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(54) **METAL NANOPARTICLE ENHANCED SEMICONDUCTOR FILM FOR FUNCTIONALIZED TEXTILES**

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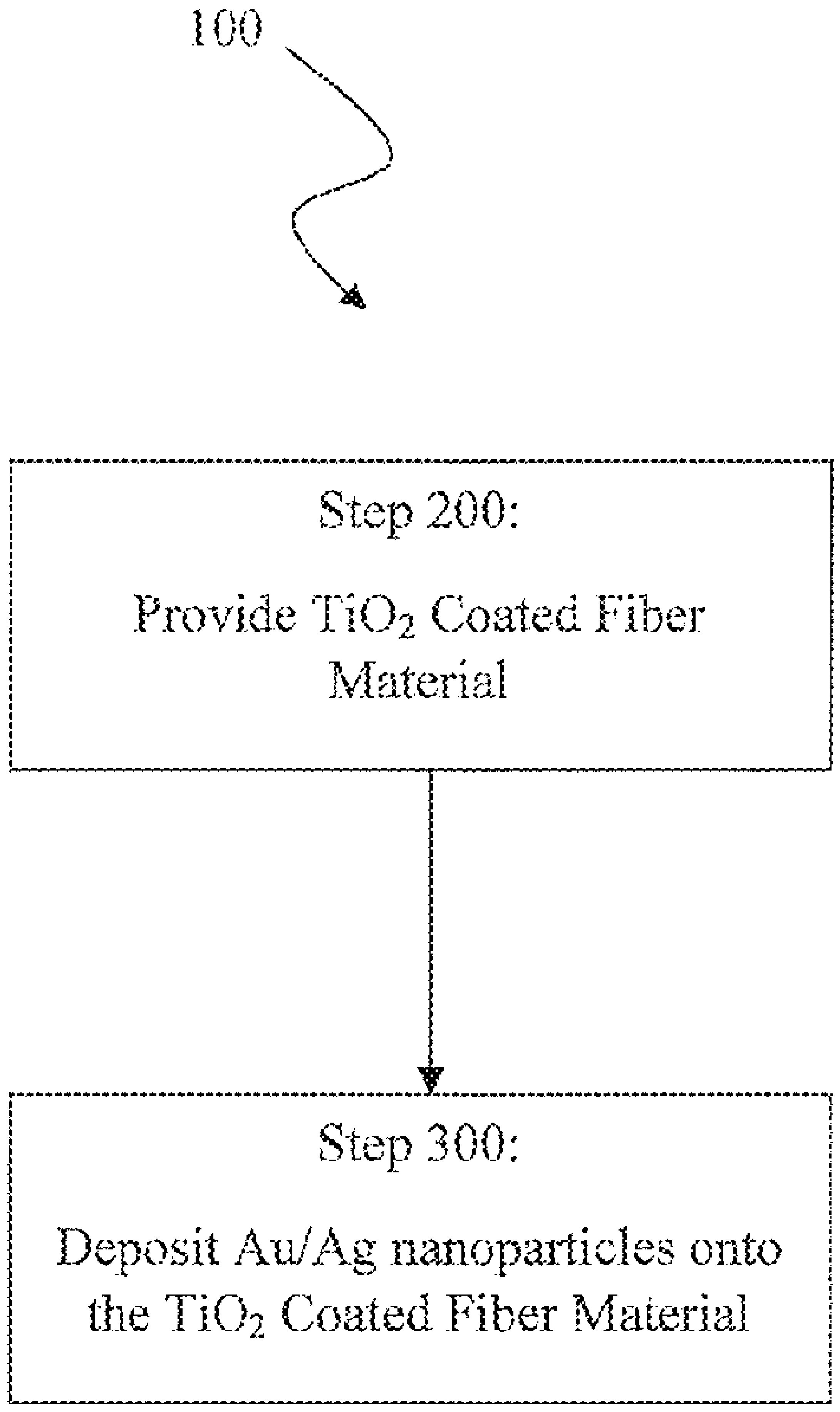
(57) **ABSTRACT**

A method for forming a metallic nanoparticle and semiconductor coated surface, such as the surface of a fiber or other material is provided. The method can include the steps of coating at least one surface of a material, for example a textile material, with a semiconducting layer, and providing metallic nanoparticles on the semiconducting layer. The steps for coating a surface of a material with a semiconducting layer can include forming a titanium dioxide film on the surface of the textile or other material. The steps for depositing and/or providing metallic nanoparticles on the semiconducting layer can include immersing a surface having a semiconductor layer into a metallic nanoparticle precursor solution, drying the semiconductor layer, and exposing the semiconductor layer on the surface to UV radiation. The metallic nanoparticles can include gold and/or silver nanoparticles. Also disclosed are surface treated materials having a semiconductor layer thereon, wherein the semiconductor layer is treated to include metallic nanoparticles. The surface treated materials may comprise surfaces of a textile material, such as fibers. The surface treated materials are anti-microbial and resistant to peeling, as well as non-toxic to biological surfaces, such as skin. Treated fiber materials may be used in garments, masks, and other products that contact the skin, that are free of toxic/rash side effects.



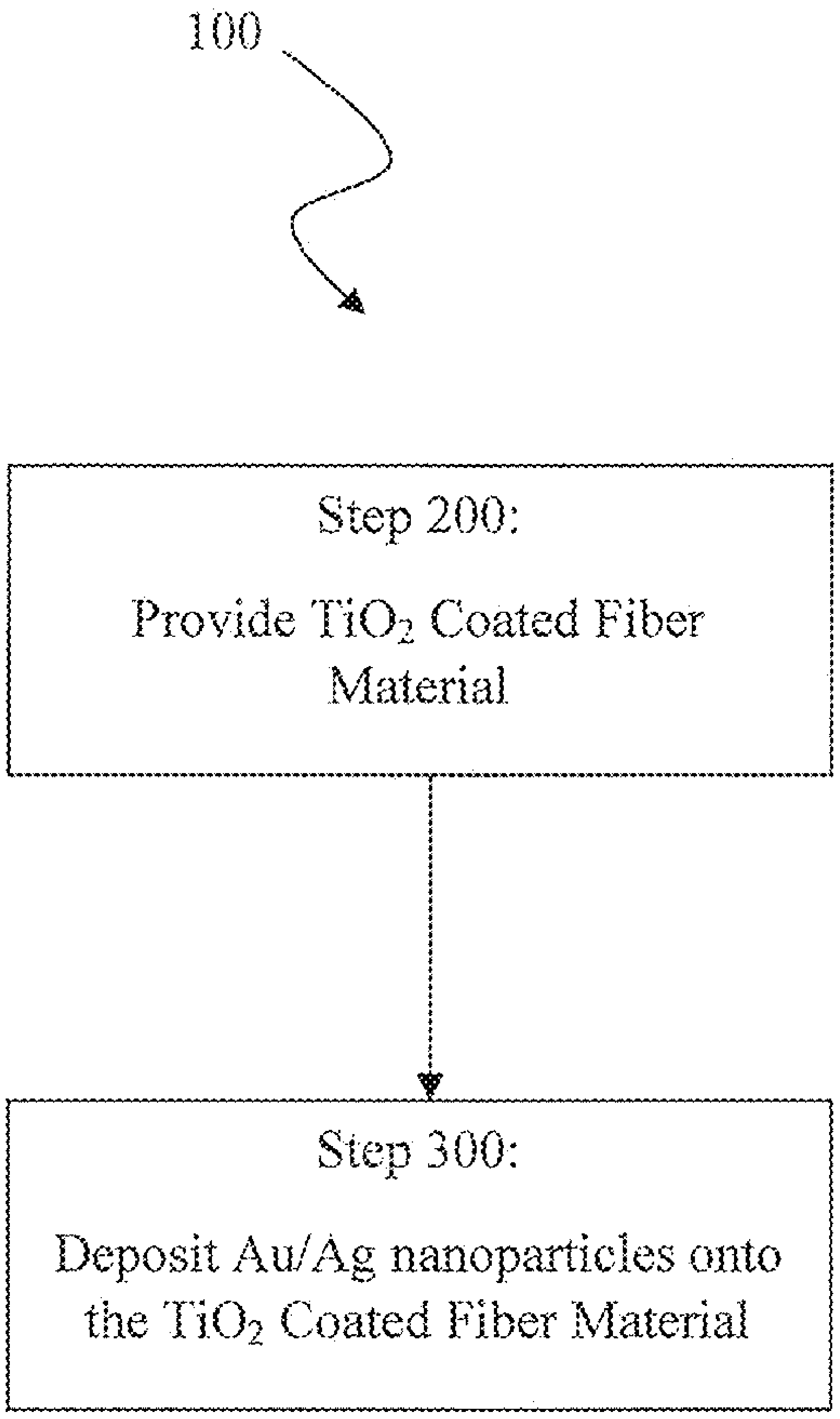

100
Step 200:
Provide TiO_2 Coated Fiber Material
Step 300:
Deposit Au/Ag nanoparticles onto the TiO_2 Coated Fiber Material

FIG. 1

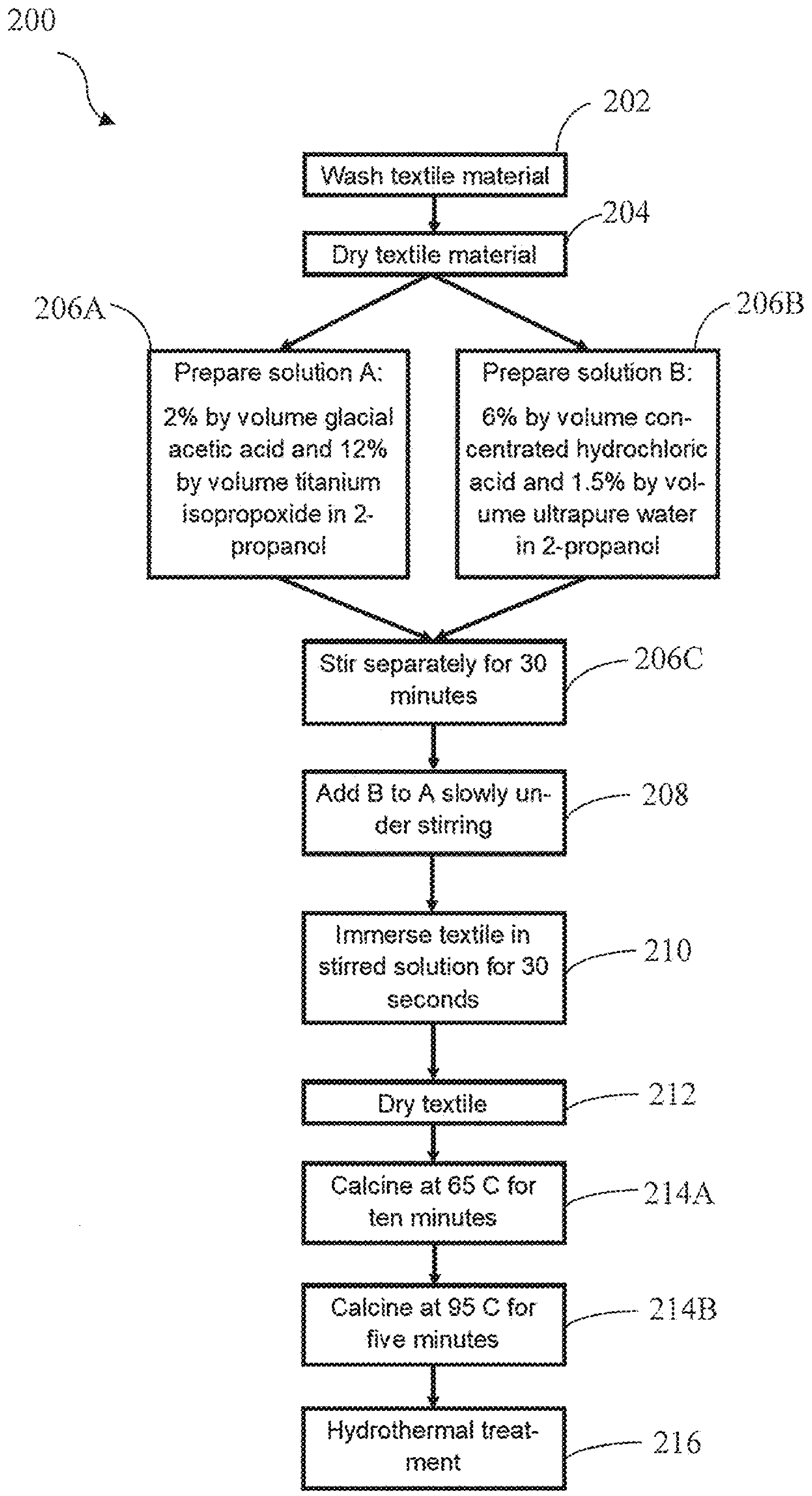

200
202
Wash textile material
204
Dry textile material
206A
Prepare solution A:
2% by volume glacial acetic acid and 12% by volume titanium isopropoxide in 2-propanol
206B
Prepare solution B:
6% by volume concentrated hydrochloric acid and 1.5% by volume ultrapure water in 2-propanol
Stir separately for 30 minutes
206C
Add B to A slowly under stirring
208
Immerse textile in stirred solution for 30 seconds
210
Dry textile
212
Calcine at 65 C for ten minutes
214A
Calcine at 95 C for five minutes
214B
Hydrothermal treatment
216

FIG. 2

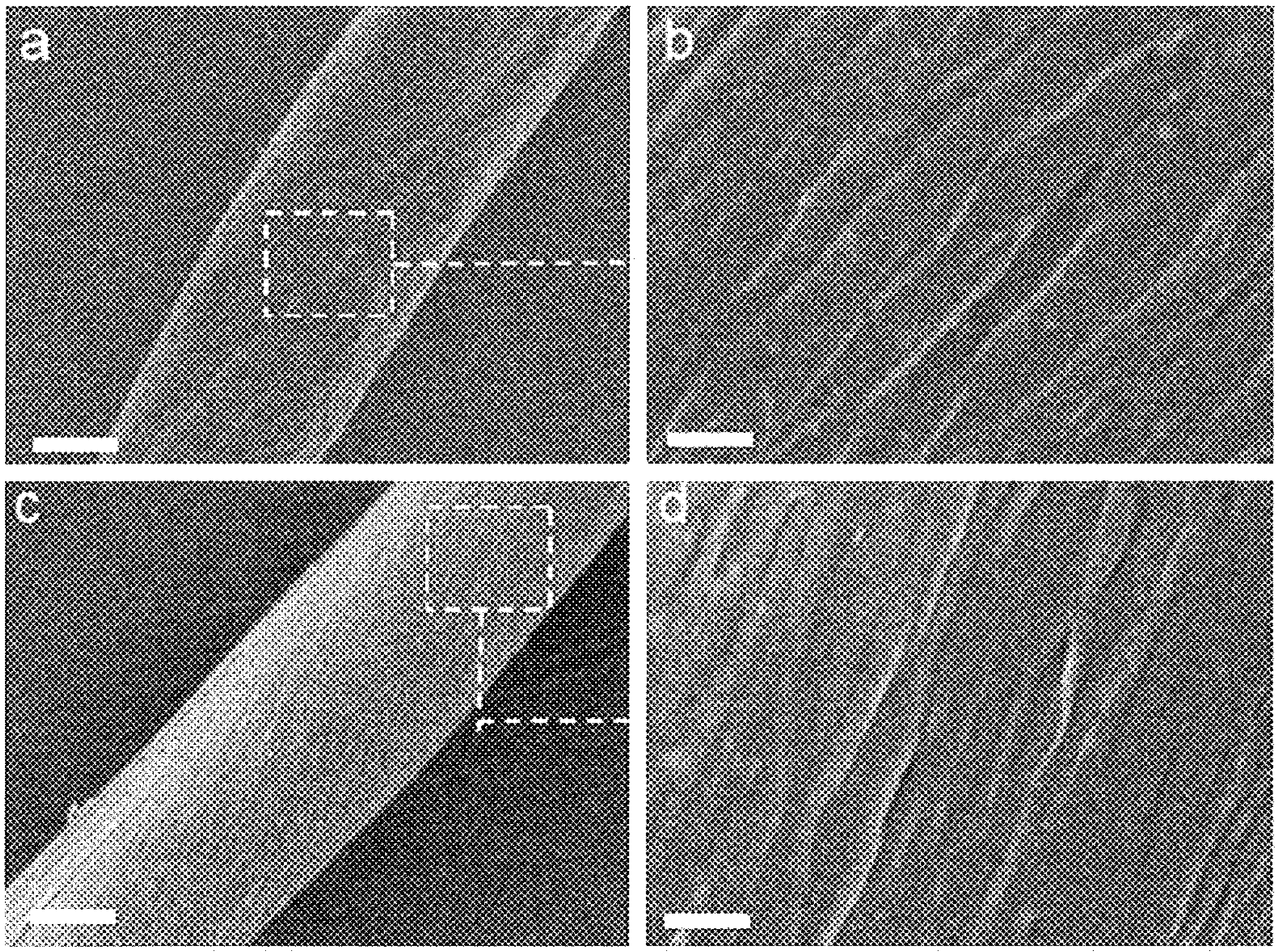


FIG. 3

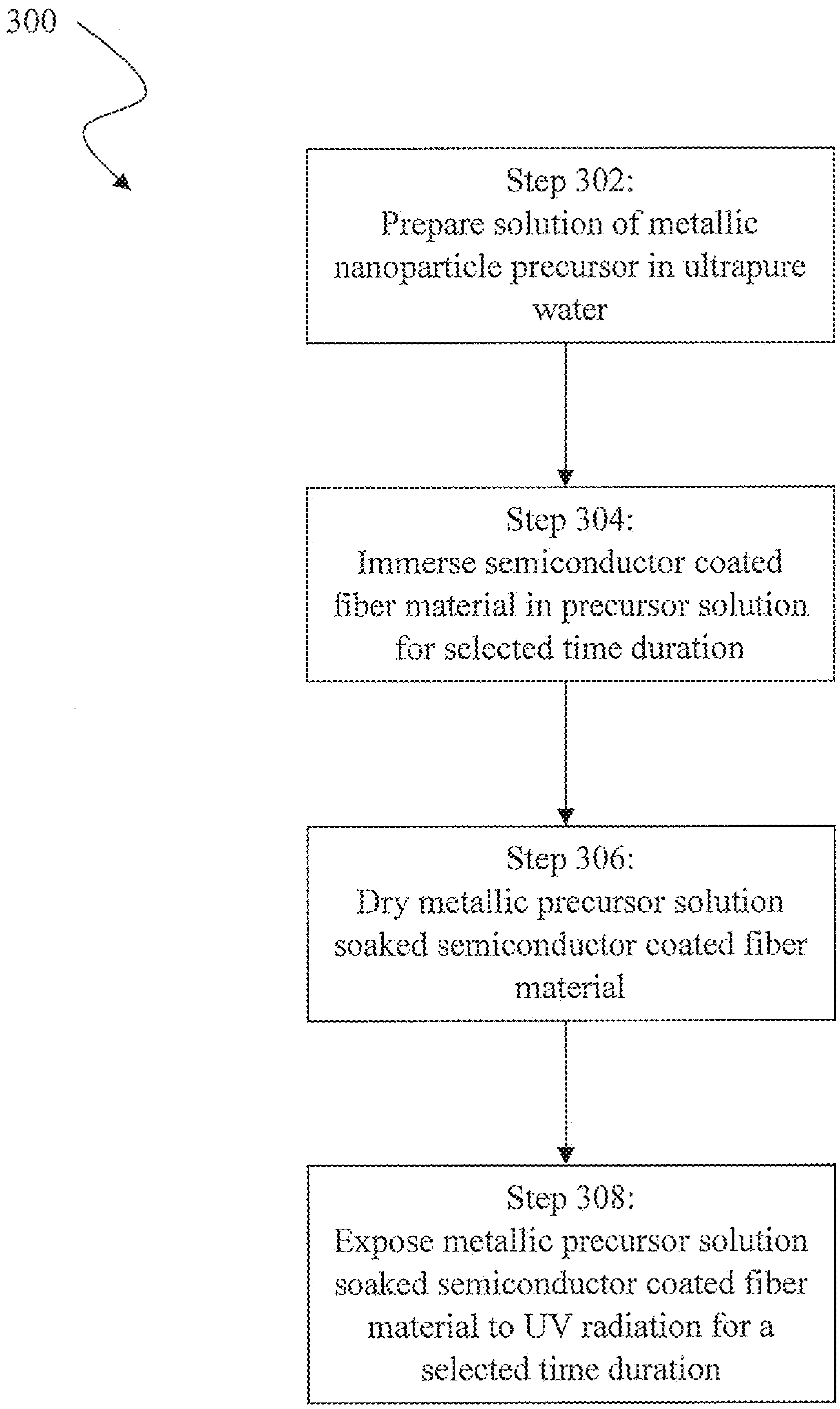

300
Step 302:
Prepare solution of metallic nanoparticle precursor in ultrapure water
Step 304:
Immerse semiconductor coated fiber material in precursor solution for selected time duration
Step 306:
Dry metallic precursor solution soaked semiconductor coated fiber material
Step 308:
Expose metallic precursor solution soaked semiconductor coated fiber material to UV radiation for a selected time duration

FIG. 4A

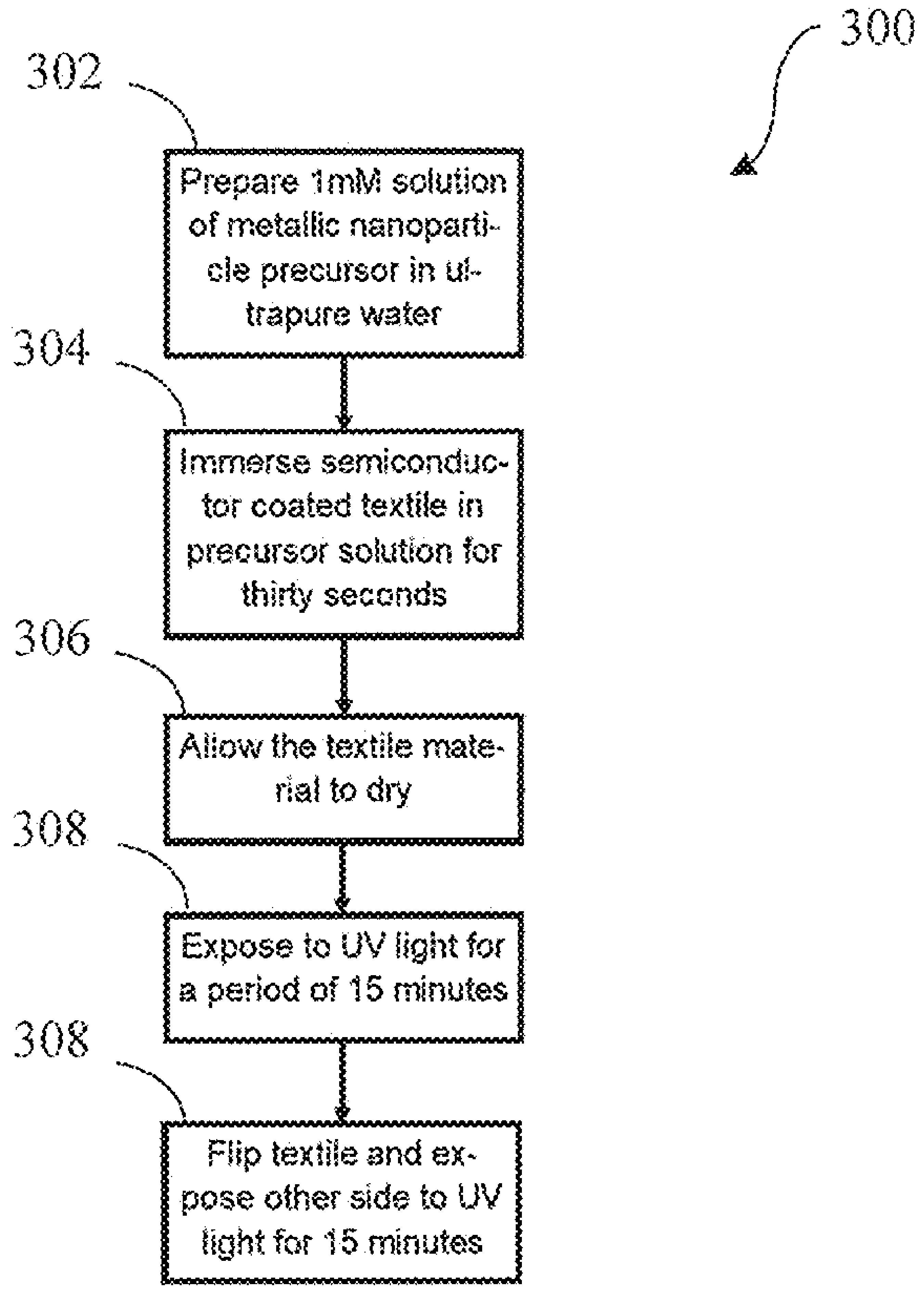

300
302
Prepare 1mM solution of metallic nanoparticle precursor in ultrapure water
304
Immerse semiconductor coated textile in precursor solution for thirty seconds
306
Allow the textile material to dry
308
Expose to UV light for a period of 15 minutes
308
Flip textile and expose other side to UV light for 15 minutes

FIG. 4B

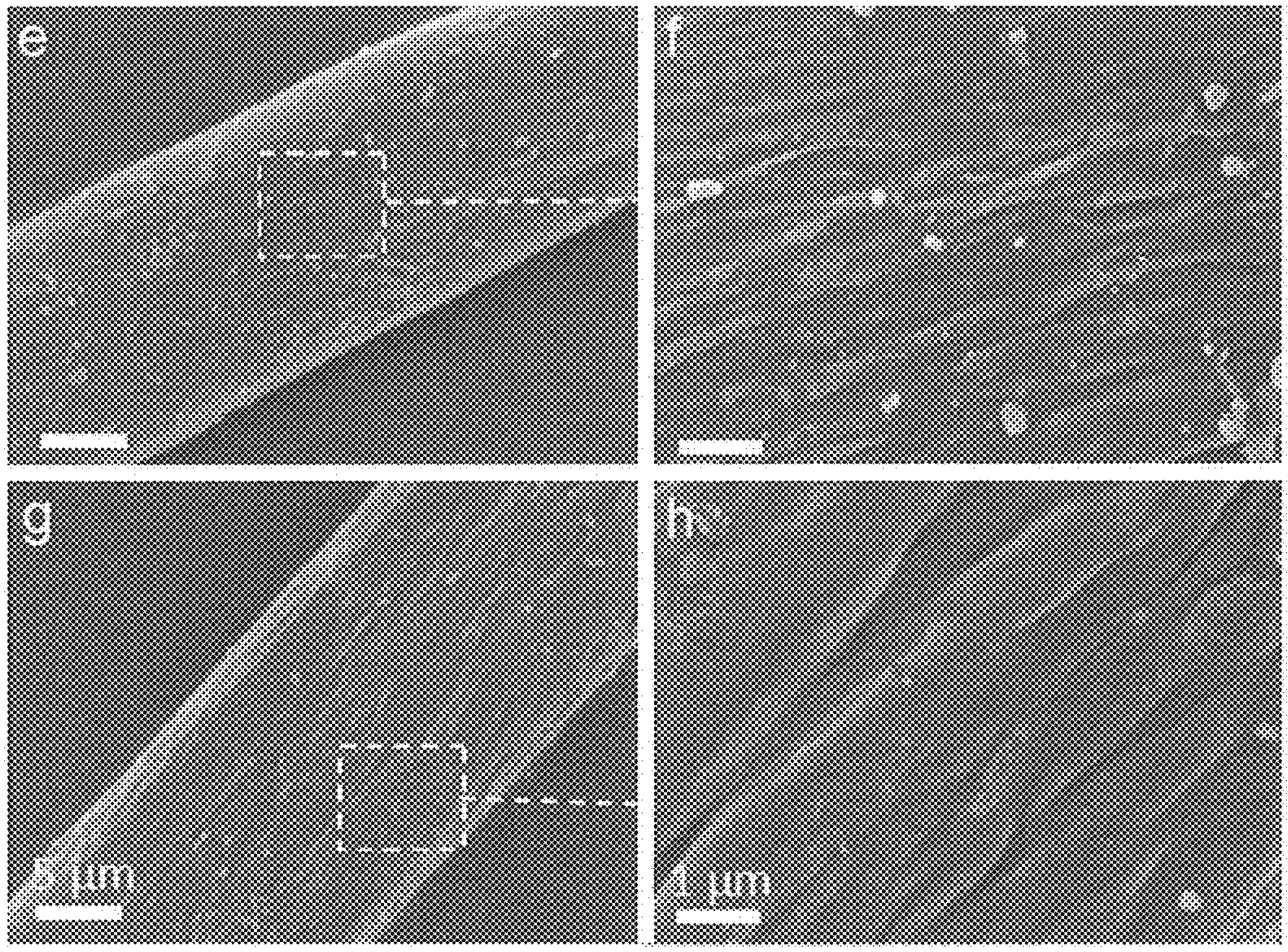


FIG. 5

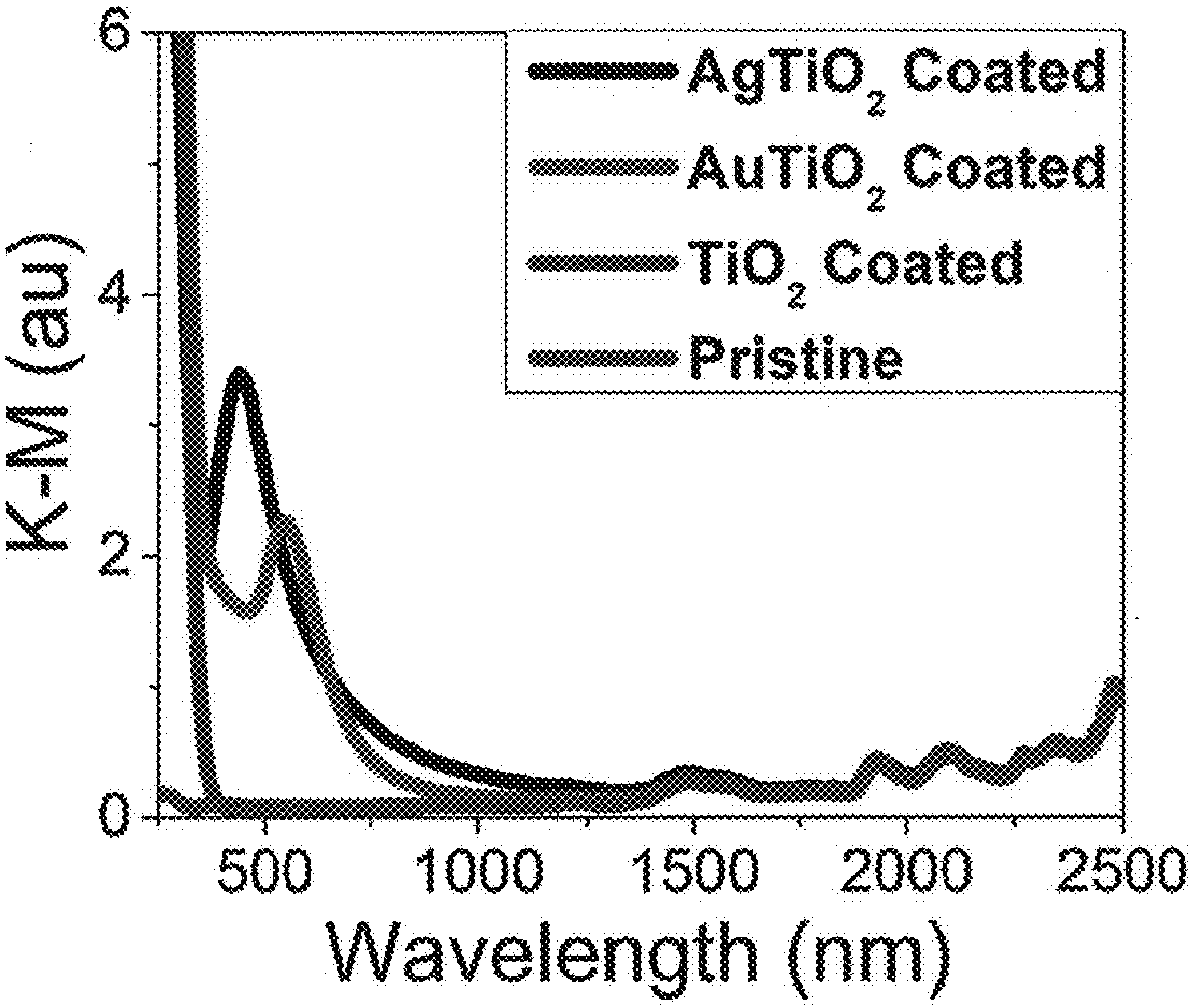

AgTiO$_2$ Coated
AuTiO$_2$ Coated
TiO$_2$ Coated
Pristine
K-M (au)
0
2
4
6
500
1000
1500
2000
2500
Wavelength (nm)

FIG. 6

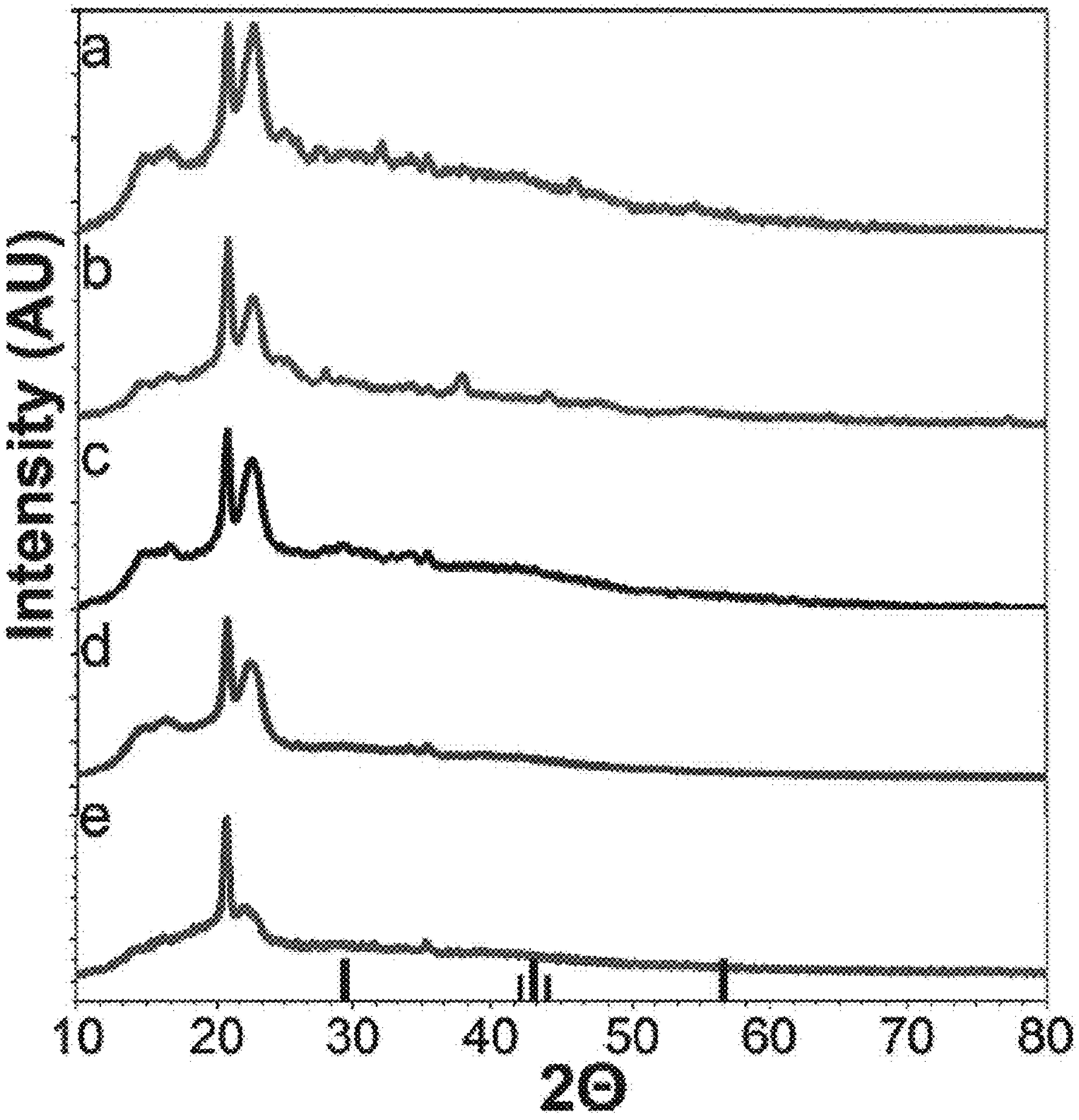


FIG. 7

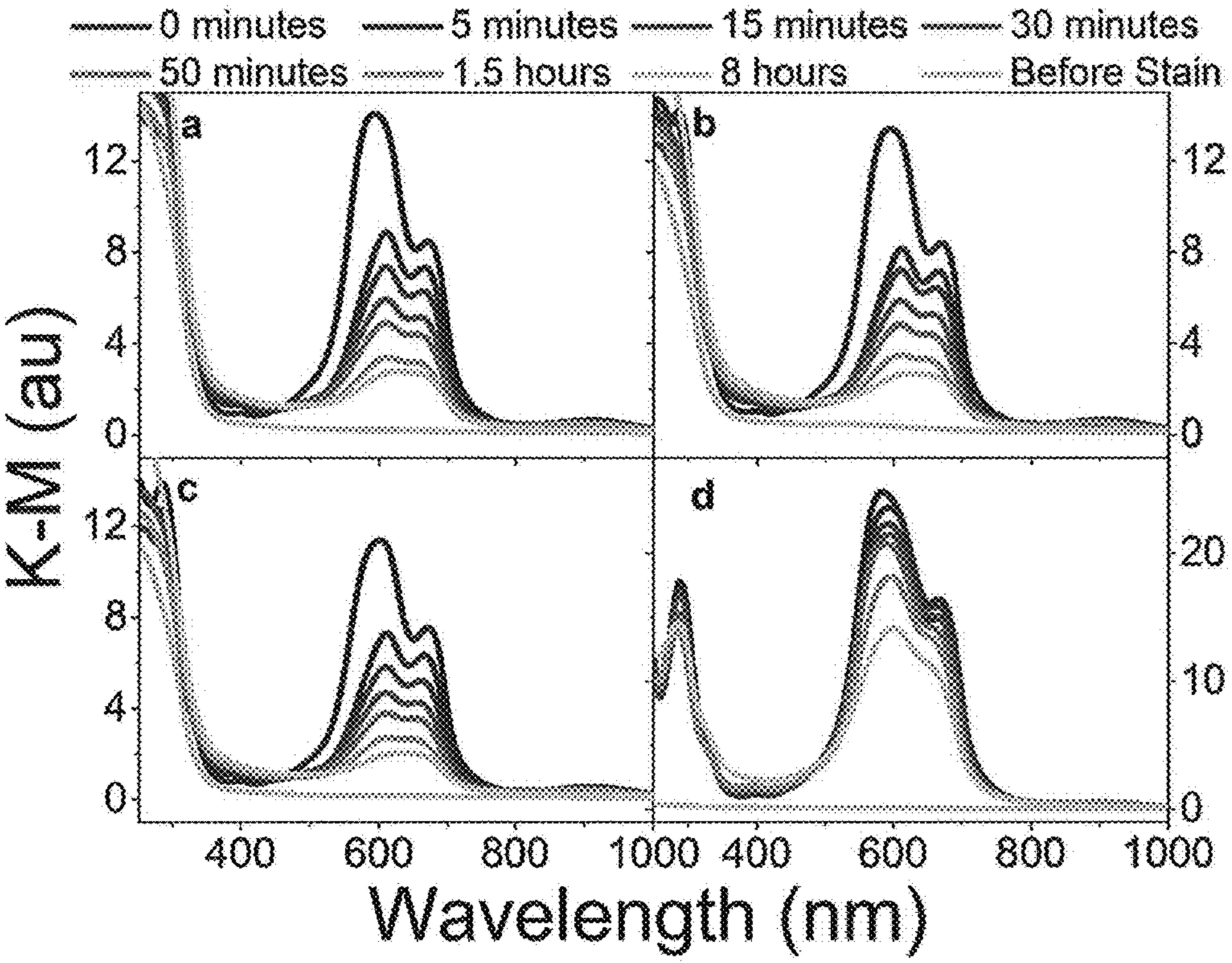

0 minutes
5 minutes
15 minutes
30 minutes
50 minutes
1.5 hours
8 hours
Before Stain
a
b
c
d
K-M (au)
Wavelength (nm)
0
4
8
12
0
4
8
12
0
4
8
12
0
4
8
12
0
10
20
400
600
800
1000
400
600
800
1000

FIG. 8

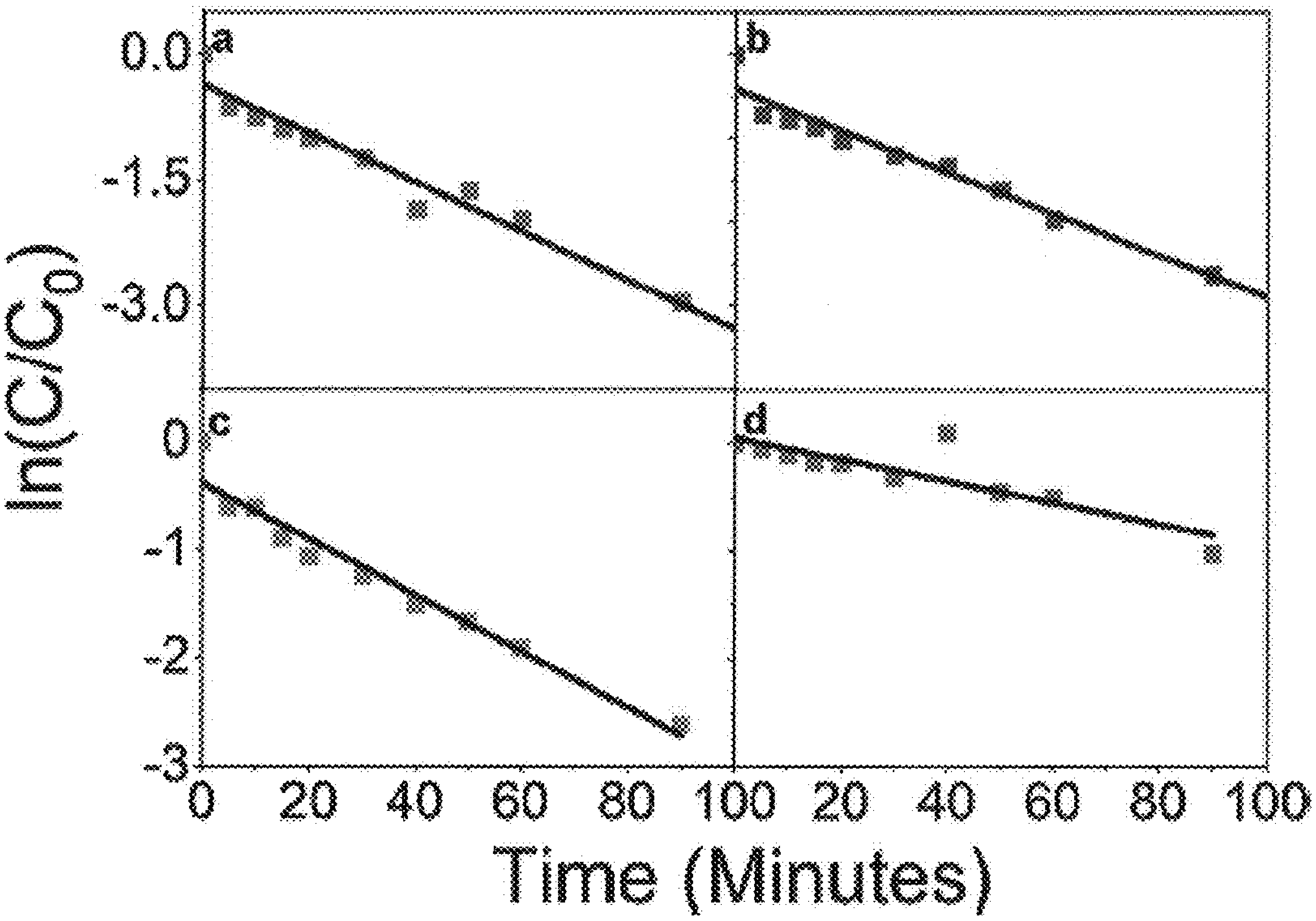

a
b
c
d
0.0
-1.5
-3.0
0
-1
-2
-3
0
20
40
60
80
100
20
40
60
80
100
$\ln(C/C_0)$
Time (Minutes)

FIG. 9

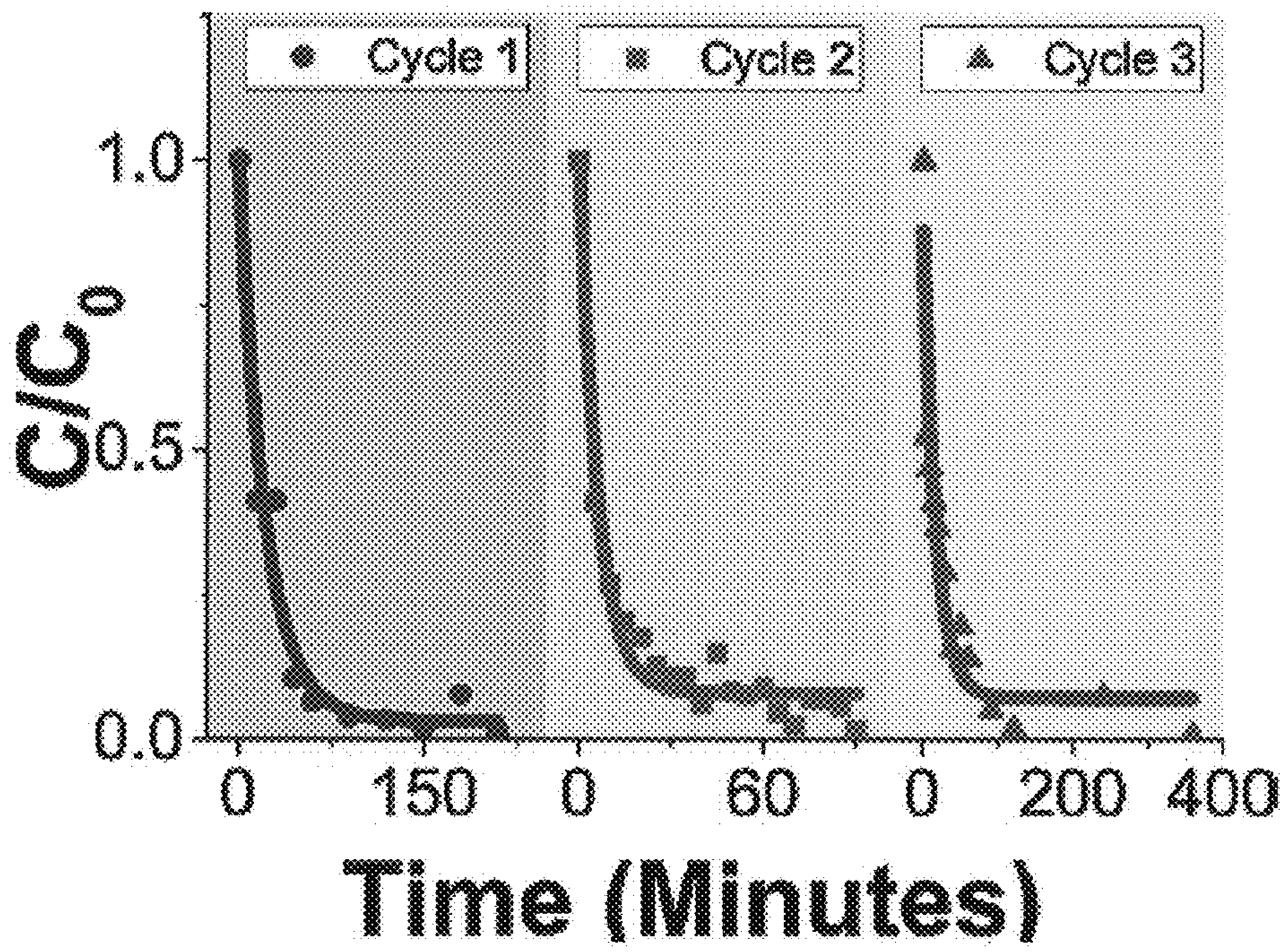

Cycle 1
Cycle 2
Cycle 3
C/C$_0$
1.0
0.5
0.0
0
150
0
60
0
200
400
Time (Minutes)

FIG. 10

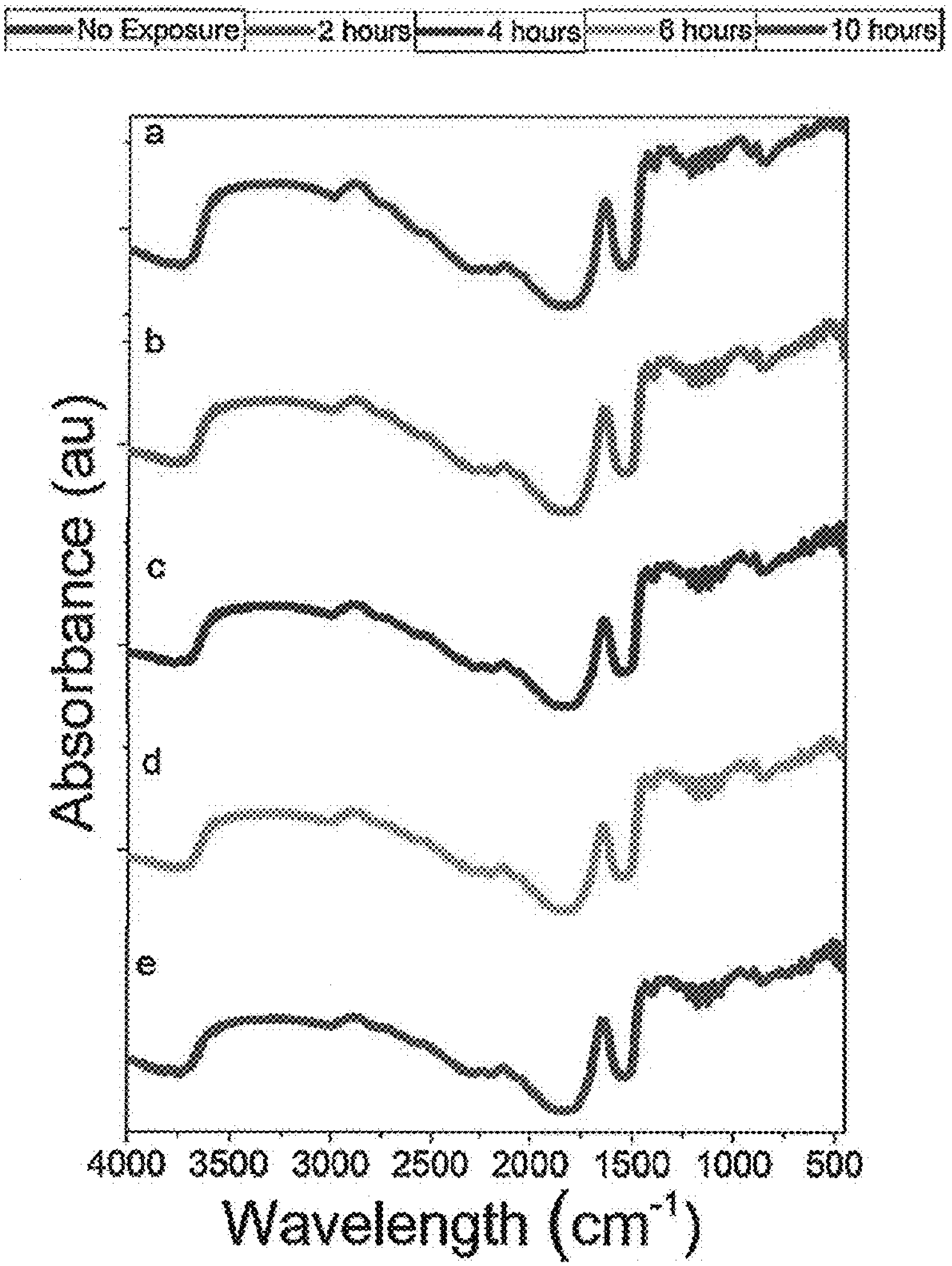

No Exposure
2 hours
4 hours
6 hours
10 hours
a
b
c
d
e
Absorbance (au)
4000
3500
3000
2500
2000
1500
1000
500
Wavelength (cm^{-1})

FIG. 11

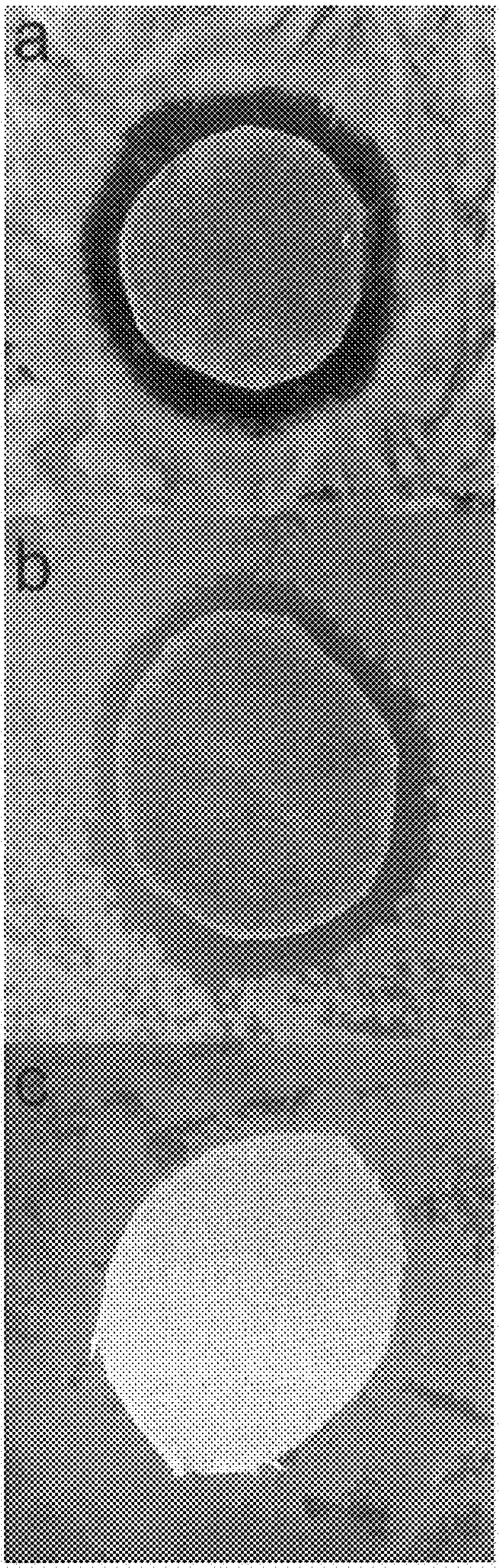


FIG. 12

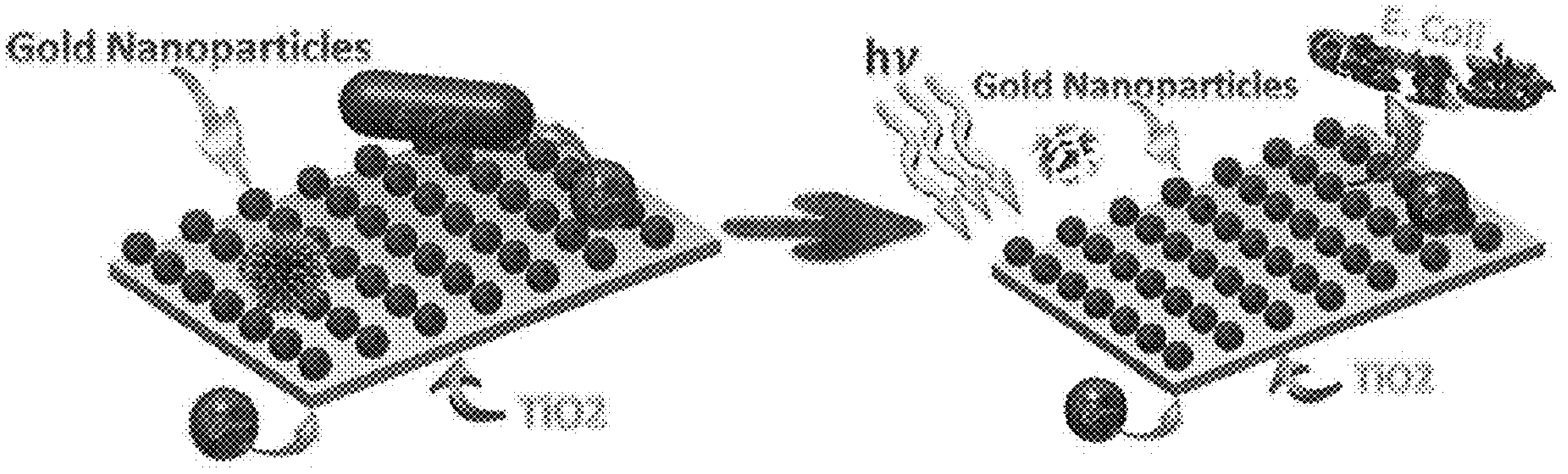


FIG. 13

METAL NANOPARTICLE ENHANCED SEMICONDUCTOR FILM FOR FUNCTIONALIZED TEXTILES

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] The present application is a continuation of U.S. patent application Ser. No. 16/843,789, filed Apr. 8, 2020, which is a continuation of U.S. patent application Ser. No. 16/818,751, filed Mar. 13, 2020, which claimed priority to U.S. Provisional Patent Application Ser. No. 62/830,953, filed Apr. 8, 2019, the contents of which are specifically incorporated herein by reference.

GOVERNMENT LICENSE RIGHTS

[0002] This invention was made with government support under D01_W911SR-14-2-0001-0003 awarded by the Department of Defense. The government has certain rights in the invention.

FIELD OF THE INVENTION

[0003] This invention relates to the field of surface coatings and methods for providing a surface coating to a material, as a method of treating a material, for example a textile material, such that at least one surface of the material comprises a nanostructured coating is provided. The invention also relates to the field of nanostructured coatings that are self-cleaning, anti-microbial, and radiation-protective. The invention further relates to the field of semiconducting metal oxide thin film coatings, as semiconducting metal oxide thin film coating comprising metallic nanoparticle incorporated to a semiconducting film is provided, the film providing an active photocatalyst layer imparting the above characteristics to a surface having the film provided thereon. The invention also relates to the field of methods for providing a thin film to a surface, as a method for generating a thin, homogenous, nanostructured film of titanium dioxide on a cellulosic substrate and generating noble metal nanoparticles (silver and gold) directly on the titanium oxide surface to provide a treated surface is provided. The treated surface enhances photocatalytic activity at the surface, and renders the treated surface self-cleaning and antimicrobial. A surface treated with a titanium dioxide coating process alone does not possess these characteristics. The invention also relates to methods of treating materials and surfaces of other natural or synthetic substrates, other semiconductor-based thin films, and other noble/common metallic nanoparticles.

BACKGROUND OF THE INVENTION

[0004] Conventional fabric treatment methods aim to provide stain resistance, extend the lifetime of the textile material, or provide anti-microbial action through the use of chemicals that seal and protect the fabric, or through treatment methods that leave the fabric innately resistant to stains. Treatment methods that rely on semiconducting materials being deposited on a textile typically rely on complicated methods ill-suited to scaling to industrial scale, and also typically yield a textile material that is impregnated by and/or decorated with discrete semiconductor nanotubes or nanoparticles, which both have the disadvantage of being more readily removed from the fabric and less photocatalytically active than a thin, uniform film. Sol-gel based treatment techniques are one of the developed procedures for depositing a surface photocatalytic coating on textile materials.

[0005] While advancements have been made in the development of advanced textile materials with a photocatalytic film or layer, current methods and techniques are inadequate because they are ill-suited to large scale production and they have limited self-cleaning, anti-microbial, and radiation-protective properties. Accordingly, a need exists for an improved advance textile or fiber materials with self-cleaning, anti-microbial, and radiation-protective properties that overcome the aforementioned problems.

SUMMARY OF THE INVENTION

[0006] The method and system of this invention center around the innovative concept of methods for generating a nanostructured photocatalytic system on at least one surface of a material, for example a textile material, using simple, scalable methods. The invention allows a nanostructured photocatalytic system to be constructed using a sol-gel based synthetic method for depositing a semiconducting thin film that coats the fabric, provides a surface for photocatalytic chemical reactions to occur, and itself absorbs UV light preventing the penetration of the material by UV radiation. Noble metal nanoparticles are grown on this semiconducting surface by a solution-based coating method followed by irradiation with UV light which, together with the already deposited semiconducting layer, acts to reduce the noble metal precursors, and generate nanoparticles on the semiconducting surface. These nanoparticles are variably sized, which allows for the absorption (and thus the photochemical utilization) of a range of incident radiation that wouldn't be absorbed by the semiconducting oxide layer alone. These nanoparticles are also capable as acting as electron acceptors for the photo-generated electrons from the oxide surface, which absorbs incident high-energy UV radiation. The nanoparticles thus help to reduce charge recombination and also generate additional excitons from the absorption of incident light at a longer wavelength than that absorbed by the semiconducting material. The tandem semiconducting oxide layer/nanoparticle system exhibits more efficient photocatalytic performance than other methods, and the synthetic techniques used in this invention are facile and scalable.

[0007] According to one embodiment of the present invention, a method is provided for the deposition of thin, uniform semiconducting films and subsequent decoration of said film with noble metal nanoparticles grown directly on the semiconducting film surface.

[0008] According to one embodiment of the present invention, this method provides a means for the large-scale facile manufacture of textile materials with said coating, which lends the finished materials self-cleaning, antimicrobial, and UV-protective properties.

[0009] According to one embodiment of the present invention, a method is provided for the direct reduction of gold chloride and silver nitrate (gold and silver nanoparticle precursors) on the semiconducting surface under intense UV radiation during the manufacturing process, thus enabling the direct growth of the nanoparticles on the oxide surface and improving manufacturing time compared to the utilization of various chemical reducing agents and/or the separate growth of the nanoparticles and subsequent deposition onto the semiconductor-coated fabric, which would further complicate manufacture.

[0010] According to one embodiment of the present invention, a method is provided for coating all fibrous/non-fibrous textile materials with a semiconducting layer and nanoparticles to lend them anti-microbial, self-cleaning, and radiation-protective properties.

[0011] The present invention advances the art of treating textile materials with the aim of obtaining a textile material that has self-cleaning, anti-microbial, or radiation protective properties, and, in addition, provides an improved method for the application of the coating in a scalable manufacturing process.

[0012] Other aspects and advantages of the present invention will be apparent from the following detailed description of the preferred embodiments of the accompanying drawing figures.

DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWING

[0013] A clear understanding of the methodology employed and results obtained by this novel treatment technique can be had by referencing the appended drawings which illustrate the method and results of the innovative treatment technique, although it will be understood that such drawings depict preferred embodiments of the invention and, therefore, are not to be considered as limiting its scope with regard to other embodiments which the invention is capable of contemplating.

[0014] Accordingly, in the accompanying drawing, which forms a part of the specification and is to be read in conjunction therewith in which like reference numerals are used to indicate like or similar parts in the various views:

[0015] FIG. **1** is a schematic representation of a methodology used to construct a metallic nanoparticle semiconducting film-coated textile material in accordance with one embodiment of the present invention;

[0016] FIG. **2** is a schematic representation of a methodology used to deposit the semiconducting film onto a textile material in accordance with one embodiment of the present invention;

[0017] FIG. **3** is an SEM image showing an uncoated pristine fiber material at low and high magnification (a, b) and a TiO_2 coated fiber material at low and high magnification (c, d) in accordance with one embodiment of the present invention;

[0018] FIG. **4**A is a schematic representation of a methodology used to deposit and/or grow metallic nanoparticles directly on the surface of fiber material having a semiconducting layer coated thereon in accordance with one embodiment of the present invention;

[0019] FIG. **4**B is a schematic representation of a methodology used to deposit and/or grow metallic nanoparticles directly on the surface of fiber material having a semiconducting layer coated thereon in accordance with another embodiment of the present invention;

[0020] FIG. **5** is a SEM image showing an Ag—TiO_2 coated fiber material at low and high magnification (e, f) and an Au—TiO_2 coated fiber material a low and high magnification (g, h) in accordance with one embodiment of the present invention;

[0021] FIG. **6** is a graph containing the ultraviolet and visible absorption spectra of an uncoated pristine fiber material, a TiO_2 coated fiber material, an Ag—TiO_2 coated fiber material, and an Au—TiO_2 coated fiber material in accordance with one embodiment of the present invention;

[0022] FIG. **7** is a graph showing XRD spectra for (a) pre-exposure Ag—TiO_2 coated fiber material, (b) pre-exposure Au—TiO_2 coated fiber material, (c) pre-exposure TiO_2 coated fiber material, (d) pre-exposure pristine uncoated fiber material, and (e) post-exposure TiO_2 coated fiber material in accordance with one embodiment of the present invention;

[0023] FIG. **8** is a graph showing the ultraviolet and visible absorption spectra of (a) Ag—TiO_2 coated fiber material, (b) Au—TiO_2 coated fiber material, (c) TiO_2 coated fiber material, and (d) pristine uncoated fiber material, after staining with methylene blue dye and exposure to simulated solar light (1.5 sun intensity) over a measured interval of time to quantify the self-cleaning efficacy in accordance with one embodiment of the present invention;

[0024] FIG. **9** is a graph showing the rate of stain extinction of (a) Ag—TiO_2 coated fiber material, (b) Au—TiO_2 coated fiber material, (c) TiO_2 coated fiber material, and (d) pristine uncoated fiber material, after staining with methylene blue dye and exposure to simulated solar light (1.5 sun intensity) over a measured interval of time in accordance with one embodiment of the present invention;

[0025] FIG. **10** is a graph showing the C/C0 data for an Ag—TiO_2 coated fiber material over repeated cycles of staining and UV exposure in accordance with one embodiment of the present invention;

[0026] FIG. **11** is a graph of the FTIR spectra for Au—TiO_2 coated fiber material after repeated exposure to simulated solar light for exposure times of (a) no exposure, (b) two hours, (c) four hours, (d) six hours, and (e) ten hours in accordance with one embodiment of the present invention;

[0027] FIG. **12** is an image of a Kirby-Baur disk diffusion test for antimicrobial activity with (a) Au—TiO_2 coated fiber material, (b) Ag—TiO_2 coated fiber material, and (c) pristine uncoated fiber material in accordance with one embodiment of the present invention; and

[0028] FIG. **13** is a schematic representation of the antimicrobial activity of Au—TiO_2 coated fiber material before and after light exposure in accordance with one embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0029] The invention will now be described with reference to the drawing figures, in which like reference numerals refer to like parts throughout. For purposes of clarity in illustrating the characteristics of the present invention, proportional relationships of the elements have not necessarily been maintained in the drawing figures.

[0030] The following detailed description of the invention references specific embodiments in which the invention can be practiced. The embodiments are intended to describe aspects of the invention in sufficient detail to enable those skilled in the art to practice the invention. Other embodiments can be utilized, and changes can be made without departing from the scope of the present invention. The present invention is defined by the appended claims and the description is, therefore, not to be taken in a limiting sense and shall not limit the scope of equivalents to which such claims are entitled.

[0031] The present invention is directed to gold and/or silver titanium dioxide coated fibers or textile materials **10**. Such fibers **10** of the present invention have been shown to have substantial benefits, including being self-cleaning, antimicrobial, and protective against UV radiation. The present invention is also directed to a method **100** for constructing metallic nanoparticle and semiconductor layer textile materials. According to one embodiment, method **100** includes procedures for depositing and/or growing gold/silver nanoparticles onto a nanostructured titanium dioxide (TiO_2) film applied to a textile material or fiber surface. As described in greater detail herein, the method **100** of the present invention can be utilized to apply a uniform and high surface area film of TiO_2 onto a cotton fiber or other textile material, and subsequently directly incorporate gold/silver nanoparticles on the nanostructured TiO_2 surface of the fiber/textile material. The method **100** described herein can produce a TiO_2 film that is substantially homogenous with uniformly distributed Au/Ag nanoparticles on the TiO_2 film distributed using photocatalytic reduction method.

[0032] According to one embodiment the Ag—TiO_2 coated textile material **10** of the present invention was observed to have the largest improvement in rate of stain extinction compared to the untreated fibers with a methylene blue stain. According to one embodiment, the Au and/or Ag—TiO_2 coated textile material **10** of the present invention were observed to have the largest improvement versus untreated fibers when stained with Congo red. The Ag/Au—TiO_2 coated textile material **10** can maintain consistent photocatalytic activity over multiple cycles and have resistance to degradation, which was verified using Fourier transform infrared spectroscopy (FTIR). The Ag/Au—TiO_2 coated textile material **10** are also configured for efficient anti-microbial activity, which was confirmed by exposure of the fibers to bacterial culture (*Escherichia coli*) and direct observation of antimicrobial activity.

[0033] As described herein, the present invention is directed to a method **100** for depositing and/or growing nanostructured gold and silver nanoparticles on the surface of natural fibers (i.e., textile materials) that have been coated with TiO_2. The TiO_2 coating can be applied utilizing a sol-gel based method that uniformly coats the fiber material; however, other methods can also be suitably used. TiO_2 is a well-known photo-catalyst that has been extensively tested and shown to effectively decompose a wide range of organic substances under irradiation with solar light, including methylene blue, isothiazolin-3-ones, formaldehyde, acid orange, phenol, coffee/wine stains, and even the chemical warfare agent Soman. The innate photocatalytic effectiveness of TiO_2 is very high, even under artificial room lighting a layer of TiO_2 possesses sufficient photocatalytic activity to completely mineralize an approximately 1 μm thick hydrocarbon layer every hour, and therefore can be suitable for a surface photocatalytic coating to produce self-cleaning fibers and textile materials.

[0034] The gold and silver nanoparticles can be applied via direct reduction of $AuCl_3$ and/or $AgNO_3$ by UV radiation as described herein. Ag/Au—TiO_2 coated fibers **10** created through method **100** of the present invention have demonstrated self-cleansing and anti-microbial properties. Silver nanoparticles have been shown to have antibacterial activity and have been shown to reduce the incidence of electron/hole recombination when used in conjunction with TiO_2, which should improve photocatalytic activity. Gold nanoparticles have been shown to decrease the bandgap of TiO_2 which improves overall photocatalytic activity and allows for the photocatalytic destruction of certain organic under visible-only/UV filtered lighting conditions where a TiO_2 coating alone is ineffective. As described herein, method **100** of the present invention is directed to procedures for successfully depositing and growing gold and silver nanoparticles onto a TiO_2 coating layer that coats the surface of a textile or fiber material.

[0035] Referring to FIG. **1**, method **100** according to one embodiment of the present invention is illustrated schematically. As shown, method **100** begins with an initial step **200** that includes providing a fiber/textile material and coating the textile material with a TiO_2 coating. As further shown in FIG. **1**, method **100** includes a subsequent step **300** that includes depositing gold and/or silver nanoparticles onto the surface of the TiO_2 fiber/textile material. Method **100** and steps **200** and **300** incorporated into method **100** for providing an Au/Ag—TiO_2 coated fiber material **10** will now be described in greater detail with reference to the several figures.

[0036] Referring to FIG. **2**, step **200** and the methodology for coating the fiber or textile material (referred to herein as a fiber material for simplicity) with a thin film of titanium dioxide via a sol-gel method can take place in several steps as described below. At step **202**, the fiber material can be washed and cleaned. According to one embodiment the fiber material at step **202** can be thoroughly cleaned via washing with acetone at an elevated temperature for a suitable period of time (e.g., hours) to remove any impurities that may be present (such as natural fats). In other embodiments, any suitable cleaning method can also be utilized. Next, at step **204**, the fiber can be dried. According to one embodiment, the drying process of step **204** can include drying the fiber material at room temperature or other suitable temperature for a suitable period of time (for example, 12 hours).

[0037] Next, at step **206**, a TiO_2 nanosol coating solution can be prepared for coating the fiber material. The coating solution can include the preparation of two solutions: solution A and solution B. As shown by step **206**A, solution A can be prepared by combining approximately 2% by volume acetic acid and 12% by volume titanium isopropoxide in approximately 86% by volume 2-propanol and mix vigorously for approximately 30 minutes as represented by step **206**C. According to one embodiment, solution A can comprise 50 mL of 2-propanol, 1 mL of acetic acid, and 5.91 mL of titanium isopropoxide; however, it is recognized that other percentage-by-volume amounts can suitably be used. As shown by step **206**B, solution B can be prepared by combining approximately 6% by volume of concentrated hydrochloric acid and approximately 1.5% ultrapure water in approximately 92.5% of 2-propanol and mix vigorously for approximately 30 minutes as represented by step **206**C. According to one embodiment, solution B can comprise 50 mL of 2-propanol, 3 mL concentrated hydrochloric acid, and 0.72 mL of ultrapure water; however, it is recognized that other percentage-by-volume amounts can suitably be used.

[0038] Next, at step **208**, solutions A and B can be mixed together and combined. According to one embodiment, step **208** includes the procedure of slowly adding solution B into solution A while under vigorous stirring (e.g., 400-800 rpm) solution A until the solutions A and B are thoroughly combined to form the nanosol coating solution.

[0039] Next, at step **210**, the fiber material can be immersed in the nanosol coating solution for approximately 30 seconds and removed. Depending on the particular application of method **100**, the prepared nanosol coating solution can continue to be used for as long as 7 days before it loses its integrity and precipitating out TiO_2 and becoming qualitatively opaque instead of transparent. The ability to reuse the prepared nanosol coating solution for an extended period of time and provide cost and efficiency benefits for large-scale productions of Au/Ag—TiO_2 coated fiber material **10**.

[0040] Next, at step **212**, the fiber material can be dried. According to one embodiment, the drying process at step **212** can include drying the fiber material for approximately 24 hours at room temperature under normal atmospheric conditions.

[0041] Next, at step **214**, the fiber material can be calcined in order to remove any residual solvent. According to one embodiment, as shown in FIG. **2**, step **214** can include a sub-step **214**A where the fiber material is calcined at approximately 65° C. for approximately 10 minutes and a sub-step **214**B where the fiber material is calcined at approximately 90-95° C. for approximately 5 minutes under normal atmospheric conditions.

[0042] Next, at step **216**, the calcined fiber material can be hydrothermally treated to remove excess oxide left behind from the nanosol coating process. According to one embodiment, the process at step **216** can include boiling the fiber material in ultrapure water for a period of approximately 3 hours.

[0043] FIG. **3** illustrates the effect of the TiO_2 coating process described in step **200**. FIGS. **3**(*a*) and **3**(*b*) provide SEM images at low and high magnification, respectively of a cotton fiber material that was not treated with the TiO_2 coating of step **200**. FIGS. **3**(*c*) and **3**(*d*) provide SEM images at low and high magnification, respectively, of a TiO_2 coated cotton fiber material that was treated with the TiO_2 coating of step **200**. The differences between (a) and (b) of FIG. **3** and (c) and (d) demonstrate how the coating process of step **200** creates a thin, essentially uniform coating on the surface of the fiber material, and that the coating process of step **200** results in quality adhesion of the coating to the surface of the fiber material without significant cracking or other surface deformities. The coating process of step **200** can also result in a coating that is thin enough so as to allow for flexing of the fiber material without the coating cracking or becoming separated from the fiber material surface.

[0044] Referring to FIGS. **4**A and **4**B, step **300** of the method **100** for constructing Ag/Au—TiO_2 coated fibers **10** is described in greater detail. As schematically illustrated in FIG. **4**A and described below, step **300** can include several steps for depositing/growing gold and/or silver nanoparticles on the surface of the TiO_2 coated fiber material. Step **300** can begin at step **302** where a metallic nanoparticle precursor solution is prepared. According to one embodiment, the precursor is prepared by diluting a solution of gold chloride ($AuCl_3$) with ultrapure water to create a 100 mL precursor solution of 1 mM $AuCl_3$. According to another embodiment, the precursor is prepared by diluting a solution of silver nitrate ($AgNO_3$) in ultrapure water to create a 100 mL precursor solution of 1 mM $AgNO_3$. In other embodiments, greater or lesser concentrations of gold chloride or silver nitrate can suitably be used to for the precursor solution.

[0045] Next, at step **304**, the TiO_2 coated fiber material can be immersed in the precursor solution for a suitable period of time and then removed. According to one embodiment, the preferred time period is approximately 30 seconds.

[0046] Next, at step **306**, the metallic nanoparticle-TiO_2 coated fiber material (i.e., $AuCL_3$—TiO_2 coated fiber material or $AgNO_3$—TiO_2 coated fiber material) can be allowed to dry for a suitable period of time. According to one embodiment, during step **306**, the coated fiber material is left to dry at room temperature under normal atmospheric conditions for approximately 24 hours (however, other temperatures, conditions and time periods can also be suitably used during step **306**).

[0047] Next, at step **308**, the metallic precursor solution-TiO_2 coated fiber material is exposed to UV radiation for a suitable period of time as shown in FIG. **4**A. According to one embodiment, the $AuCL_3$or $AgNO_3$—TiO_2 coated fiber material is exposed to approximately 254 nm UV radiation for approximately 30 minutes. According to one embodiment, the UV radiation is applied for approximately 15 minutes on each side of the coated fiber material as shown in FIG. **4**B. Other suitable time periods for UV radiation exposure can also be suitable used in alternative embodiments. Step **308** can act to photocatalytically reduce the metallic nanoparticle precursors deposited via a solvent-based method, and can essentially activate the photocatalytic surface. The semiconducting oxide material (TiO_2) is most photocatalytically active and/or capable of reducing the metallic nanoparticle precursors when irradiated with UV light, so intense UV light can be preferable used for initial creation of the nanoparticles.

[0048] FIG. **5** illustrates the effect of the metallic nanoparticle application process described in step **300** where metallic nanoparticles (e.g., Au or Ag nanoparticles) are deposited and/or grown the TiO_2 coated surface of the fiber material. As shown in FIGS. **3**(*a*) and (*b*) and described above, the fiber material includes natural surface folds, which increase the exposed surface area of the fiber material and can improve photocatalytic efficiency by providing more sites for photoreactions to take place and for the anchoring of nanoparticles. As shown in FIGS. **3**(*c*) and (*d*), the application of the TiO_2 coating on the surface of the fiber material results in a slight reduction in the fold definition. Subsequently, as illustrated in FIGS. **5**(*e*)-(*h*), after the TiO_2-coated fiber material is immersed in the metallic nanoparticle precursor solution, removed, dried and exposed to UV radiation through steps **302**-**308**, the growth of metallic nanoparticles gold and silver nanoparticles on the TiO_2 coated fiber materials is visible on the SEM images of FIG. **5**. FIGS. **5**(*e*) and (*f*) show Ag—TiO_2 coated fiber material **10** at low and high magnification, respectively, while FIGS. **5**(*g*) and (*h*) show Au—TiO_2 coated fiber material **10** at low and high magnification, respectively.

[0049] Referring to FIG. **6**, the UV-Visible absorption spectra of Ag/Au—TiO_2 coated fiber materials **10** prepared following the steps of method **100** outlined above is shown, and the clear offset of the gold and silver nanoparticle coated fiber material is visible. As shown in FIG. **6**, the relatively wide absorption peaks of the gold and silver nanoparticle peaks are due to the range of nanoparticle sizes generated by the reduction method used above. Peak width and peak offset can be both important for the photocatalytic efficacy of the textile coating. It is apparent that the absorption contribution of the nanoparticles allows the semiconducting layer to absorb incident near-UV/visible photons which enhance the photocatalytic efficiency.

[0050] FIG. **6** illustrates the development of Au and Ag nanoparticles under UV radiation where the Ag/Au—TiO_2

coated fiber materials **10** were formed using 5 mM precursor solutions of $AgNO_3$and $AuCl_3$. The gold peak in the embodiment illustrated in FIG. **6** is at 547 nm, which matches what would be expected if the gold nanoparticles took on roughly spherical shapes and have an average size of 60-80 nm (calculated utilizing available data concerning nanoparticle size and max wavelength of UV-vis absorption). Further, the width of the peak indicates that nanoparticles constituting a range of sizes were directly generated on the TiO_2 surface coating. The silver nanoparticle peak in the embodiment illustrated in FIG. **6** is at 440 nm, which matches what would be expected if the average size of the nanoparticles were between 40 and 50 nm. The intense absorption present in the UV-vis spectra of all TiO_2 coated samples in the UV region is due to the absorption profile of plain TiO2. Because the gold and silver nanoparticle peaks occur in the visible region of the spectra it should be noted that the fiber materials may take on a characteristic purple (in the case of gold) or brown (in the case of silver) color after deposition of the nanoparticles but prior to staining, which matches the coloration found in the literature when dealing with comparatively large gold and silver nanoparticles. FIG. **6** further illustrates UV protective properties of the Ag/Au—TiO_2 coated fiber materials **10** over untreated cotton, as the absorption of all samples but pristine can be seen to dramatically increase in the UV region of the spectra.

[0051] FIG. **7** illustrates the XRD spectra for (a) pre-exposure Ag—TiO_2 coated fiber materials, (b) pre-exposure Au—TiO_2 coated fiber materials, (c) pre-exposure TiO_2 coated fiber materials, (d) pre-exposure pristine uncoated fiber materials, and (e) post-exposure TiO_2 coated fiber materials.

[0052] FIG. **8** illustrates the UV-Vis absorption spectra of (a) Ag—TiO_2 coated fiber materials, (b) Au—TiO_2 coated fiber materials, (c) TiO_2 coated fiber materials, and (d) pristine uncoated fiber materials after staining with methylene blue dye and exposing the fiber material to simulated full-spectrum solar light (1.5 sun intensity) over a variety of time intervals. The area contained by the peak can be directly related to the intensity of the appearance of the stain on the fiber material and thereby also to the concentration of the dye molecules remaining on the surface of the Ag/Au—TiO_2 coated fiber materials by Beer's law. As also shown in FIG. **8**, the rate of stain extinction/fiber self-cleaning is dramatically increased on the Ag/Au—TiO_2 coated fiber materials as the methylene blue stain is being destroyed by the Ag/Au—TiO_2 coating at a faster rate than what occurs with the pristine uncoated fiber material.

[0053] As shown in FIG. **9**, the breakdown of methylene blue proceeds much more rapidly for the fiber samples that have been coated with TiO_2, and further improvement of the rate of decay is obtained when gold or silver nanoparticles are deposited on the TiO_2-coated fibers. FIG. **9** illustrates the integration of the area contained by the peaks in FIG. **8** and allows for determination of the rate of stain removal from the textile materials. The rate of stain removal observed for the Ag/Au—TiO_2 coated fiber materials is of the first order, and was observed to proceed more rapidly for the Ag/Au—TiO_2 coated fiber materials than for either the only TiO_2 coated fiber materials or the untreated fiber material, providing direct quantitative verification of the enhancement in photocatalytic activity obtained with this treatment methodology. The extinction of methylene the adsorbed stain can be seen to follow a roughly first order rate of decay, where the rate of decay can be determined by $\ln([C]/[C]_0)=-kt$ (illustrated by the plot of FIG. **9**).

[0054] FIG. **10** illustrates repeated testing cycles of the Ag/Au—TiO_2 coated fiber materials to illustrate that the photocatalytic activity of the Ag/Au—TiO_2 coated fiber materials does not decrease over time. As shown, following three cycles of staining followed by exposure to simulated sunlight until the stain was virtually eliminated, the Ag/Au—TiO_2 coated fiber materials displayed remarkable consistency of stain removal over multiple cycles, with the obtained rate constants of stain removal being virtually the same. As further illustrated by FIG. **10**, the kinetic rates of stain degradation do not change over multiple staining cycles for the Ag/Au—TiO_2 coated fiber materials, and the photo-catalytic activity of the produced Ag/Au—TiO_2 coating is stable even over a significant length of time.

[0055] FIG. **11** illustrates FTIR spectra of the Ag/Au—TiO_2 coated fiber materials after repeated exposure to simulated solar light for exposure times of (a) no exposure, (b) two hours, (c) four hours, (d) six hours, and (e) ten hours. As shown, the spectra for the Ag/Au—TiO_2 coated fiber materials remains unchanged over time indicating minimal degradation. Additionally, the surface coating is not being damaged during the process of stain removal, and the photocatalytic activity of the Ag/Au—TiO_2 coated fiber materials appear to remain roughly unchanged over multiple staining/stain removal events. The concentration of the stain also has no apparent effect on the rate of stain removal, as staining for the first two cycles was performed using a 0.001% w/v methylene blue solution, and staining for the third cycle used a 0.1% w/v solution and no difference in extinction rate was observed. This suggests that the photocatalytic activity of the Ag/Au—TiO_2 coating does not decrease with increased stain saturation, at least at practical levels of staining.

[0056] Staining with Congo red was also performed to evaluate the photocatalytic performance with a different, less easily broken-down stain. In general, the extinction of Congo red can be seen to proceed more slowly than methylene blue, with the rate of extinction of Congo red stained on pristine fiber material being roughly half that of methylene blue stained on pristine fiber material. The improvement in the rate of stain extinction of the Ag/Au—TiO_2 coated fiber materials over the pristine fiber material was also less pronounced when Congo red was tested, with a 1 mM Ag/Au—TiO_2 coated fiber material sample demonstrating the best performance in this case with a 65% improvement in the rate of stain removal when compared to the pristine fiber material. Congo red taking longer to degrade is expected as it has been found to take roughly twice as long as methylene blue to photocatalytically degrade, however the decrease in the photocatalytic effect of the Ag/Au—TiO_2 coated fiber materials is notable. This effect can be partially accounted for by the fact that Congo red, while having its main absorption peak at 496 nm, also has two absorption peaks in the UV region at 236 and 338 nm. Because of this, it is likely that some of the incident photocatalytically useful UV and near UV radiation was absorbed by the Congo red stain itself rather than interacting with the Ag/Au—TiO_2 coating layer, decreasing the apparent efficiency of the catalytic coating. Compounds such as Congo red which absorb high-energy incident radiation are a good example of why Au/Ag nanoparticle-based photosensitizers are important for photocatalytic applications; by decreasing the bandgap of TiO_2 and increasing the wavelength range in which photons can be harnessed for photocatalysis, compounds which inherently absorb high-energy incident photons can still be degraded. This is likely the reason that the majority of the nanoparticle coated samples displayed better performance than the fiber material coated with TiO_2 only when stained with Congo red.

[0057] Additionally, the Au—TiO_2 coated fiber materials displayed markedly better photocatalytic activity than the Ag—TiO_2 coated fiber materials when stained with Congo red (S7), and the reason for this could be explained by the higher wavelength of the gold nanoparticle peak relative to the silver peak, and thus the decreased overlap with the Congo red peaks. This strongly suggests that electron transfer is taking place between the gold nanoparticles and the TiO_2 coating, and that the gold nanoparticles are acting as photosensitizers. A complicating factor in interpreting the kinetic data directly is the non-first order rate of stain extinction observed for the samples not impregnated with nanoparticles, which was also observed in previous works. This complicates direct comparison of the kinetic constants with one another however qualitatively it can still be seen that the rate of stain extinction is improved for the metallic nanoparticle impregnated samples (See FIG. **8**).

[0058] The fiber materials' stability of photocatalytic activity over time, and confirmation that the cellulose was not being photocatalytically destroyed was provided by FTIR analysis of the Au—TiO_2 coated fiber materials at regular intervals after UV exposure (See FIG. **11**). Degradation of the fiber would be evidenced by changes in the FTIR spectra corresponding to destruction of the cellulosic backbone, however no changes in the spectra are observed. Characteristic peaks that can be observed include a broad O—H stretching band at 3378 cm−1, the C—H stretching band at 2900 cm−1, and the H—O—H bending band at 1650 cm−1, which is observed to be more intense in the Au—TiO_2 coated fiber material than in the pristine fiber material, however this may also be due to the somewhat hydrophobic nature of the potassium bromide used to prepare the fibers for FTIR analysis. The TiO_2 band is expected to appear at ~700 cm−1, and indeed the Au—TiO_2 absorption spectra lack the "dip" observed in the spectra of pristine cotton near 700 cm−1, which suggests that the TiO_2 while not immediately visible is indeed present as a relatively broad peak. Reduction of the intensity of C—H stretching band at 2900 cm−1 was also observed. Overall, the consistency of the FTIR spectra after ten hours of exposure to simulated solar light suggests that the Au—TiO_2 coated fibers possesses long-term photo stability.

[0059] Referring to FIGS. **12** and **13**, the antimicrobial properties of the prepared fabric material were examined via the Kirby-Baur disk diffusion method using gram negative *E. coli.* bacteria. The nanoparticle coated fiber samples are expected to show antimicrobial activity in addition to the stain cleansing properties. As shown in FIG. **12**, a zone of exclusion is clearly visible around the Au—TiO_2 coated fiber material (a) and the semiconductor and Ag—TiO_2 coated fiber material (b), but not around the TiO_2 coated fiber material alone (c), indicating that the metallic nanoparticles directly grown on the semiconducting surface lend the material antimicrobial properties.

[0060] Testing of the anti-microbial properties of the Ag/Au—TiO_2 coated fiber materials demonstrated that the prepared fiber samples were resistant to gram negative *E. coli* microbial contamination as evidenced by the zone of inhibition that was present around the fibers after inoculation and incubation of the plates (See FIG. **12**). It should be noted that the degree of *coli* inhibition for the gold and silver nanoparticle coated samples was about equivalent. This result was expected given the widespread study and utilization of silver nanoparticles for their bactericidal properties, and the recent utilization of gold nanoparticles for the same purpose. The TiO_2 and pristine cotton fiber material samples exhibited little to no bacterial inhibition, which is notable as some limited degree of bactericidal activity would be expected simply from the reducing/oxidizing potential generated by the TiO_2 layer, and while the oxide alone likely generates some antimicrobial activity, it is apparently much more pronounced with the gold and silver nanoparticle containing samples. It is likely however that bacteria located directly on the illuminated fiber samples coated with TiO_2 only would be quickly removed by the oxidizing power of the TiO_2 and the reactive species generated at the surface, as *E. coli, Staphylococcus aureus,* and *Pseudomonas aeruginosa,* the bacteria responsible for common skin infections/MRSA (methicillin-resistant *Staphylococcus aureus*) and hospital-acquired antibiotic resistant infections respectively, have each been experimentally observed to be killed rapidly on illuminated TiO_2 surfaces.

[0061] Furthermore, the toxic compounds produced by bacteria can themselves be certainly decomposed by the catalytic action of TiO_2. However, this localized effect is insufficient if the fiber is to be deployed as clothing material, as the entirety of the fiber should be kept free from microbes, not just the outermost exposed surface, thus the relatively large zone of exclusion provided by the incorporation of gold and silver nanoparticles is desirable. One proven mechanism of bactericidal action for both gold and silver nanoparticles includes the disruption of cysteine/disulfide bonds in the proteins on the exterior of bacterial cell walls leading to decreased cell wall integrity, direct inhibition of ATP production, ribosomal activity, and DNA degradation.

[0062] Free radical generation has also been proposed to be an active bactericidal mechanism for silver nanoparticles. The reaction between silver nanoparticles and the membrane structures of both gram positive and gram negative is not fully understood, however the formation of "pits" in the out membranes due to the presence of silver nanoparticles, leading to increased membrane permittivity and ultimately cell death has been observed. However there remains a strong argument for the free radicals generated by silver nanoparticles to be the main causal mechanism behind the antimicrobial effects, as the inclusion of an antioxidant in one study was found to eliminate the anti-microbial action of silver nanoparticles. Furthermore, it has been suggested that the evolution of silver ions produced from the silver nanoparticles via their oxidation by the holes produced on the TiO_2 layer may be another mechanism by which the TiO_2/Ag nanoparticle hybrid surface exhibits antimicrobial activity, as a similar mechanism has been observed with TiO_2/copper hybrid surfaces. Our results suggest that some combination of the above outlined plays an active role in improving the antimicrobial activity of the nanoparticle coated fiber samples, and further elucidation of the mechanism behind the observed antimicrobial properties could be had testing the nanoparticle coated fibers in the presence of an antioxidant. The gold and silver nanoparticle coated fiber materials showed similar antibacterial activity. FIG. **13** demonstrates the mechanism behind the most active bactericidal pathway in this photocatalytically active material, namely, the generation of electrons and holes that react through the mechanisms outlined above to destroy bacteria in proximity to the photocatalytically active nanostructured surface.

[0063] In some embodiments, the method provides for treating a textile fiber material with a sol-gel based method, as outlined above, so as to facilitate the deposit of a semiconducting thin film (TiO_2) on at least one surface of the textile material. In this manner, metallic (Ag/Au) nanoparticles, for example silver, gold or both silver and gold, metallic nanoparticles are grown directly on the oxide surface via the photocatalytic reduction method outlined above. This treatment method provides for the creation of a photocatalytically active fiber material, that is scalable using techniques carried out at normal atmospheric pressure, (about 1 atmospheric pressure), and require only that the material be capable of withstanding 95° C. temperatures for a short period of time. Another important feature of the method **100** is the use of the nanoparticles to allow the absorption and photocatalytic utilization of near-UV and visible incident photons which improves photocatalytic activity by allowing for the useful harnessing of more incident light. The metallic nanoparticles impart an antimicrobial feature to the surface of a material, for example the surface of a fiber material, another unique feature imparted to the surfaces and fiber materials provided as part of the invention.

[0064] The present invention allows for the treatment of fibrous and non-fibrous textile materials and the production of a hybrid semiconductor/metallic nanoparticle based photocatalytic (self-cleaning), antimicrobial, and UV radiation protective system on the textile surface. The treatment technique allows the textile material to be treated without the use of either vacuum or pressurized conditions, and the textile material is required only to withstand dry annealing at 95 C and hydrothermal treatment in boiling water, both mild conditions compared to more exotic treatment methodologies.

[0065] While the present invention has been described in terms of particular embodiments and applications, in both summarized and detailed forms, it is not intended that these descriptions in any way limit its scope to any such embodiments and applications, and it will be understood that many substitutions, changes and variations in the described embodiments, applications, and details of the method and system illustrated herein and of their operation can be made by those skilled in the art without departing from the spirit of this invention.

[0066] From the foregoing, it will be seen that this invention is one well adapted to attain all the ends and objects hereinabove set forth together with other advantages which are obvious, and which are inherent to the structure. It will be understood that certain features and sub combinations are of utility and may be employed without reference to other features and sub combinations. This is contemplated by and is within the scope of the claims. Since many possible embodiments of the invention may be made without departing from the scope thereof, it is also to be understood that all matters herein set forth or shown in the accompanying drawings are to be interpreted as illustrative and not limiting.

[0067] The constructions described above and illustrated in the drawings are presented by way of example only and are not intended to limit the concepts and principles of the present invention. Thus, there has been shown and described several embodiments of a novel invention. As is evident from the foregoing description, certain aspects of the present invention are not limited by the particular details of the examples illustrated herein, and it is therefore contemplated that other modifications and applications, or equivalents thereof, will occur to those skilled in the art. The terms "having" and "including" and similar terms as used in the foregoing specification are used in the sense of "optional" or "may include" and not as "required". Many changes, modifications, variations and other uses and applications of the present construction will, however, become apparent to those skilled in the art after considering the specification and the accompanying drawings. All such changes, modifications, variations and other uses and applications which do not depart from the spirit and scope of the invention are deemed to be covered by the invention which is limited only by the claims which follow.

What is claimed is:

1. A method for providing a surface having a metallic nanoparticle semi-conductor layer comprising:

providing a semi-conducting layer on the surface; and

treating said semi-conductor layer on the surface to provide metallic nanoparticles on said semi-conductor layer, comprising:

immersing said semi-conductor layer in an aqueous solution comprising a precursor solution, said precursor solution comprising metallic nanoparticles, to provide a precursor solution-treated semi-conductor layer;

drying said precursor solution-treated semi-conductor layer at room temperature;

exposing said dried precursor solution-treated semi-conductor layer to ultraviolet radiation for a selected time duration; and

providing metallic nanoparticles on the semi-conductor layer, to provide a surface having a metallic nanoparticle semi-conductor layer.

2. The method of claim **1**, wherein said precursor solution comprises gold chloride ($AuCL_3$) and ultrapure water.

3. The method of claim **2**, wherein said precursor solution comprises silver nitrate ($AgNO_3$) and ultrapure water.

4. The method of claim **1**, wherein said semi-conductor layer is immersed in said precursor solution for approximately 30 seconds.

5. The method of claim **1** wherein said semi-conductor layer is dried at room temperature under normal atmospheric conditions for approximately 24 hours.

6. The method of claim **5**, wherein said dried semiconductor layer is exposed to about 254 nm UV radiation for approximately 30 minutes.

7. The method of claim **6**, wherein said dried semiconductor layer is exposed to about 254 nm UV radiation for approximately 15 minutes.

8. A material comprising a surface, said surface comprising a semi-conductor layer containing metallic nanoparticles, wherein said semi-conductor layer is resistant to peeling and is non-toxic.

9. The material of claim **8** wherein said surface is a surface of a textile material and said textile material is anti-microbial and self-cleaning.

10. The material of claim **8** wherein the metallic nanoparticles comprise gold nanoparticles, silver nanoparticles, or a combination thereof.

11. The material of claim **8** wherein the textile material comprises a fiber.

12. A textile material comprising fibers having a metallic nanoparticle semi-conductor film, wherein said film comprises a nanostructured titanium dioxide film and metallic nanoparticles.

13. The textile material of claim **12** wherein the metallic nanoparticles comprise gold, silver, or a combination of gold and silver nanoparticles.

14. The textile material of claim **12** wherein said textile material is resistant to *E. coli* microbial contamination, mechanical peeling and is non-toxic.

15. A face mask comprising the textile material of claim **12**.

16. A garment comprising the textile material of claim **12**.

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