



(51) International Patent Classification:

G02B 26/02 (2006.01) G02B 6/12 (2006.01)
G02B 6/00 (2006.01) G02B 26/00 (2006.01)

(21) International Application Number:

PCT/US2018/014747

(22) International Filing Date:

22 January 2018 (22.01.2018)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/448,581 20 January 2017 (20.01.2017) US

(72) Inventors; and

(71) Applicants: LIU, Guoliang [US/US]; Suite 2250, 1700 Kraft Drive, Blacksburg, Virginia 24060 (US). KHAN, As-sad U. [US/US]; Suite 2250, 1700 Kraft Drive, Blacksburg, Virginia 24060 (US).

(74) Agent: VOGT, Keith A.; VOGT IP, Suite 200, 1033 South Blvd., Oak Park, Illinois 60302 (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, JO, 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))

(54) Title: PLASMONIC NANOPARTICLE LAYERS WITH CONTROLLED ORIENTATION

(57) Abstract: An article comprising one or more layers of plasmonic nanoparticles located between opposing layers of dielectric materials.

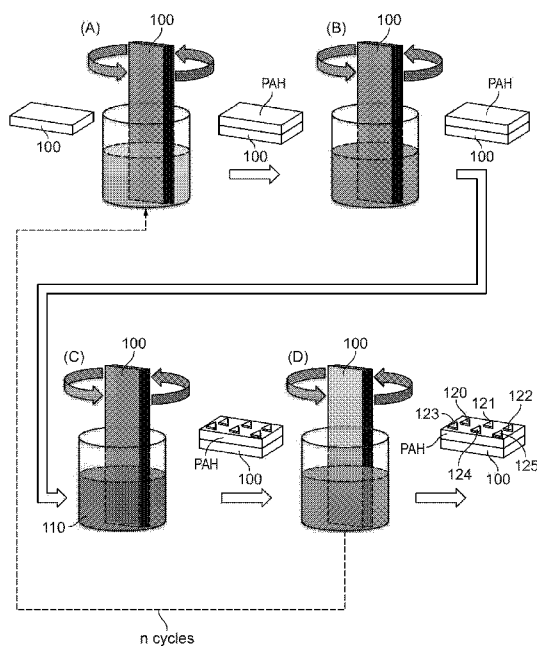


FIG. 1



TITLE

Plasmonic Nanoparticle Layers with Controlled Orientation

RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application No. 62448581, filed
5 January 20, 2017.

BACKGROUND OF THE INVENTION

[0002] Plasmonic nanoparticles are particles whose electron density may be coupled with
electromagnetic radiation of wavelengths that are far larger than the particle due to the
nature of the dielectric-metal interface between the medium and the particles. Articles
10 incorporating plasmonic nanoparticles have use in applications ranging from solar cells,
sensing, spectroscopy to cancer treatment.

BRIEF SUMMARY OF THE INVENTION

[0003] In one embodiment, the present invention provides methods that provide articles
having plasmonic nanoparticles by applying the particles using the layer-by-layer technique.
15 The method results in the formation of composite films of polyelectrolytes and plasmonic
nanoparticles.

[0004] In other embodiments, the present invention provides methods that form
nanoprisms having plasmonic properties.

[0005] In other embodiments, the present invention provides a layer of plasmonic
nanoparticles located between opposing layers of dielectric materials. The plasmonic
20 nanoparticles may be at least two different metals, have different plasmonic resonance
wavelengths.

[0006] In other embodiments, the plasmonic nanoparticles may be configured to absorb,
reflect, scatter, and transmit light.

25 [0007] In other embodiments, the layer of plasmonic nanoparticles may be comprised of
oriented nanoparticles, randomly oriented nanoparticles, or combinations thereof.

[0008] In other embodiments, the present invention provides an article comprising a
plurality of layers of plasmonic nanoparticles located between opposing layers of dielectric
materials. In other embodiments, at least two layers have plasmonic nanoparticles having
30 different plasmon resonance wavelengths. In other embodiments, at least two layers have
plasmonic nanoparticles having the same plasmon resonance wavelengths.

[0009] In yet other embodiments, each layer has plasmonic nanoparticles configured to
absorb, reflect, scatter, and transmit light.

[00010] In yet other embodiments, the layers of plasmonic nanoparticles are oriented parallel to substrate or layers, randomly oriented in all directions or has combinations thereof.

[00011] In other embodiments, the present invention provides an article comprising layers of nanoparticles wherein one of the layers has oriented plasmonic nanoparticles and at least one other layer has randomly oriented nanoparticles.

[00012] In other embodiments, the present invention provides an article comprising a plurality of layers of plasmonic nanoparticles sandwiched between layers of dielectric materials which may have different thicknesses, the same thicknesses or combinations thereof.

[00013] In other embodiments, the present invention provides an article comprising a plurality of layers wherein at least two layers of plasmonic nanoparticles have different surface densities, the same surface densities or combinations thereof.

[00014] In other embodiments, the dielectric material is a polymer.

[00015] In other embodiments, the present invention provides an article comprising a plurality of layers of plasmonic nanoparticles wherein at least two layers of the plasmonic nanoparticles have plasmonic nanoparticles having the same or different metals.

[00016] In other embodiments, the present invention provides an article comprising a plurality of layers of plasmonic nanoparticles wherein at least two layers of the plasmonic nanoparticles having the same or different metal oxides.

[00017] In other embodiments, the present invention provides an article comprising a plurality of layers of plasmonic nanoparticles wherein at least one layer of the plasmonic nanoparticles has metal plasmonic nanoparticles and another layer of the plasmonic nanoparticles has metal oxide plasmonic nanoparticles.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS

[00018] In the drawings, which are not necessarily drawn to scale, like numerals may describe substantially similar components throughout the several views. Like numerals having different letter suffixes may represent different instances of substantially similar components. The drawings illustrate generally, by way of example, but not by way of limitation, a detailed description of certain embodiments discussed in the present document.

[00019] Figures 1A, 1B, 1C and 1D are schematics that show a layer-by-layer assembly used in one embodiment of the present invention.

[00020] Figure 2 is the top view of a detector assembly used to measured optical properties (%T, %R, and %A) for an embodiment of the present invention.

[00021] Figures 3A, 3B and 3C are schemes for randomly distributed nanoplates in polymer matrix, corresponding optical image of the film and film cross-section SEM image showing nanoparticle.

[00022] Figures 3D, 3E and 3F are schemes for oriented nanoplates on substrate prepared by layer-by-layer assembly, corresponding optical image and SEM image showing most particles are lying flat on the substrate for an embodiment of the present invention.

[00023] Figures 3G and 3H show %T, %R, and %A spectrum plotted as a function of wavelength (400 – 2000 nm) at different angles (6° to 75°) at 1° increment for an embodiment of the present invention.

[00024] Figure 4A shows an optical image of colloidal solution of Ag nanoparticles of increasing sizes from a – h in accordance with an embodiment of the present invention.

[00025] Figure 4B shows representative TEM images of the colloidal nanoparticles where the size can be seen increasing for an embodiment of the present invention.

[00026] Figure 4C shows extinction spectra of the corresponding nanoparticles in Figure 4A for an embodiment of the present invention.

[00027] Figure 4D shows an optical image of one monolayer of Ag nanoparticles on glass slides showing various colors and increasing size from a–h in accordance with an embodiment of the present invention.

[00028] Figure 4E shows the corresponding representative scanning electron microscope (SEM) image of the deposited Ag nanoparticles in Figure 4D for an embodiment of the present invention.

[00029] Figures 4F shows the percentage transmittance, reflectance, and absorptance of the nanoparticles films for an embodiment of the present invention.

[00030] Figure 5A shows an incubation time study showing the optical image of glass slides which were placed in nanoparticles solution for various times for embodiments of the present invention.

[00031] Figure 5B is a corresponding SEM images of the deposited nanoparticles on glass slides shown in Figure 5A for an embodiment of the present invention.

[00032] Figure 5C shows percentage transmittance and reflectance of the corresponding samples for an embodiment of the present invention.

[00033] Figure 6 depicts the maximum percentage transmittance plotted for all the different incubation times shown in Figure 5 at different angles.

[00034] Figure 7 shows the percentage coverage, transmittance, and reflectance as a function of incubation time for an embodiment of the present invention for three different sizes of nanoparticles.

[00035] Figure 8A is an optical image of glass slides with selected samples of Ag nanoparticles having different number of layers deposited on top of each other depicting a more dense color as the number of layer increases,

[00036] Figure 8B is a corresponding SEM images of selected layers shown in Figure 8A where the top layer is not coated with polymer.

[00037] Figure 8C is a corresponding SEM images of selected layers (Fig. 8B) where the top layer is coated with a thin polymer layer.

[00038] Figure 8D is percentage transmittance, reflectance, and absorptance respectively through Ag nanoparticles films having various number of layers.

[00039] Figure 9A is an optical image of two different size of nanoparticles where **a** represents bigger nanoplates, **b** represents smaller nanoplates, and **a+b** represents combination of these layers of particles.

[00040] Figure 9B represents the corresponding SEM images of Figure 9A.

[00041] Figure 9C shows the percentage transmittance, reflectance, and absorptance of the two layers of different sizes of nanoparticles (**a+b**).

[00042] Figures 10A, 10B, 10C, 10D, 10E and 10F are 3D contour plots for *p*- and *s*-polarized light passing through a composite film of Ag nanoparticle and PAH. The heat maps show the intensity of light wavelengths stopped most and defines the range.

[00043] Figures 11A and 11B illustrate an article having multiple layers of plasmonic nanoparticles.

DETAILED DESCRIPTION OF THE INVENTION

[00044] Detailed embodiments of the present invention are disclosed herein; however, it is to be understood that the disclosed embodiments are merely exemplary of the invention, which may be embodied in various forms. Therefore, specific structural and functional details disclosed herein are not to be interpreted as limiting, but merely as a representative basis for teaching one skilled in the art to variously employ the present invention in virtually any appropriately detailed method, structure or system. Further, the terms and phrases

used herein are not intended to be limiting, but rather to provide an understandable description of the invention.

[00045] As shown in Figures 1A-1D, some embodiments of the present invention provide a layer-by-layer technique used to prepare composite films of polyelectrolytes and plasmonic nanoparticles on articles or substrates. In a preferred embodiment, Ag plasmonic nanoparticles may be used.

[00046] As shown for one embodiment, a substrate or article 100, which may be a clean glass slide, is first dipped in dilute solution (10 mM) of polyelectrolyte solution (Figure 1A) followed by rinsing step with deionized (DI) water (Figure 1B). It is then dipped in nanoparticles solution 110 for various times (Figure 1C) and rinsed afterwards with DI water (Figure D).

[00047] The use of polyelectrolytes in thin films is known to those of skill in the art for one embodiment poly (allylamine hydrochloride) (PAH) cationic polymer and poly (acrylic acid) (PAA) anionic polymer were used for multiplayer thin film fabrication resulting in the deposition of plasmonic nanoparticles 120-124 as shown in Figure 1D.

[00048] The Si-O on glass slides or other substrates provides a negative charge and PAH which is cationic polymer can electrostatically attach to the glass slides or substrates. Strong oxidation agents like RCA can also be used to increase the negative charge on glass slides or substrates. PAH can saturate the surface with a monolayer, hence giving rise to a positive surface charge overall. The Ag nanoparticles may be negatively charged. In other embodiments, the Ag nanoparticles are citrate-capped and hence negatively charged and can be electrostatically deposited on the PAH layer. The glass slides or substrates may be rinsed with water between all deposition steps.

[00049] Orientation of plasmonic nanoplates have a prominent effect on their optical properties. Figures 3A-F show two different cases where the nanoparticles are either randomly distributed in a PMMA matrix or they are oriented on substrate using PAH. The optical properties in Figure 3G-H show that the % reflectance is minimum for randomly distributed nanoparticles (G) while it increases for the oriented nanoparticles (H). As shown in Figure 3A, plasmonic nanoparticles 130-135 are randomly oriented in all directions to layer 140. As shown in Figure 3D, plasmonic nanoparticles 160-165 are oriented parallel to layer 170.

[00050] In a preferred embodiment, Ag nanoprisms were synthesized using seed mediated process in aqueous medium. Figures 4A and 4C show the optical image and extinction peaks

of the colloidal solution. For plate like nanoparticles in the visible range (400 - 700 nm), sharp colors can be seen owing to the in-plane dipole. When the in-plane dipole is above 700 nm, it does not impart the intense color, instead light colors are observed because of the in-plane quadrupole peaks associated with plate like structures. The in-plane quadrupole is a characteristic of plate like nanoparticles. Figure 4B shows a typical TEM images for selected nanoparticles and it was observed that majority of nanoparticles were prismatic in shape except the smaller nanoparticles which were more rounded.

[00051] In yet other embodiments, a dipping machine may be used. Using a dipping machine, these nanoparticles were deposited on glass slides or substrates using a layer-by-layer technique. Figure 4D shows the optical image of the glass slides after the nanoparticles were deposited on it. The dipping time (i.e. incubation) was 120 min for these samples and therefore the glass slides have dark colors due to high density of nanoparticles as can be evidenced from the SEM images in Figure 4E. Based on the nanoparticle sizes, the transmittance spectrum can be seen in Figure 4F. The optical measurements were taken using Cary Universal Measurement Accessory (UMA) with Cary 5000, the schematic of which is shown in Figure 2. Here non-polarized light was used. Transmittance profiles revealed that the wavelength of light being stopped by various size of nanoparticles is dependent on their localized surface plasmonic peak position. It was also revealed that the smaller nanoparticles have lower reflectance compared to bigger nanoparticles as can be seen in Figure 4F. Reflectance of light increases as the size of plate as reported in previous studies. The % absorbance spectrum can be seen in Figure 4F. These nanoparticles have higher absorbance than reflectance.

[00052] Incubation time also plays a role in using polyelectrolytes for depositing plasmonic nanoparticles. Figure 5A shows the optical image of the nanoparticles deposited on substrates for different time intervals. The color becomes more and more intense as the incubation time is increased. Corresponding FE-SEM image in Figure 5B revealed that the nanoparticles density increases from 10–300 min. Physically from the optical image and SEM images it can be witnessed that the films become saturated around 120 min but looking at the % transmittance (%T) and % reflectance (%R) in Figure 5C, which show a shoulder peak increasing. The shoulder peak appearance may be attributed to the interparticle spacing being decreased and in some cases overlapping, leading to localized surface plasmon coupling (LSPC) effect. Hence as the incubation time increases more and more particles come closer to each other and overlap leading to this coupling phenomena. The %

transmittance also reveals that as the density of nanoparticles increases, more light is being stopped at the localized surface plasmon resonance (LSPR) of nanoparticles. A point is reached where the maximum transmittance at the LSPR of nanoparticles stops while the coupling effect keeps increasing. Similarly, % reflectance increases as the density of the nanoparticles increases. The coupling effect also leads to reflectance of higher wavelength light as can be witnessed in Figure 5C. The maximum transmittance of sample 5 is plotted as function of incidence angle in Figure 6. The surface coverage, % T, and % R is plotted as a function of incubation time for three different sizes ($a < b < c$) in Figure 7. It can be quantitatively seen that around 90 min the surface starts to saturate with no significant increase in the surface coverage. The maximum surface coverage is around 55% for Figure 5, 300 min sample and hence still 45% of the surface is empty which can be useful for light transmittance.

[00053] Decreasing transmittance can be done either through using a longer incubation time or using multiple layers of nanoparticles on top of each other. Figure 8A show optical images of multilayer samples. Their corresponding SEM images for selected samples are also shown in Figure 8B and 8C respectively. PMMA is used as a spacer between two layers of nanoparticles which helps in keeping the nanoparticles apart and helps in avoiding undesirable coupling. If PMMA is not used and only PAH-PAA are used, then we will see a lot of undesirable coupling effects. Decreasing transmittance and increasing reflectance and absorbance for a LSPR are shown in Figure 8D. Thus, increasing the number of layers also leads to blocking other higher wavelengths of light.

[00054] This multiple layer strategy can also be applied to prepare samples with two different types of nanoparticles. For example, shown in Figure 9 is an example of big nanoparticles in NIR range which are useful for heat reflecting windows and another layer of smaller nanoparticles absorbing in visible region can be added for aesthetic purposes. This filtering ability can be applied to many useful applications. The nanoparticles are well separated in SEM images in Figure 9B and the plasmonic peaks are well separated in Figure 9C.

[00055] In coating applications, it is important to know the absorbance of the films as that defines the color being imparted. Therefore, polarization dependence of the optical properties of these films was plotted in Figures 10A-10F. In Figures 10A-C, *p*-polarized was used and the transmittance, reflectance, and absorbance was measured at different angles from 6° to 58° with 1° increment. Similarly, *s*-polarized was plotted in Figures 9D-F. These

3D contour plots gave an idea into the exact range of wavelength where the light is not transmitted and is either reflected or absorbed.

[00056] **Materials and Methods**

[00057] Materials: Silver nitrate (>99.9999%) (204390), sodium borohydride (>99.99%) (480886), sodium citrate tribasic dihydrate (>99.0%) (S4641), ascorbic acid (>99.0%) (A5960), poly(allylamine hydrochloride) (PAH) (average M_w - 17,500 g mol⁻¹) (283215), poly(acrylic acid) ((PAA) (M_v -450,000 g mol⁻¹), and poly(sodium 4-styrenesulfonate) (PSSS) (average M_w -1,000 Kg mol⁻¹) (434574) were purchased from Sigma-Aldrich and used as received. Plain glass microscope slides (25 x 75 mm) (Cat. No. 12-544-4) were bought from Fisher Scientific and used as the substrate or article. Other substrates of various materials, sizes and shapes may also be used. Nanoparticle synthesis was carried out in ultrapure deionized (DI) water obtained from Thermo Scientific™ Barnstead™ GenPure™ Pro water purification system at 17.60 MQ-cm, while rinsing steps of the glass slides after deposition in polyelectrolyte or nanoparticles solutions were carried out with DI water.

[00058] Synthesis of Ag Nanoparticles: Ag nanoparticles were synthesized following a seed-mediated method. Ag seeds may be synthesized as follows. First, 0.25 mL of PSSS (5 mg/mL) and 0.3 mL of ice-cold NaBH₄ (10 mM) aqueous solutions were added to a 5 mL solution of sodium citrate (2.5 mM) under constant stirring. Afterwards, 5 mL of AgNO₃ (0.5 mM) was added to the solution at a rate of 2 mL/min using Cole-Parmer syringe pump (Cat. No. 78-8210C). The seed solution was then immediately covered in an Al foil to prevent from light exposure. After 5 min, the stirring was stopped.

[00059] To synthesize Ag nanoparticles, 1.5 mL of 10 mM ascorbic acid solution was added to 254 mL of water under vigorous stirring, followed by the addition of a certain amount of seed solutions (ranged from 200 to 2000 μ L) to prepare nanoparticles of various sizes. Afterwards, 6 mL of AgNO₃ (5 mM) solution was added to the mixture at a rate of 2 mL/min. The solution changed color indicating the growth of Ag nanoparticles. Finally, 10 mL of sodium citrate (25 mM) solution was added to the product solution to stabilize the nanoparticles. To obtain large Ag nanoparticles with a resonance peak above 800 nm, small Ag nanoplate seeds were prepared by the addition of 75 μ L of AA and 10 μ L of Ag spherical seeds to 10 mL of water. This was followed by the addition of 3 mL of 0.5 mM AgNO₃ at 1 mL/min. Once the nanoparticles were prepared they were used as seeds to be grown into larger nanoplates. To prepare large Ag nanoparticles 150 μ L of AA was added to 20 mL of water followed by varying amounts from 0.5–1 mL of the Ag nanoplates were added to this

solution. Then 6 mL of 0.5 mM of AgNO₃ was added to this mixture at a rate of 2 mL/min. Once the synthesis was complete, 1 mL of sodium citrate was added to stabilize the nanoparticles.

[00060] Transmission Electron Microscopy (TEM): 5–10 µL of Ag nanoparticles aliquots were drop-casted on copper grids to prepare TEM samples. The samples were dried overnight at room temperature and imaged using Philips EM420 transmission electron microscope at an accelerating voltage of 120 keV.

[00061] Layer-by-Layer Fabrication of Ag Nanoparticles and Polyelectrolytes: Thin films of nanoparticle-polymer nanocomposites were prepared using a layer-by-layer (LbL) technique using dipping machine. First, two dilute solutions of cationic PAH and anionic PAA polyelectrolytes with a concentration of 10 mM (based on the monomer) were prepared in DI water. The pH of both solutions was brought to neutral (*i.e.* 7) by adding either hydrochloric acid (HCl) or sodium hydroxide (NaOH). The neutral pH helped in not degrading the nanoparticles. Two 120 mL beakers were filled with 100 mL PAH solution and 100 mL colloidal solution of as-synthesized Ag nanoparticles for deposition. Six additional beakers were filled with DI water for rinsing. All eight beakers were placed on the rotating stage of a dipping machine. The PAH solution and Ag nanoparticles were separated by three beakers of DI water. The glass slides were dipped in the PAH solution for 5 min which led to the deposition of positively charged PAH onto the glass slides due to electrostatic interaction. To remove any potentially accumulated polyelectrolyte, the glass slides were rinsed in DI water for 40 sec and this process was repeated three times. After rinsing, the glass slides were immersed in the colloidal solution of Ag nanoparticles for various amount of time (10–300 min). Ag nanoparticles had negatively charged surface due to adsorbed sodium citrate molecules therefore the nanoparticles were able to adhere onto the positively charged PAH layers attached on the glass slides. Afterwards, the glass slides were rinsed three times in DI water for 30 sec each. The deposition cycle was repeated as needed.

[00062] Random Orientation of Ag Nanoparticles: Ag nanoparticles in aqueous medium were centrifuged at 10000 rpm for 30 min and redispersed in DMF. The nanoparticles were functionalized with 1 wt.% thiol-terminated poly (methyl methacrylate) (PMMA-SH) in DMF for 24h and centrifuged again at 10000 rpm for 30 min. Supernatant was removed and the nanoparticles were redispersed in 5 wt.% PMMA-SH in Toluene. The nanocomposite films were casted on the glass surface and then kept in fume hood to vaporize the solvent for 24-48 h.

[00063] Field Emission Scanning Electron Microscopy (FE-SEM): To image the nanoparticles on glass slides, the samples were coated with high resolution Iridium with a thickness of 1.5–3 nm. They were then imaged using SEM where the WD was 4 mm, EHT was 10kV and InLens detector was used.

5 [00064] Optical Measurement using UV-Visible Near-Infrared (NIR) Spectroscopy with Cary Universal Measurement Accessory (UMA): To perform optical measurement including % absorptance, transmittance, and reflectance, we used universal measurement accessory (UMA) with Agilent Cary 5000 UV-visible-NIR spectrophotometer. A schematic of the setup is shown in Figure 2. Here the glass slide with nanoparticles was mounted on the stage
10 where the full light beam could pass through it. For Figure 4 and 5 the sample angle was 6° for % reflectance and % transmittance. In Figure 3 the angle was changed from 6° to 75° with 1° increment step and the data was plotted in Origin.

[00065] Figures 11A and 11B illustrate other embodiments of the present involving an article of manufacture. As shown in Figure 11A, article 200 is comprised of a plurality of
15 layers 201-204 which may optionally be located on substrate 210. Sandwiched between layers 200-201 are layers of plasmonic nanoparticles 220-224, 230-234 and 240-244.

[00066] Plasmonic nanoparticles 220-224, 230-234 and 240-244 may be of the same size as shown. In addition, the plasmonic nanoparticles may be configured as described above. For example, plasmonic nanoparticles 220-224, 230-234 and 240-244 may be randomly
20 orientated as shown in Figure 3A or may have the same orientation as shown in Figure 3D.

[00067] In other embodiments, plasmonic nanoparticles 220-224, 230-234 and 240-244 may have different plasmon resonance wavelengths, the same plasmon resonance wavelengths, or combinations thereof. In yet other embodiments, each layer of article 200 has plasmonic nanoparticles configured to absorb, reflect, and transmit light as well as
25 combinations thereof. In yet other embodiments, the layers of plasmonic nanoparticles of article 200 are orientated the same, randomly orientated or are combinations thereof.

[00068] Plasmonic nanoparticles 220-224, 230-234 and 240-244 may be comprised of the same metal, different metals, the same metal oxide or different metal oxides as well as combinations thereof. Plasmonic nanoparticles 220-224, 230-234 and 240-244 may also
30 have different surface densities or the same surface densities.

[00069] In other embodiments, layers 201-204 of article 200 may have different thicknesses, the same thicknesses or combinations thereof. In other embodiments, the dielectric material is a polymer, metal oxides as well as combinations thereof.

[00070] As shown in Figure 11B, article 300 is comprised of a plurality of layers 301-304 which may optionally be located on substrate 310. Sandwiched between layers 300-301 are layers of plasmonic nanoparticles 320-328, 330-336 and 340-343.

[00071] Plasmonic nanoparticles 320-328, 330-336 and 340-343 may be of varying sizes as shown. In addition, the plasmonic nanoparticles may be configured as described above. For example, plasmonic nanoparticles 320-328, 330-336 and 340-343 may be randomly orientated as shown in Figure 3A or may have the same orientation as shown in Figure 3D.

[00072] In other embodiments, plasmonic nanoparticles 320-328, 330-336 and 340-343 may have different plasmon resonance wavelengths, the same plasmon resonance wavelengths, or combinations thereof. In yet other embodiments, each layer of article 300 has plasmonic nanoparticles configured to absorb, reflect, and transmit light as well as combinations thereof. In yet other embodiments, the layers of plasmonic nanoparticles of article 300 are oriented the same, randomly oriented or are combinations thereof.

[00073] Plasmonic nanoparticles 320-328, 330-336 and 340-343 may be comprised of the same metal, different metals, the same metal oxide or different metal oxides as well as combinations thereof. Plasmonic nanoparticles 320-328, 330-336 and 340-343 may also have different surface densities or the same surface densities.

[00074] In other embodiments, layers 301-304 of article 300 may have different thicknesses, the same thicknesses or combinations thereof. In other embodiments, the dielectric material is a polymer, metal oxides as well as combinations thereof.

[00075] While the foregoing written description enables one of ordinary skill to make and use what is considered presently to be the best mode thereof, those of ordinary skill will understand and appreciate the existence of variations, combinations, and equivalents of the specific embodiment, method, and examples herein. The disclosure should therefore not be limited by the above described embodiments, methods, and examples, but by all embodiments and methods within the scope and spirit of the disclosure.

WHAT IS CLAIMED IS:

1. A structured layer comprising: a layer of plasmonic nanoparticles located between opposing layers of dielectric materials.
- 5 2. The structured layer of claim 1 wherein said plasmonic nanoparticles are at least two different metals.
3. The structured layer of claim 1 wherein said plasmonic nanoparticles include nanoparticles having different plasmonic resonance wavelengths.
- 10 4. The structured layer of claim 1 wherein said types of said plasmonic nanoparticles are configured to absorb, reflect, scatter, and transmit light.
5. The structured layer of claim 1 wherein said layer of plasmonic nanoparticles are oriented parallel to said layer.
6. The structured layer of claim 1 wherein said layer of plasmonic nanoparticles is a randomly oriented in all directions to said layer.
- 15 7. An article comprising: a plurality of layers of plasmonic nanoparticles located between opposing layers of dielectric materials.
8. The article of claim 7 wherein at least two layers have plasmonic nanoparticles having different plasmon resonance wavelengths.
9. The article of claim 7 wherein at least two layers have plasmonic nanoparticles having the same plasmon resonance wavelengths.
- 20 10. The article of claim 7 wherein each layer has plasmonic nanoparticles configured to absorb, reflect, scatter, and transmit light.
11. The article of claim 7 wherein the plasmonic nanoparticles in said layers are orientated.
- 25 12. The article of claim 7 wherein the plasmonic nanoparticles in said layers are randomly orientated.
13. The article of claim 7 wherein one of said layers has plasmonic nanoparticles oriented parallel to said layer and at least one other layer has nanoparticles randomly oriented in all directions to said layer.
- 30 14. The article of claim 7 wherein at least two layers of dielectric materials have different thicknesses.
15. The article of claim 7 wherein at least two layers of dielectric materials have the same thicknesses.

16. The article of claim 7 wherein at least two layers of plasmonic nanoparticles have different surface densities.

17. The article of claim 7 wherein at least two layers of plasmonic nanoparticles have the same surface densities.

5 18. The article of claim 7 wherein said dielectric material is a polymer.

19. The article of claim 7 wherein said dielectric material is a metal oxide.

20. The article of claim 7 wherein at least two layers of said plasmonic nanoparticles have plasmonic nanoparticles having the same or different metals.

10 21. The article of claim 7 wherein at least two layers of said plasmonic nanoparticles have plasmonic nanoparticles having the same or different metal oxides.

22. The article of claim 7 wherein at least one layer of said plasmonic nanoparticles has metal plasmonic nanoparticles and another layer of said plasmonic nanoparticles has metal oxide plasmonic nanoparticles.

15 23. The structured layer of claim 1 wherein said layer of plasmonic nanoparticles contains plasmonic nanoparticles configured to absorb, reflect, scatter, and transmit light as well as combinations thereof.

24. The article of claim 7 wherein each layer of plasmonic nanoparticles contains plasmonic nanoparticles configured to absorb, reflect, scatter, and transmit light as well as combinations thereof.

20

1/16

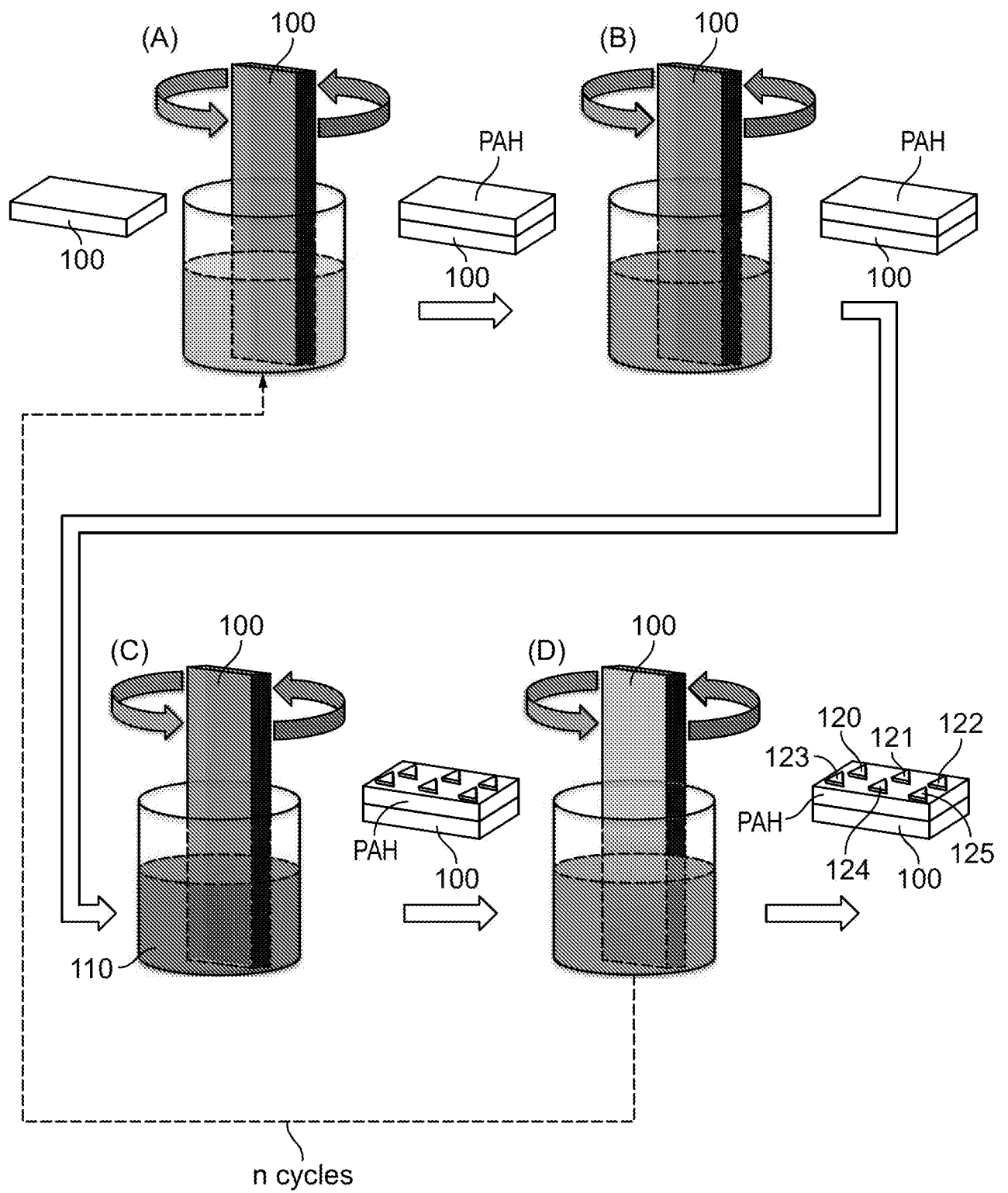


FIG. 1

2/16

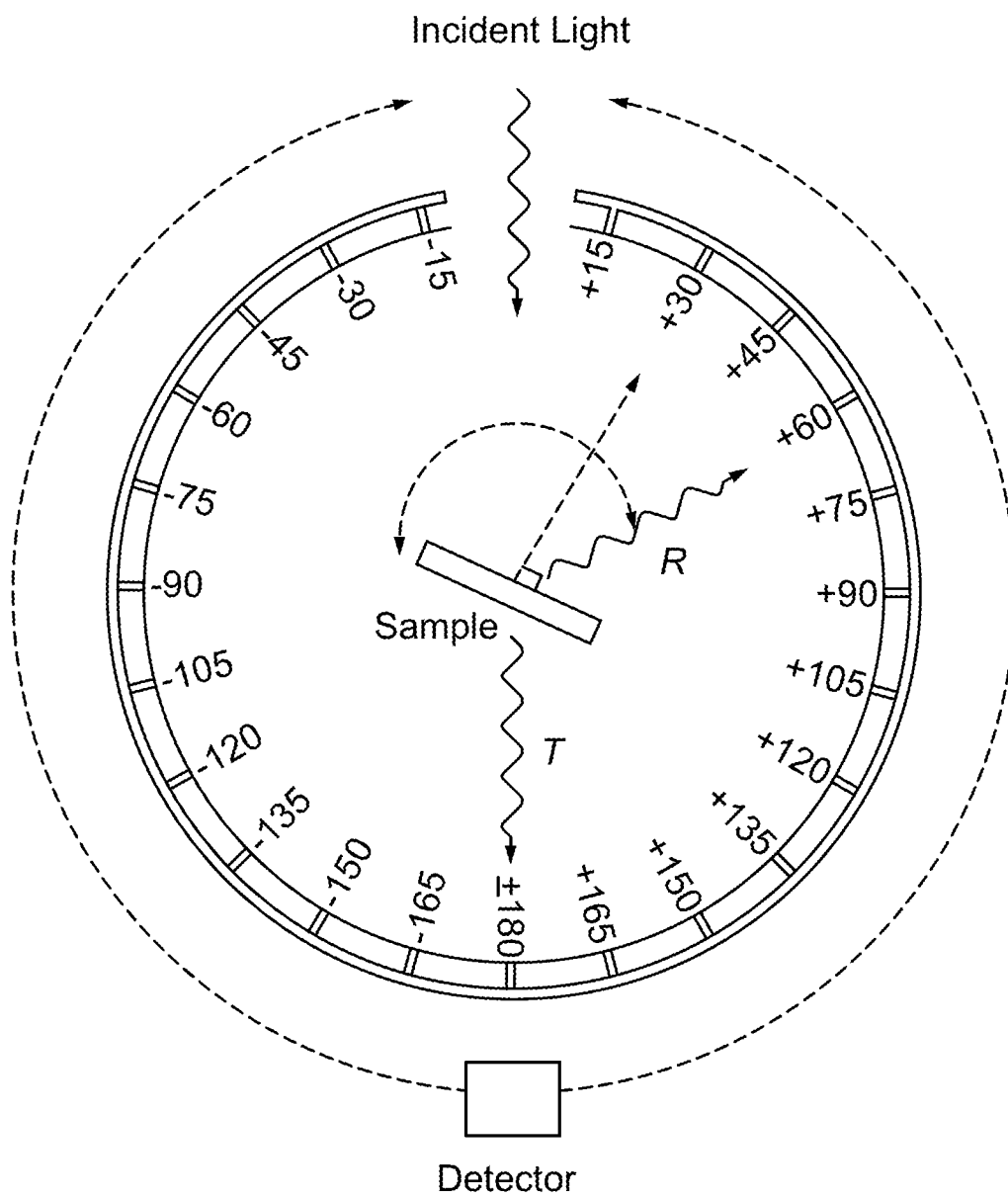


FIG. 2

3/16

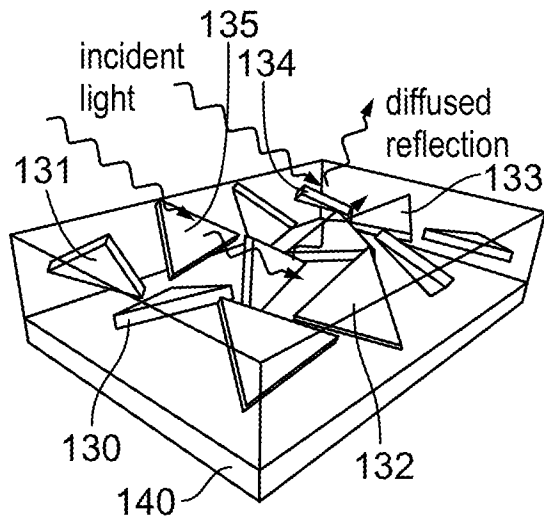


FIG. 3A

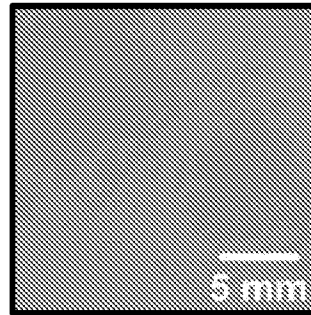


FIG. 3B

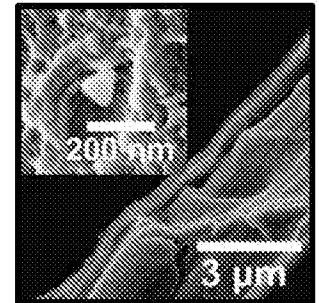


FIG. 3C

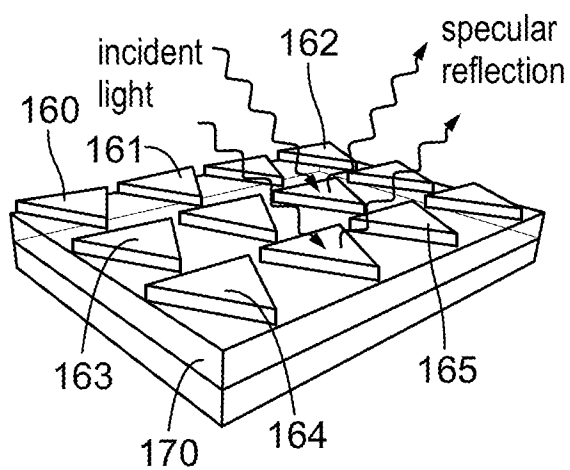


FIG. 3D

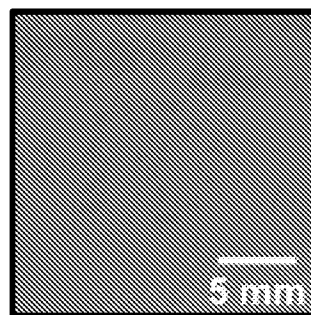


FIG. 3E

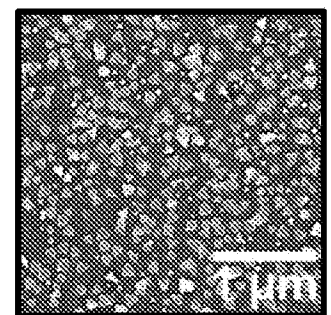


FIG. 3F

4/16

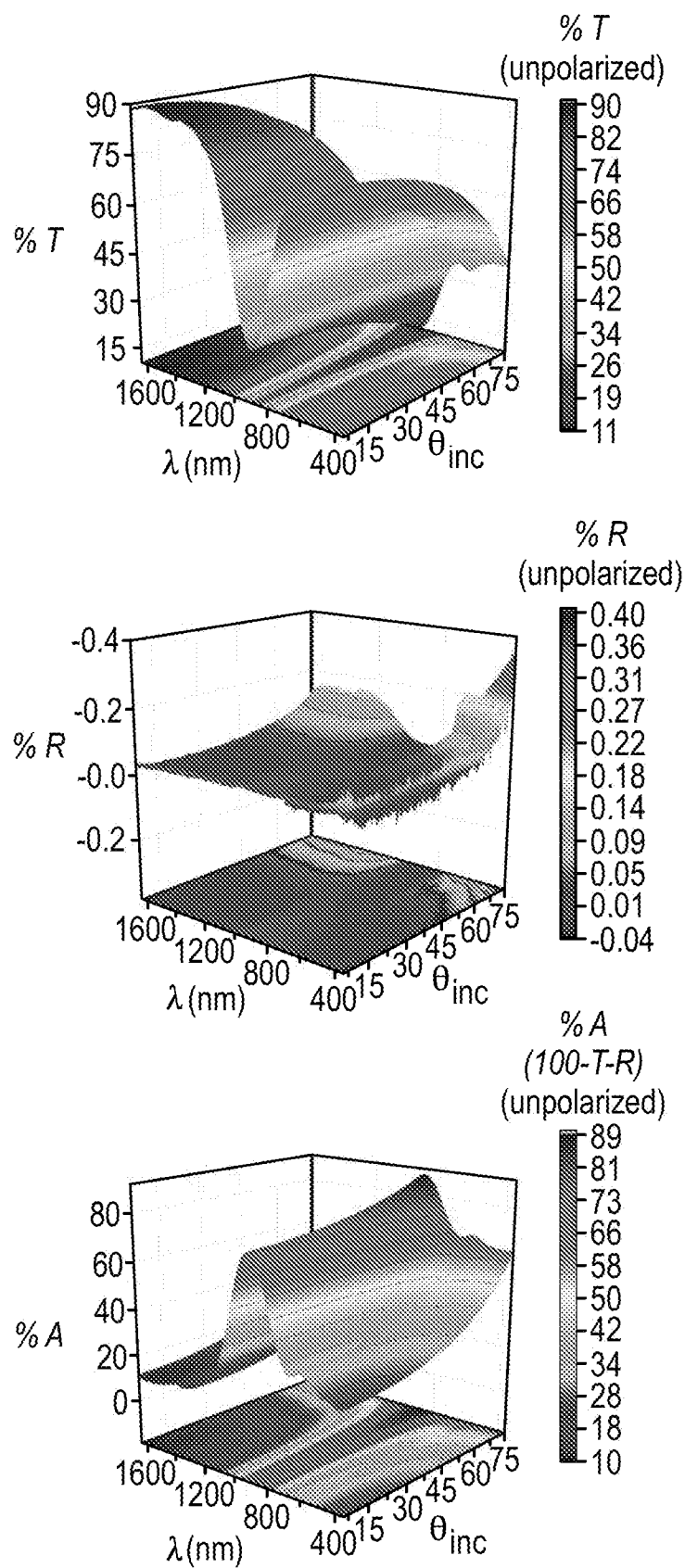


FIG. 3G

5/16

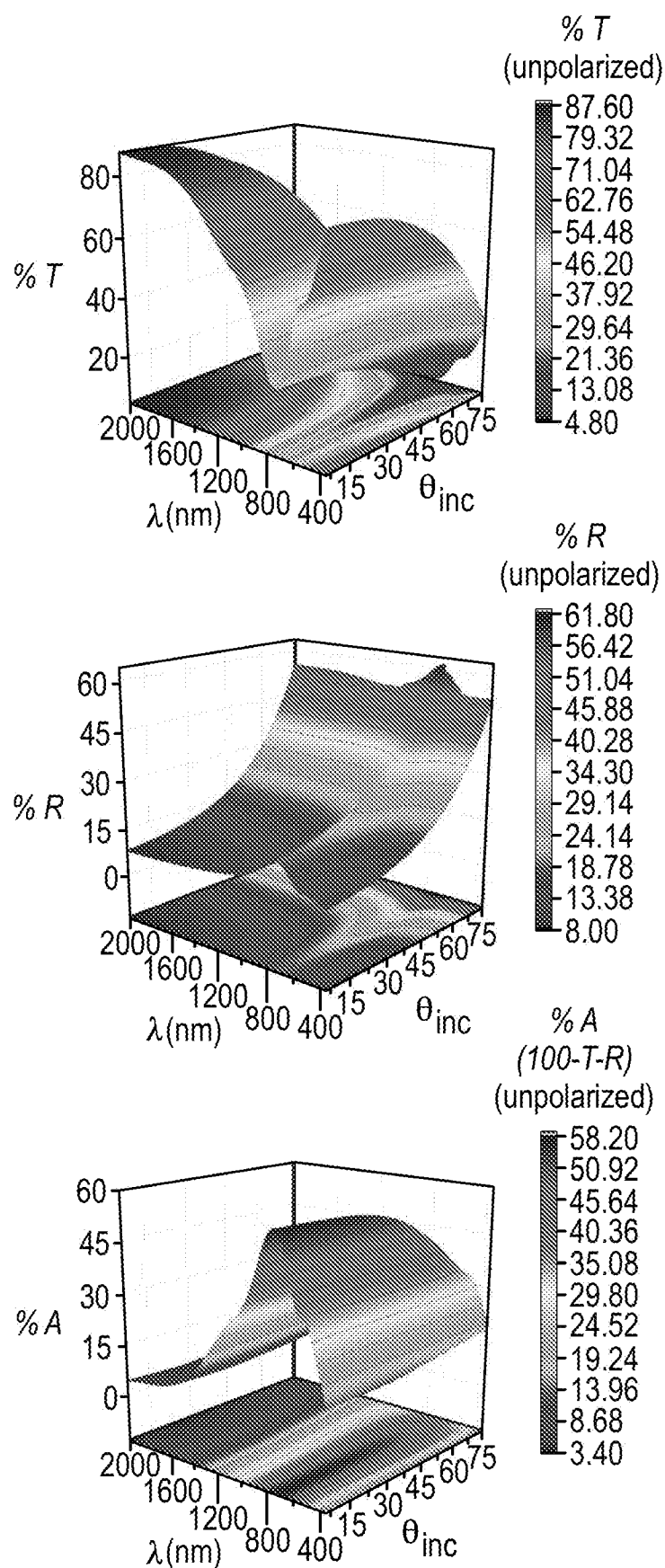


FIG. 3H

6/16

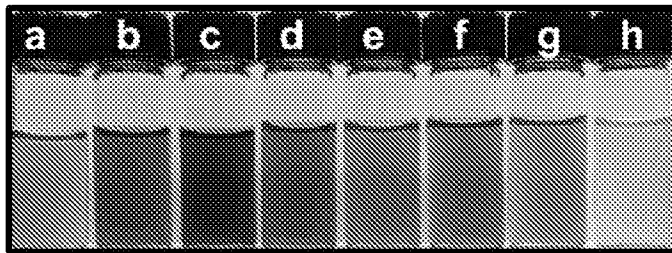


FIG. 4A

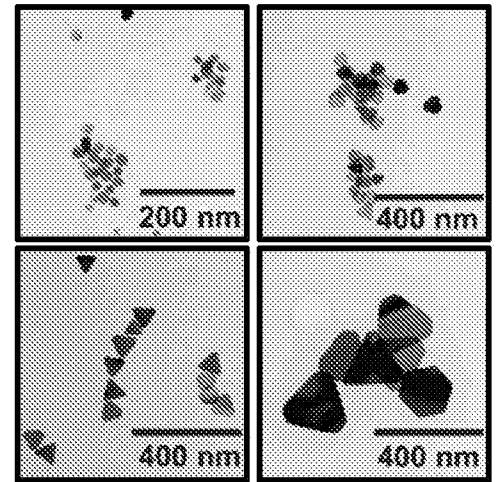


FIG. 4B

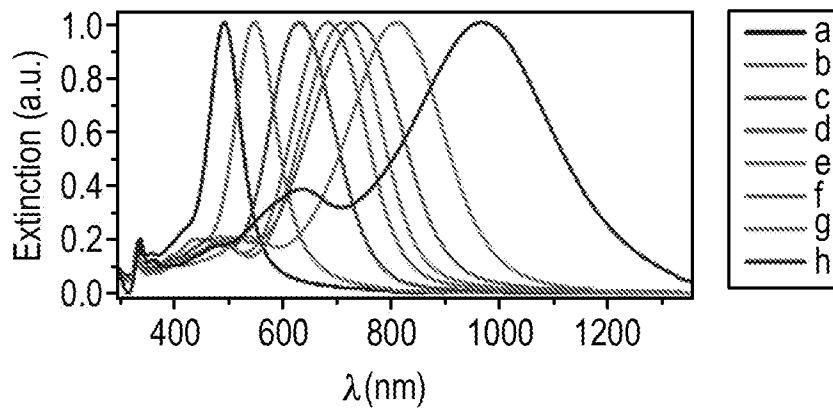


FIG. 4C

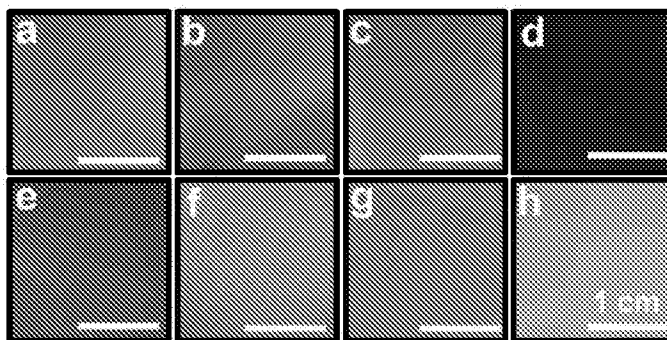


FIG. 4D

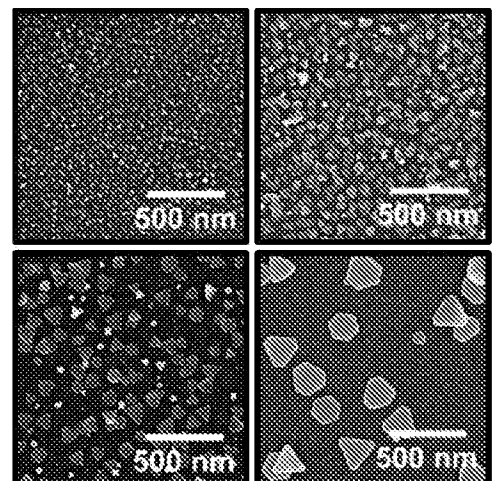


FIG. 4E

7/16

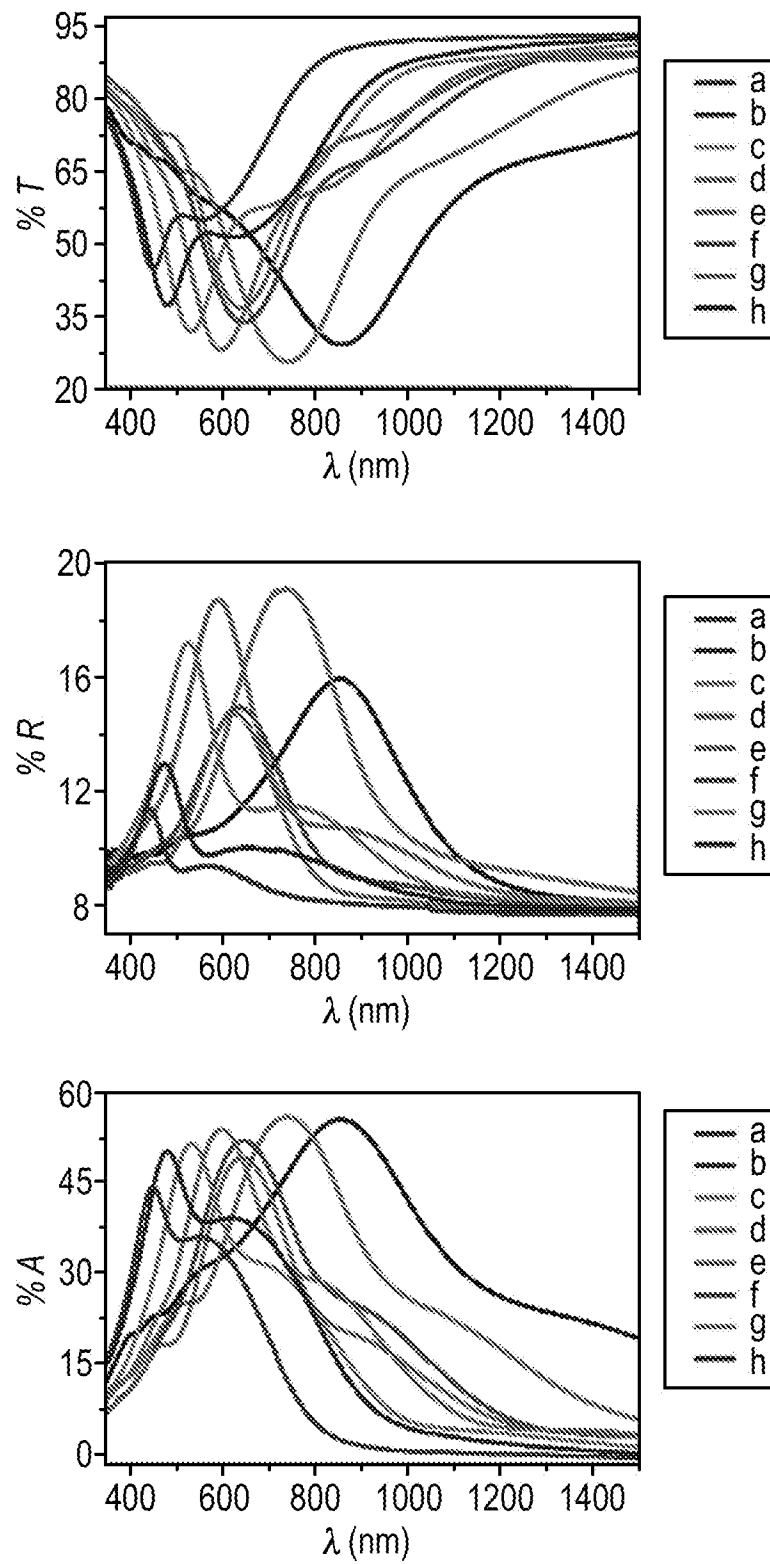


FIG. 4F

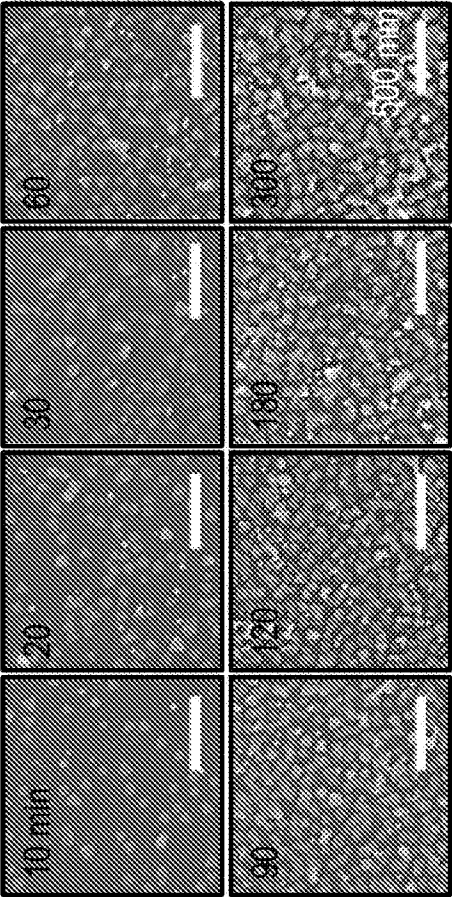


FIG. 5B

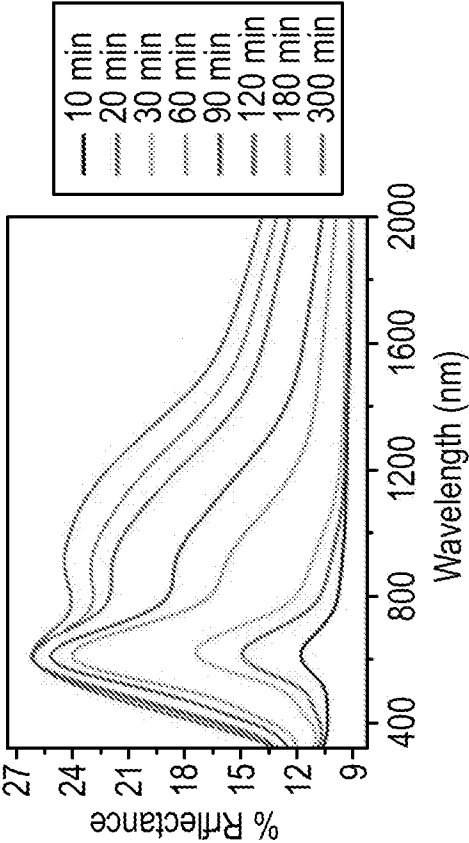


FIG. 5D

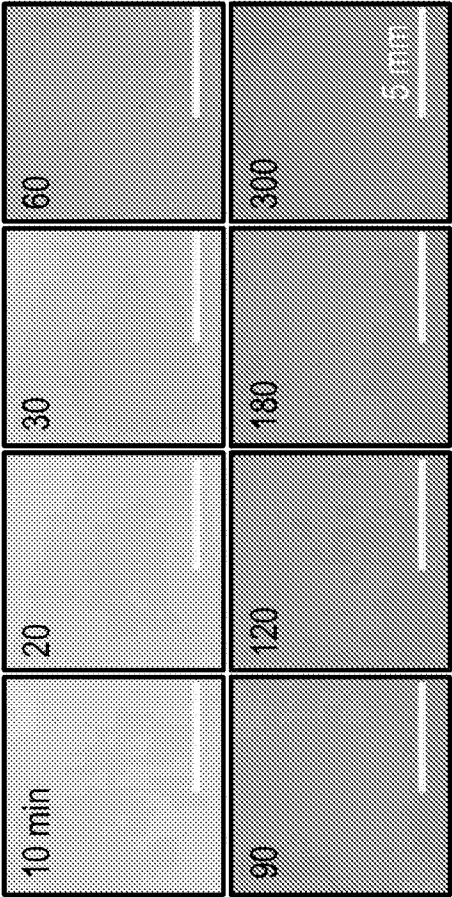


FIG. 5A

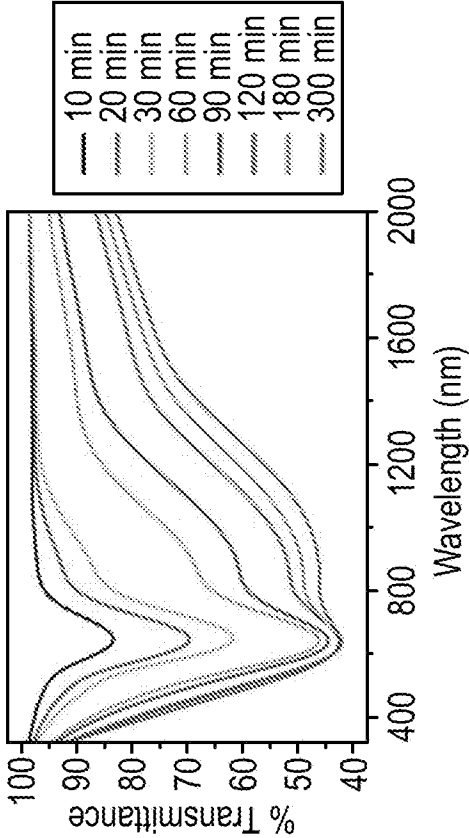


FIG. 5C

9/16

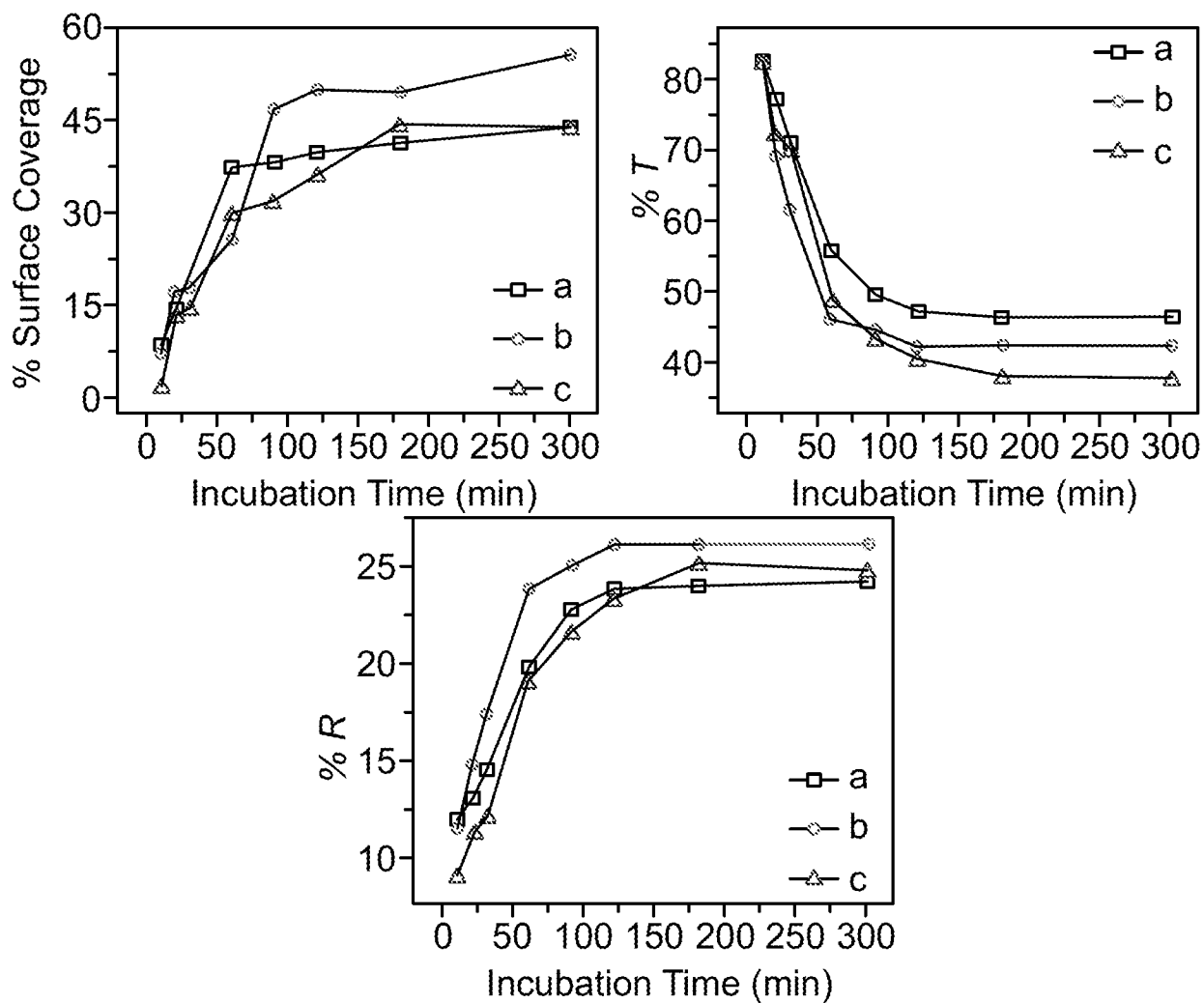


FIG. 6

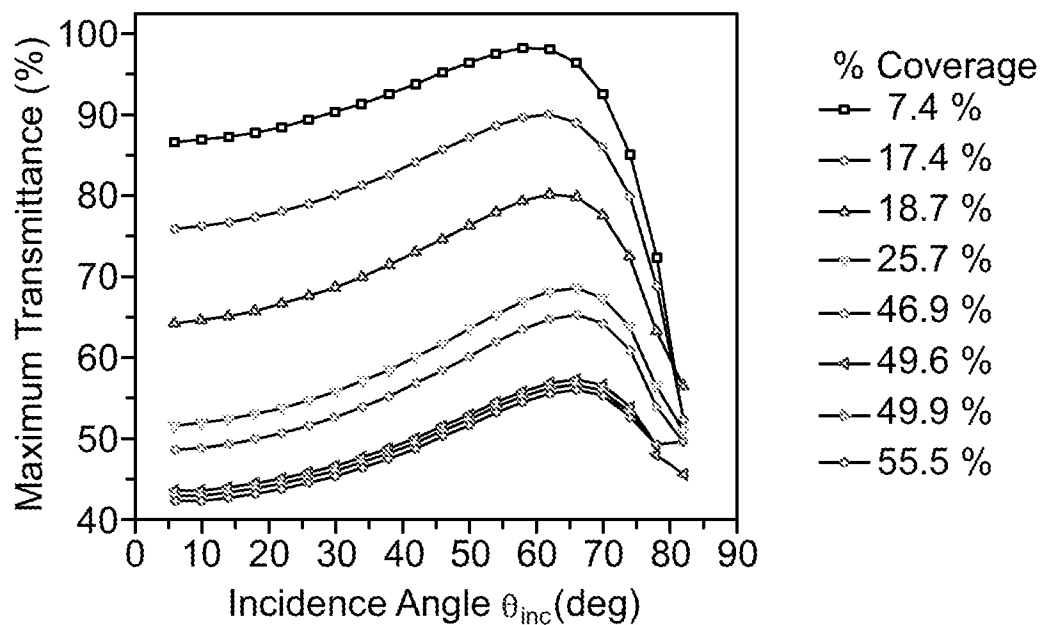


FIG. 7

10/16

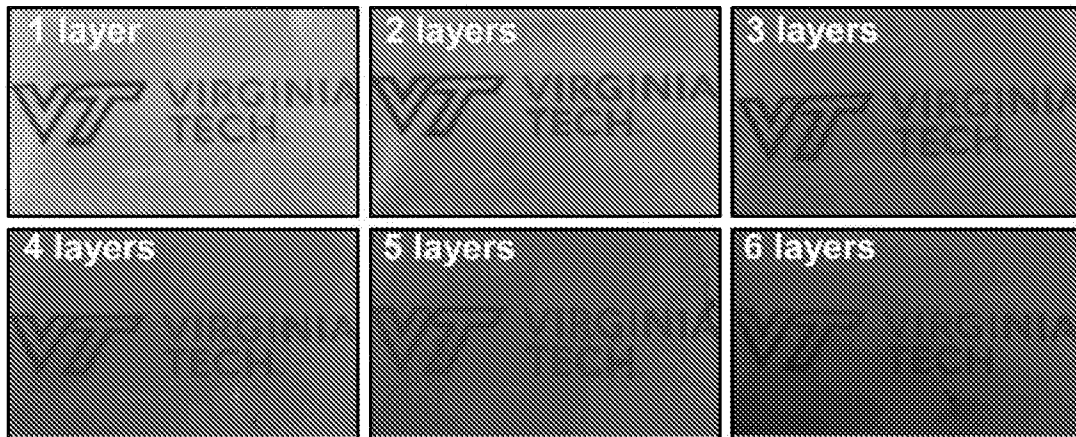


FIG. 8A

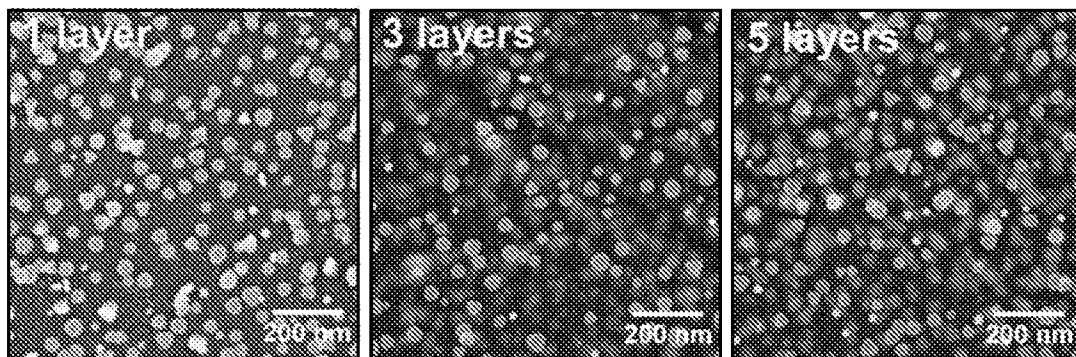


FIG. 8B

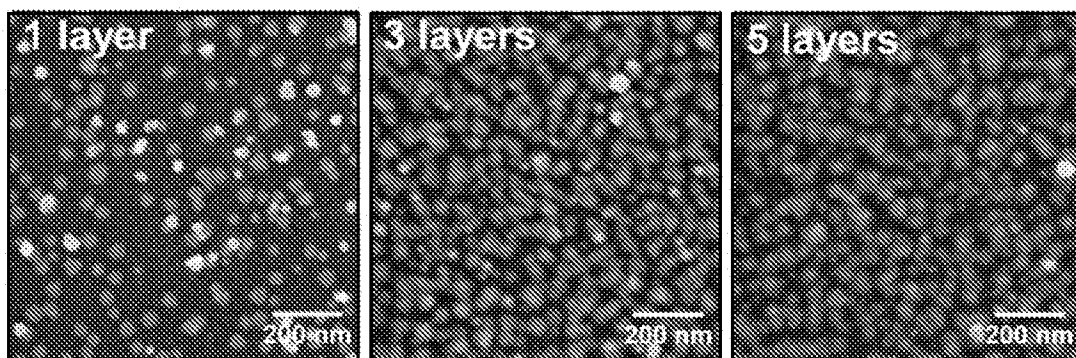


FIG. 8C

11/16

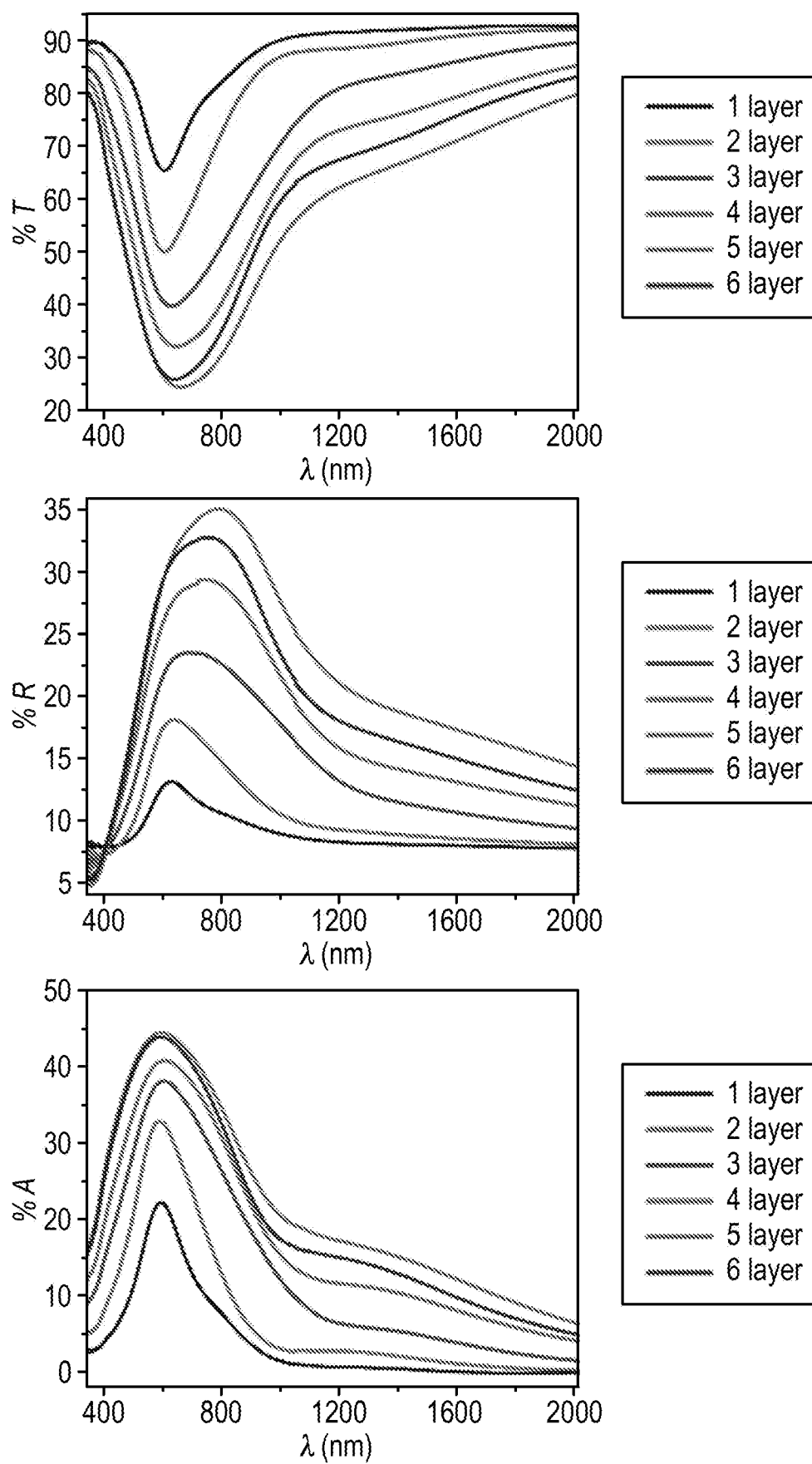


FIG. 8D

12/16

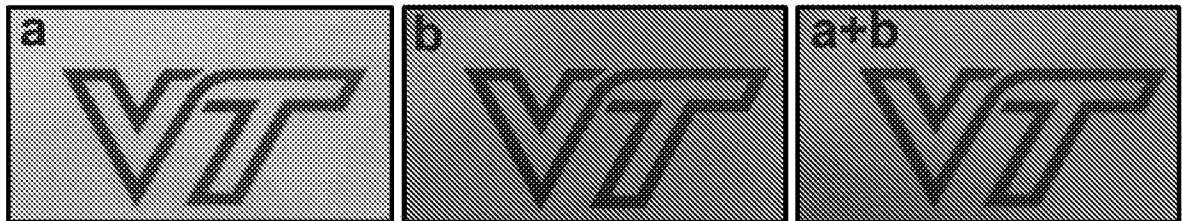


FIG. 9A

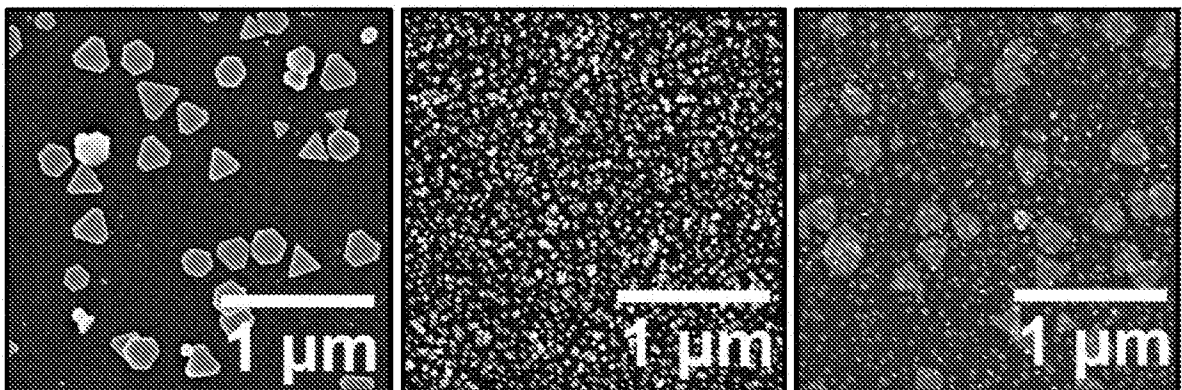
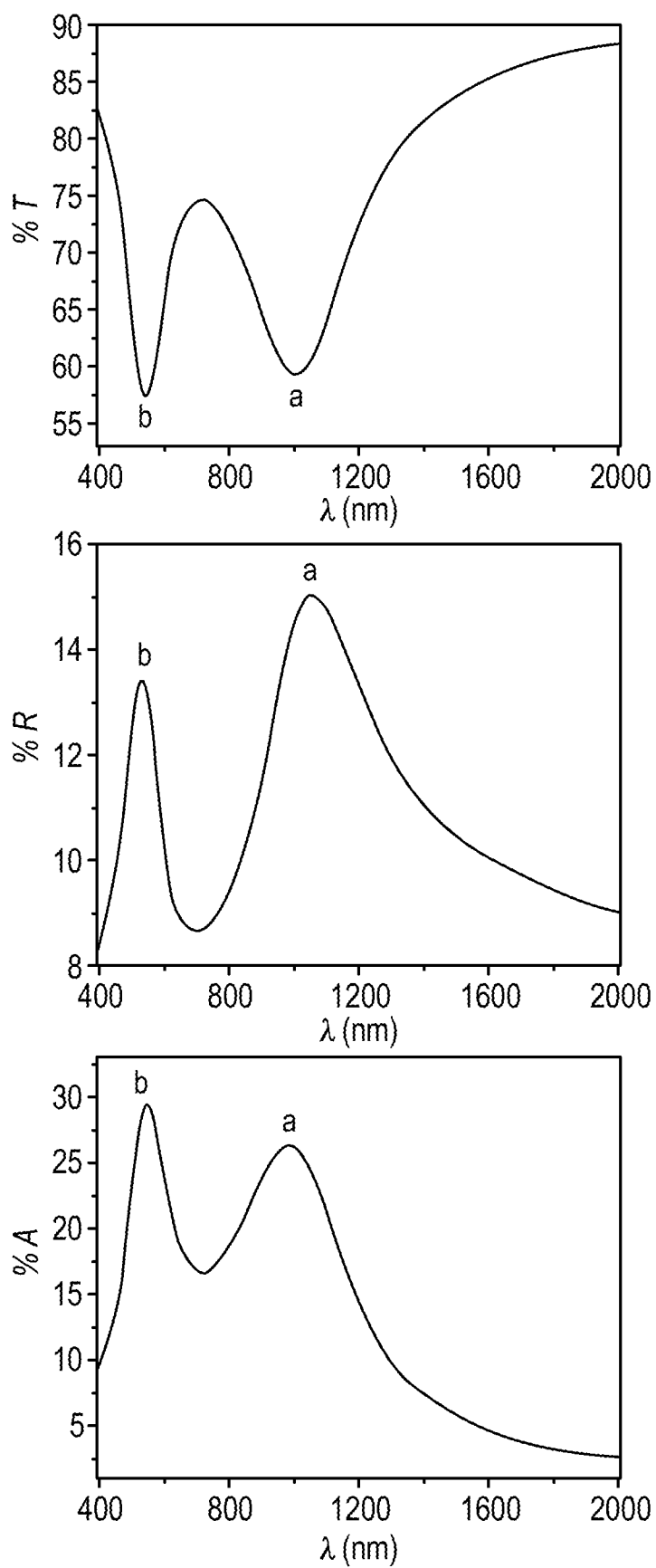


FIG. 9B

13/16**FIG. 9C**

14/16

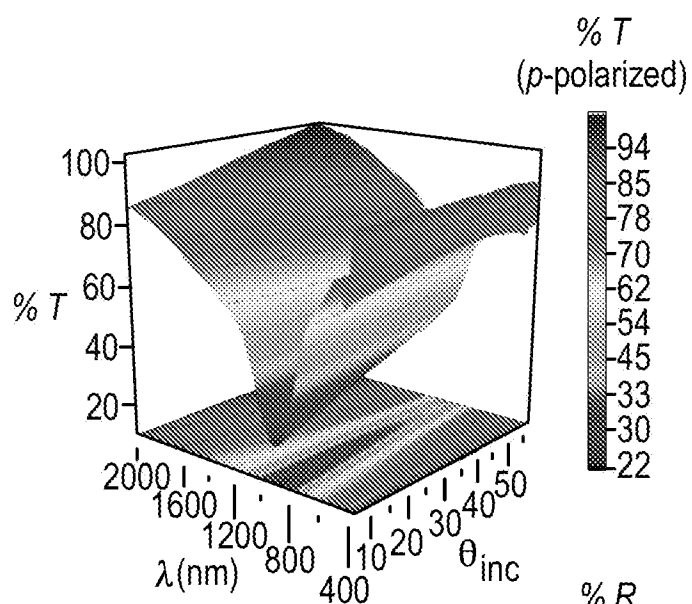


FIG. 10A

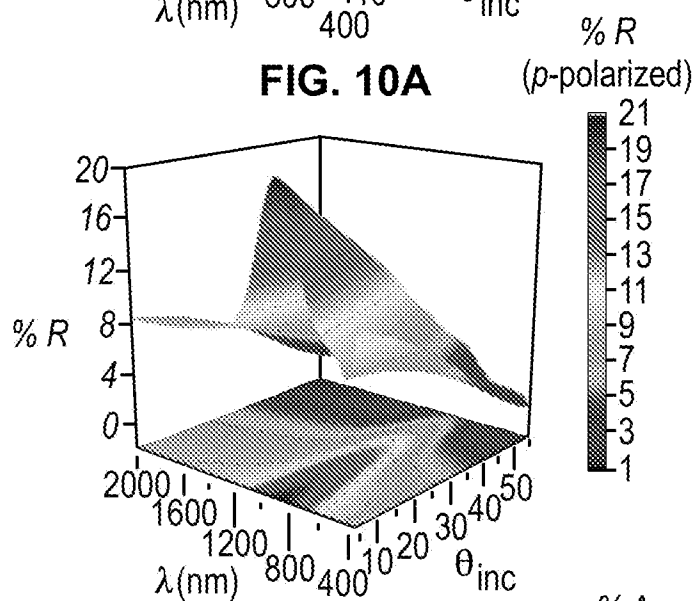


FIG. 10B

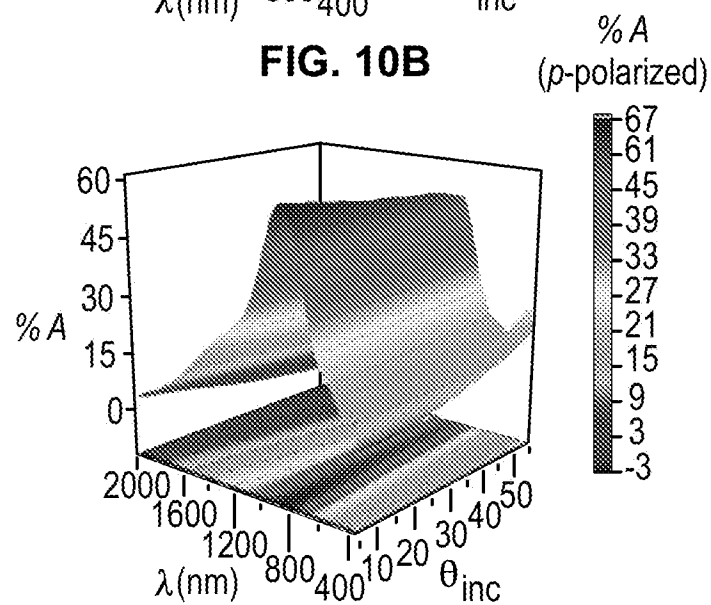


FIG. 10C

15/16

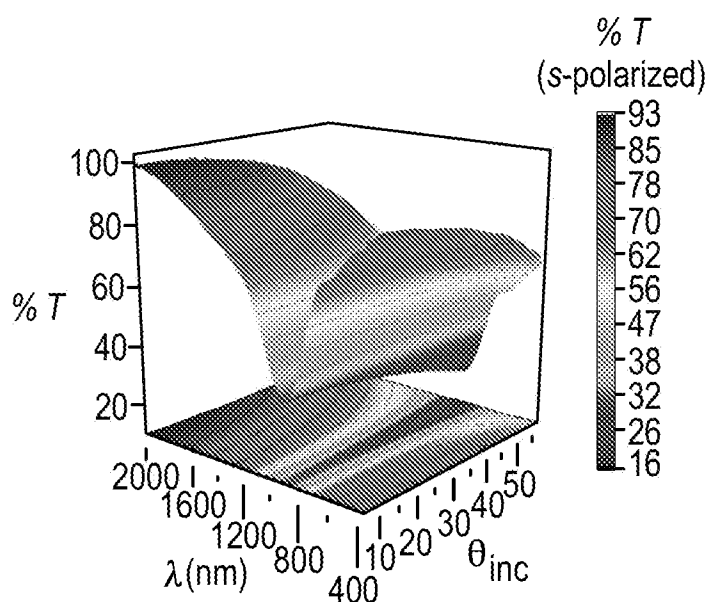


FIG. 10D

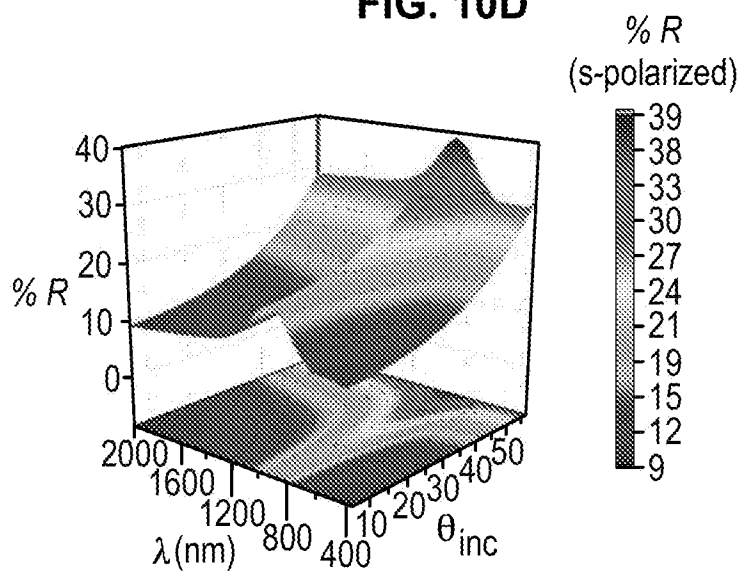


FIG. 10E

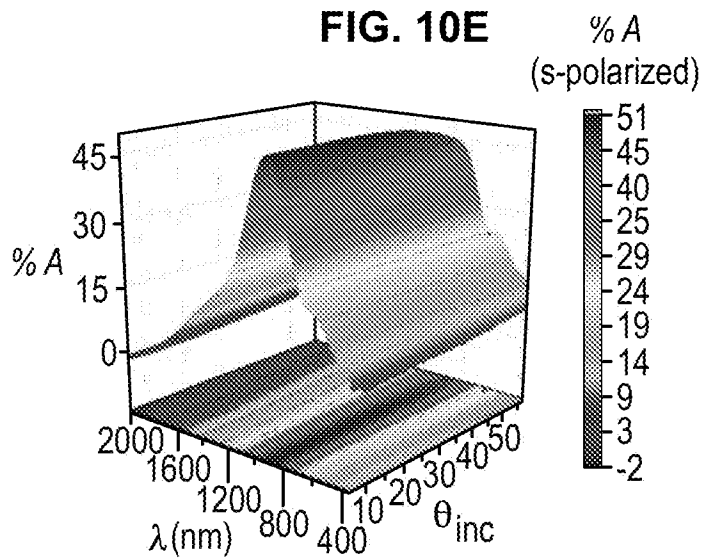


FIG. 10F

16/16

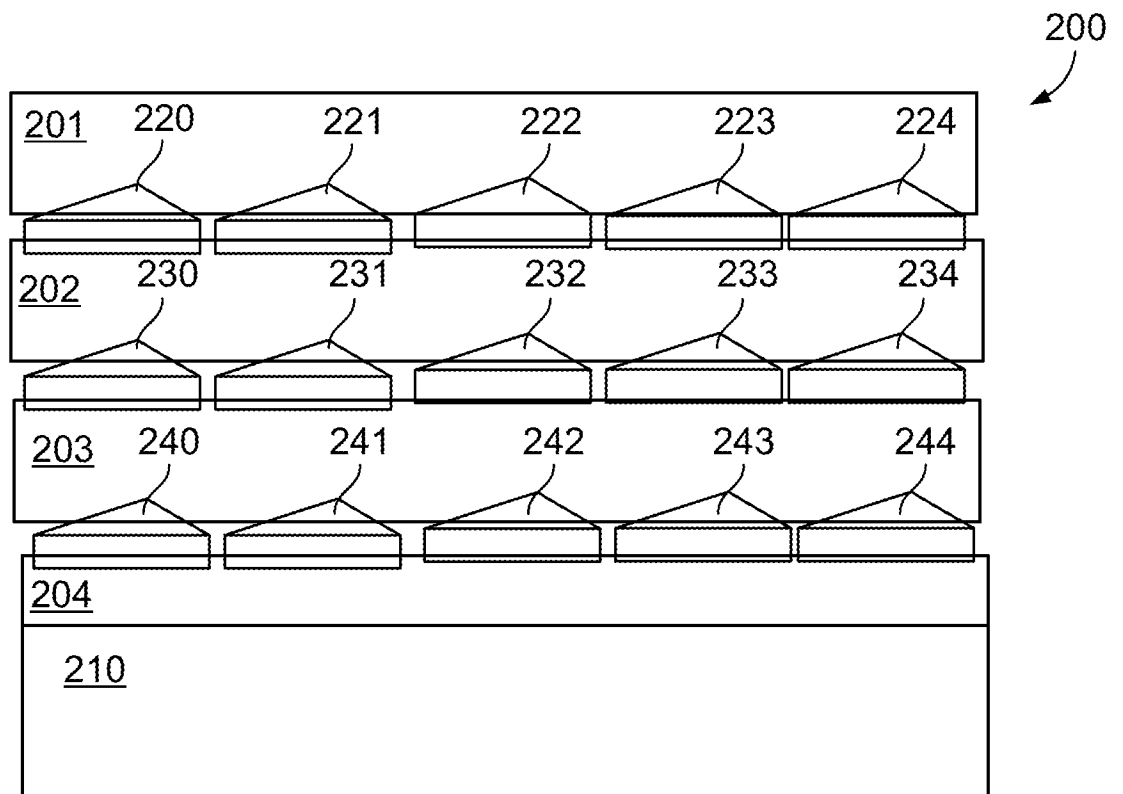


FIG. 11A

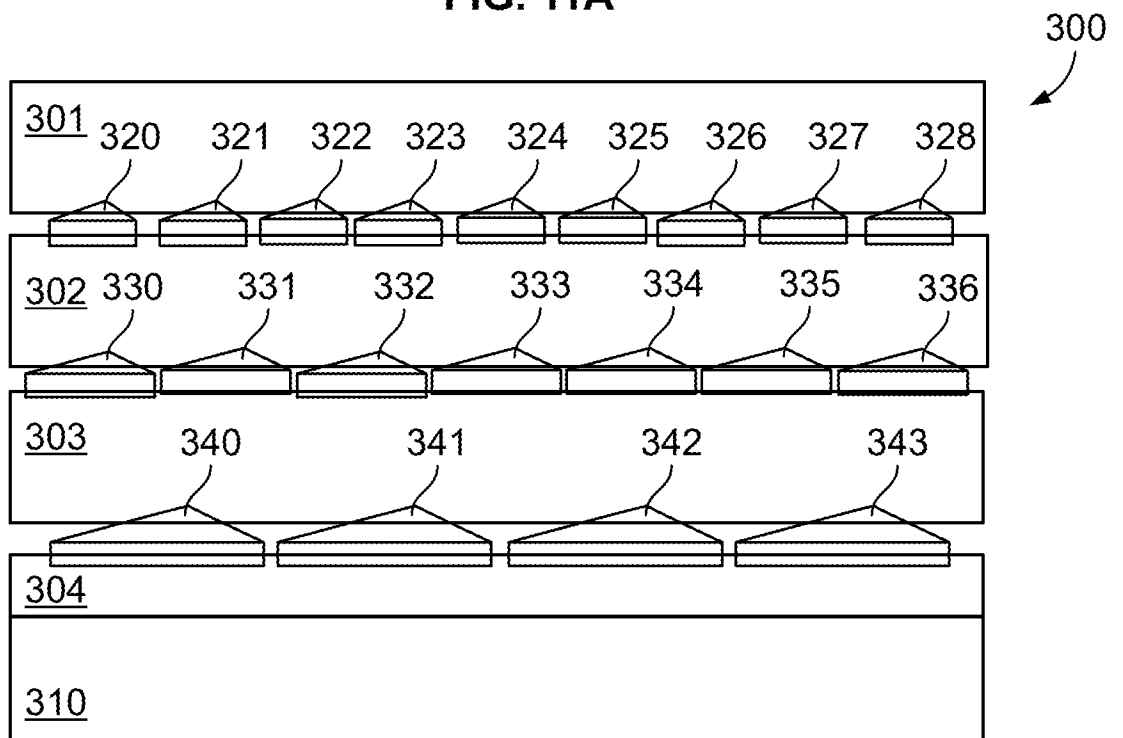


FIG. 11B

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2018/014747

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - G02B 26/02; G02B 6/00; G02B 6/12; G02B 26/00 (2018.01)

CPC - G02B 6/1226; G02B 6/00; G02B 6/12; G02B 26/00; G02B 26/02 (2018.02)

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

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.
X ---	US 2011/0109821 A1 (TANG et al) 12 May 2011 (12.05.2011) entire document	1-6, 23
Y		8, 10-12, 24
X ---	US 2006/0274315 A1 (SAITO) 07 December 2006 (07.12.2006) entire document	7, 9, 14-20
Y		8, 10-12, 21, 24
Y	US 2014/0234226 A1 (MAHMOUDI et al) 21 August 2014 (21.08.2014) entire document	21
A	NANOCOMPOSIX, Color Engineering, 30 April 2014 [retrieved on 02 March 2018]. Retrieved from the Internet: <URL: https://web.archive.org/web/20140430045440/https://nanocomposix.com/pages/color-engineering > entire document	1-24

☐ 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

02 March 2018

Date of mailing of the international search report

22 MAR 2018

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
P.O. Box 1450, Alexandria, VA 22313-1450

Facsimile No. 571-273-8300

Authorized officer

Blaine R. Copenhaver

PCT Helpdesk: 571-272-4300

PCT OSP: 571-272-7774