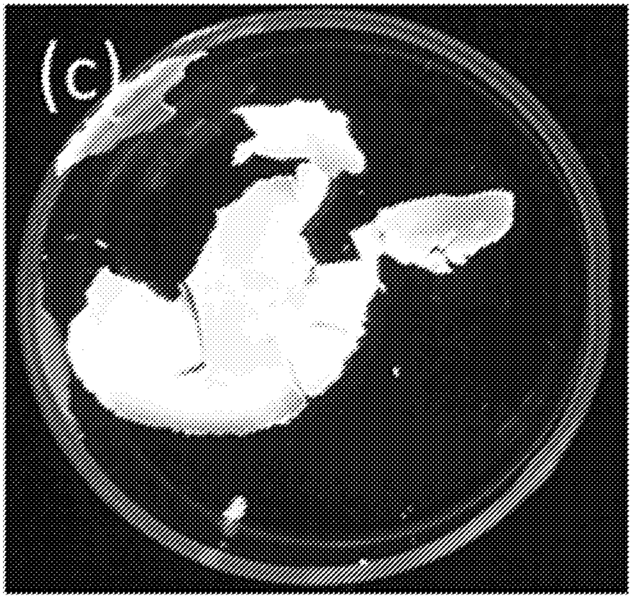


FIG. 16C

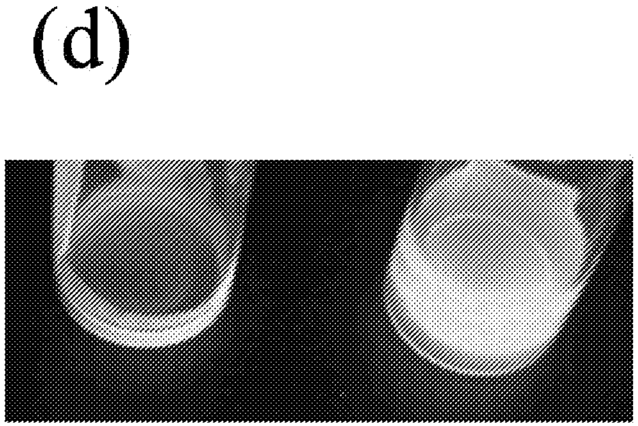


FIG. 16D

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2017/077451

A. CLASSIFICATION OF SUBJECT MATTER

H01L 21/44(2006.01)i

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)

H01L; H05K

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

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

CNABS，CNTXT，CNKI，VEN, DWPI：carbon, nitride, particle?, excitation, energy, wavelength, substance, electronic, emit +, light

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2004046261 A1 (NEC ELECTRONICS CORP) 11 March 2004 (2004-03-11) claims 1-212, pages 1-14 of description and figs. 1A-15F	1,15-18,22,28-30
A	JP 2008004615 A (EBARA CORP) 10 January 2008 (2008-01-10) the whole document	1-30
A	CN 102464887 A (达兴材料股份有限公司) 23 May 2012 (2012-05-23) the whole document	1-30
A	JP 2004014949 A (SONY CORP) 15 January 2004 (2004-01-15) the whole document	1-30

☐ 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 **27 April 2017**	Date of mailing of the international search report **16 May 2017**
Name and mailing address of the ISA/CN **STATE INTELLECTUAL PROPERTY OFFICE OF THE P.R.CHINA** **6, Xitucheng Rd., Jimen Bridge, Haidian District, Beijing 100088** **China**	Authorized officer **XIE,Shaojun**
Facsimile No. **(86-10)62019451**	Telephone No. **(86-10)62411593**

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2017/077451

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
US 2004046261 A1	11 March 2004	US 2010224995 A1	09 September 2010
		US 7842602 B2	30 November 2010
		US 2007212809 A1	13 September 2007
		US 7737555 B2	15 June 2010
		US 2007108620 A1	17 May 2007
		US 2012108060 A1	03 May 2012
		US 7687917 B2	30 March 2010
		US 8115318 B2	14 February 2012
		US 8642467 B2	04 February 2014
JP 2008004615 A	10 January 2008	None	
CN 102464887 A	23 May 2012	CN 102464887 B	04 September 2013
JP 2004014949 A	15 January 2004	None	