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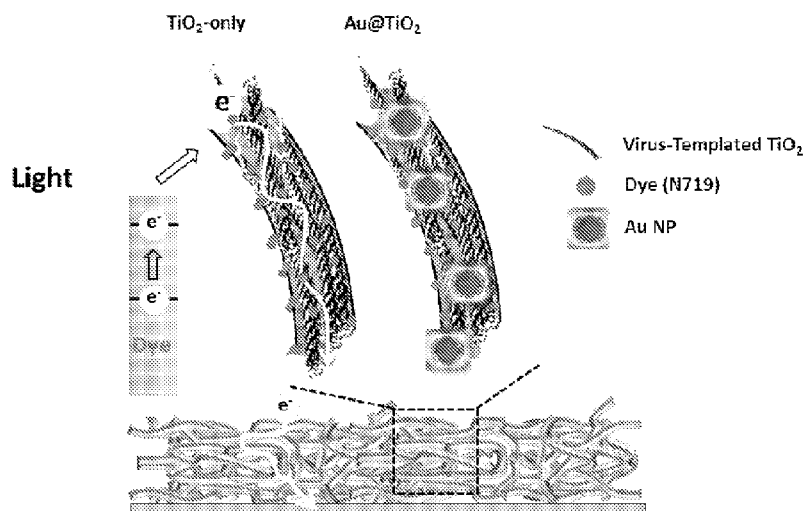
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**FIG. 3**

(57) **Abstract:** A dye-sensitized solar cell can include a photoanode including a three-dimensional scaffold of TiO₂ nanowires. In one aspect, a of making a photoanode for a dye-sensitized solar cell includes forming a network of metal-binding viruses; and nucleating TiO₂ nanoparticles on the metal-binding viruses. In another aspect, a dye-sensitized solar cell includes a photoanode including a three-dimensional scaffold of TiO₂ nanowires.

PLASMON ENHANCED DYE-SENSITIZED SOLAR CELLS

CLAIM OF PRIORITY

This application claims the benefit of prior U.S. Provisional Application No.
5 61/726,761, filed on November 15, 2012, which is incorporated by reference in its
entirety.

TECHNICAL FIELD

The present invention generally relates to plasmon enhanced dye-sensitized solar
10 cells.

BACKGROUND

The need for preserving non-renewable energy and lowering carbon dioxide
emission requires efficient and inexpensive approaches to utilize solar energy. Dye-
15 sensitized solar cells (DSSCs) are a promising technology due to their low cost and
potentially higher efficiency than silicon solar cells. DSSCs offer high internal quantum
efficiency, large surface-to-volume ratio, and a tunable absorption range.

SUMMARY

20 Viral bio-templates can be used to generate hybrid materials with unique
properties. For example, the M13 virus can be employed to create a multifunctional three-
dimensional (3-D) scaffold of photoactive material (e.g., semiconductor nanowires) to
improve the electron collection and light harvesting for an efficient dye-sensitized solar
cell (DSSC). A DSSC with virus-templated nanowire-based TiO₂ photoanodes exhibits
25 advantageous electron transport properties, characterized by a longer electron diffusion
length compared to a nanoparticle-based DSSC. Moreover, the ability of the virus to bind
metal nanoparticles can be used to increase the light absorption of dye by a localized
surface plasmon. Consequently, a virus-templated plasmon-enhanced DSSC achieves an
increased efficiency of 8.46% by improving both light harvesting and electron collection
30 simultaneously.

In one aspect, a method of making a photoanode for a dye-sensitized solar cell
includes forming a network of metal-binding viruses; and nucleating TiO₂ nanoparticles
on the metal-binding viruses.

Forming the network can include crosslinking the metal-binding viruses. The method can further include annealing the TiO₂ nanoparticles. The method can further include binding metal nanoparticles to the viruses. The metal nanoparticles can include Au or Ag.

5 In another aspect, a dye-sensitized solar cell includes a photoanode including a three-dimensional scaffold of TiO₂ nanowires. The TiO₂ nanowires can be interconnected. The photoanode can further include a plurality of a plasmon-forming nanostructures, wherein each plasmon-forming nanostructure includes a metal nanoparticle and a semiconducting oxide on a surface of the metal nanoparticle. The TiO₂ nanowires can have the dimensions of a virus template. The TiO₂ nanowires can be formed by nucleation on a virus template.

In another aspect, a method of generating solar power includes illuminating a dye-sensitized solar cell including a photoanode including a three-dimensional scaffold of TiO₂ nanowires.

15 The TiO₂ nanowires can be interconnected. The photoanode can further include a plurality of a plasmon-forming nanostructures, wherein each plasmon-forming nanostructure includes a metal nanoparticle and a semiconducting oxide on a surface of the metal nanoparticle. The TiO₂ nanowires can have the dimensions of a virus template. The TiO₂ nanowires can be formed by nucleation on a virus template.

20 Other aspects, embodiments, and features will become apparent from the following description, the drawings, and the claims.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic depiction of a dye-sensitized solar cell.

25 FIG. 2 is a schematic depiction of plasmon-forming nanoparticles.

FIG. 3 is a schematic illustration of DSSCs including a 3-D virus templated photoanode with or without additional metal nanoparticles.

FIG. 4 is a schematic illustration of a fabrication process for a 3-D porous TiO₂ photoanode, including hydrogel formation, TiO₂ nucleation, and annealing.

30 FIGS. 5A shows XRD analysis of annealed virus-templated anatase TiO₂ photoanodes; and SEM images of annealed virus-templated TiO₂ photoanodes in (FIGS. 5B-5D) top-view and (FIG. 5E) cross-section.

FIG. 6A shows electron diffusion length analysis, where L_n is the electron diffusion length and L is the photoanode thickness. FIG. 6B shows device performances for DSSCs employing the virus-templated TiO_2 -only photoanodes. The performance of nanoparticle-based DSSC is shown as a reference.

FIG. 7A is a TEM image of M13 virus. FIG. 7B is a TEM image of as-synthesized 20 nm Au nanoparticles. FIG. 7C is a TEM image of the Au nanoparticle-virus complex. FIG. 7D is a TEM image of annealed virus-templated Au@TiO_2 photoanode. FIG. 7E shows XRD analysis of virus-templated anatase Au@TiO_2 photoanode.

FIG. 8 is an SEM image of an annealed virus-templated Au@TiO_2 photoanode.

FIGS. 9A-9F demonstrate LSP-induced enhancement of optical absorption of dye-molecules in solution and in virus-templated TiO_2 thin film. FIG. 9A is an optical absorption spectra of Au nanoparticles, dye-molecules, and their mixture in solution. FIG. 9B shows net changes of dye absorption (ΔOD) due to the presence of Au nanoparticles in solution. FIG. 9C shows relative changes of effective extinction coefficient of dye ($\Delta\alpha/\alpha$) due to the presence of Au nanoparticles in solution. FIG. 9D shows optical absorption spectra of virus-templated TiO_2 and Au@TiO_2 films and their dye-adsorbed thin films ($\sim 0.6 \mu\text{m}$). FIG. 9E shows the ΔOD of dye due to the presence of Au nanoparticles in thin film. FIG. 9F shows relative changes of $\Delta\alpha/\alpha$ of dye due to the presence of Au nanoparticle in thin film. For the calculation of ΔOD and $\Delta\alpha/\alpha$: $\Delta\alpha/\alpha = \Delta OD(\lambda)/OD_{\text{dye}}(\lambda) = (OD_{\text{dye,Au}}(\lambda) - OD_{\text{dye}}(\lambda) - OD_{\text{Au}}(\lambda))/OD_{\text{dye}}(\lambda)$, where $OD_{\text{dye}}(\lambda)$, $OD_{\text{Au}}(\lambda)$, and $OD_{\text{dye,Au}}(\lambda)$ are the optical densities at wavelength λ of pure dye solution, Au nanoparticle solution, and their mixture solution with the same concentrations of dye and Au nanoparticles, respectively. For the solid-state thin films, the net absorption of dye-molecule is $OD_{\text{dye}}(\lambda) = OD_{\text{dye,TiO}_2}(\lambda) - OD_{\text{TiO}_2}(\lambda)$.

FIGS. 10A-10C show spectral responses of virus-templated TiO_2 -only and Au@TiO_2 DSSCs. FIG. 10A shows the IPCE spectra of the DSSCs with and without the presence of Au nanoparticles. FIG. 10B shows the net change of IPCE ($\Delta IPCE$) and FIG. 10C the relative changes ($\Delta IPCE/IPCE$) due to the presence of Au NPs. $\Delta IPCE(\lambda)/IPCE = IPCE_{\text{Au@TiO}_2}(\lambda) - IPCE_{\text{TiO}_2\text{-only}}(\lambda)/IPCE_{\text{TiO}_2\text{-only}}(\lambda)$. $IPCE_{\text{Au@TiO}_2}(\lambda)$ and $IPCE_{\text{TiO}_2\text{-only}}(\lambda)$ are the IPCE at wavelength λ for virus-templated Au@TiO_2 and TiO_2 -only DSSCs, respectively.

FIG. 11 shows the effect of LSPs on the performance of DSSCs. The dependence of PCE (FIG. 10A) and J_{SC} (FIG. 10B) on the concentration of Au nanoparticles in

photoanodes with the different film thickness. FIG. 10C shows current density of the most efficient virus-templated Au@TiO₂ DSSC (Au weight percent = 0.8 wt. %, η = 8.46%, FF = 74%, ~15.1 μ m) and TiO₂-only DSSC.

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DETAILED DESCRIPTION

There is a constantly growing demand for fabricating cost-effective energy conversion devices. Dye-sensitized solar cells (DSSCs) have attracted great attention for high power conversion efficiency (PCE; in some cases exceeding 12%) and the low cost of materials and solution-based fabrication processes.

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Dye-sensitized solar cells (DSSCs) are a promising solution-processed photovoltaic technology. The key components of DSSC contain dye-molecules which absorb light, and titanium dioxide (TiO₂, e.g., mesoporous TiO₂) thin films which collect photo-generated electrons (photoanodes). The power conversion efficiency (PCE) of DSSCs is mainly determined by the light harvesting and the electron collection. In general, to efficiently harvest light and collect electrons, different design criteria of material system need to be considered. For efficient electron collection, nanostructures of TiO₂ with high aspect ratio, such as nanorods, nanotubes and nanofibers, have been proven to be effective, compared to the commonly used architecture of photoanodes composed of randomly-packed nanoparticles (NPs). However, the reduced surface area of one-dimensional (1-D) structures leads to insufficient dye adsorption and thus restricts the light harvesting. As a result, achieving sufficient light harvesting requires developing strong-absorbing dye-molecules or various mechanisms to increase optical absorption, e.g. localized surface plasmon (LSP)-enhanced optical absorption by using metal NPs. Therefore, different functional materials are required for the electron collection and the light harvesting, which makes it attractive to exploit an approach to assembling different functional components together into a homogeneously distributed composite with a three-dimensional (3-D) structure.

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A 3-D viral network can template nanowires for improved electron transport in DSSCs. The viral network can also bind metal nanoparticles and incorporate them uniformly in the photoanodes for the LSP-enhanced light harvesting of dye-molecules. The 3-D network of the virus-templated photoanodes can be directly formed on the substrate, and the porosity of the nanowire thin film can be controlled.

Templated by a cross-linked virus hydrogel scaffold, the TiO₂ nanowires promote the electron transport from photo-excited dyes to the current collector (FIG. 3) in the photoanodes, resulting in an increasing electron diffusion length compared to the conventional NP-based photoanodes. In addition, the M13 virus can bind metal nanoparticles (e.g., gold nanoparticles) prior to the template-synthesis of TiO₂. The metal nanoparticles provide LSP to improve the photo-absorption of dye-molecules adsorbed on the Au@TiO₂ nanocomposites (FIG. 3). As a result, the 3-D LSP-enhanced virus-templated photoanodes exhibits efficient electron collection and improved light absorption simultaneously.

With reference to FIG. 1, solar cell 100 includes substrate 110 (e.g., glass) which supports current collector 120. Current collector 120 is proximate to photoanode 140 such that current can flow between photoanode 140 and current collector 120. Photoanode 140 can be a porous layer. Photoanode 140 can include porous layer 150 of a photoanode material. The photoanode material includes nanoparticles 160 of the photoanode material. The nanoparticles can be dispersed within a matrix. Nanoparticles 160 can be discrete nanoparticles, or can be interconnected by the matrix (which may also include or be made of the photoanode material), or the nanoparticles can include a mixture of discrete and interconnected nanoparticles. Porosity in layer 150 can exist between and among nanoparticles 160. Light absorbing dye 170 is optionally adsorbed and/or covalently bound on the photoanode material. FIG. 1 illustrates dye 170 adsorbed to nanoparticles 160.

Photoanode 140 also includes electrolyte 180. Electrolyte 180 is in contact with, and can be suffused through, the porosity of porous layer 150. Electrolyte 180 is also in contact with conductive layer 190 (i.e., the cathode). Conductive layer 190 can be, for example, a layer of platinum (Pt). Conductive layer 190 is covered by cover layer 200, which is transparent, e.g., glass.

With reference to FIGS. 1 and 2, photoanode 140 can further optionally include nanostructures 210. FIG. 2 illustrates two configurations of nanostructures; features of these configurations may be found in various combinations as explained below.

nanostructures 210 can be plasmon-forming nanostructures. nanostructures 210 can be composite nanostructures, i.e., including two or more different materials in a single nanostructure. nanostructures 210 can include a metal nanoparticle 220 and an oxide 230 on a surface of the metal nanoparticle. Metal nanoparticle 220 can be, for example, silver

(Ag), gold (Au), or a combination of these. Oxide 230 can be a semiconducting oxide, such as, for example, TiO_2 .

Metal nanoparticle 220 can have any of a variety of shapes, including spherical, oblate, elongated, rod-shaped, wire-shaped, cubic, tetrahedral, octahedral, or another regular or irregular shape. A combination of metal nanoparticles having different shapes can be used. Metal nanoparticles having various shapes, and methods for making these, are known in the art. Methods for formation of an oxide on a surface of a metal nanoparticle are also known. Oxide 230 can partially (as shown on the left of FIG. 2) or substantially fully (as shown on the right) coat the metal nanoparticle 220. Nanoparticles 210 can be referred to as "M@oxide nanoparticles," simply as "M@oxide," or "core-shell nanoparticles," when they include a metal (M) nanoparticle 220 which is substantially fully coated by oxide 230. For example, a silver metal nanoparticle 220 substantially fully covered by TiO_2 can be referred to as an Ag@TiO_2 nanoparticle, or simply Ag@TiO_2 .

In some instances, oxide 230 can include or be made of the same material(s) as found in the photoanode material, e.g., the material(s) that are found in or make up nanoparticles 160, or the material(s) that are found in or make up the optional matrix in which nanoparticles 160 are dispersed. For example, photoanode 140 can include a TiO_2 matrix in which TiO_2 nanoparticles 160 can be dispersed. Optionally, plasmon-forming nanoparticles 210 where oxide 230 is TiO_2 are also dispersed in the TiO_2 matrix.

Composite materials, such as nanocomposite materials, can provide advantageous properties that non-composite materials cannot. For example, nanocomposites including plasmon-forming nanostructures can be useful in a variety of applications, including optoelectronic devices, such as light emitting devices, and photovoltaics, e.g., dye-sensitized solar cells. Metal nanoparticles, with an optional semiconducting oxide on the surface of the metal nanoparticle, can be plasmon-forming nanostructures.

Localized surface plasmon (LSP) has potential for improving performance of DSSCs for the unique capability to improve the light absorption of dye with minimal impact on other material properties. Generally, there are three types of plasmonic light-trapping geometries, including far-field scattering, near-field LSP, and surface plasmon polaritons at the metal/semiconductor interface (see, e.g., Atwater, H. A.; Polman, A., *Nature Mater.* 2010, 9, 205-213, which is incorporated by reference in its entirety). Surface plasmon arising from metal nanoparticles has been applied to increase the optical absorption and/or photocurrent in a wide range of solar cell configurations, e.g., silicon

solar cells, organic solar cells, organic bulk heterojunction solar cells, CdSe/Si heterostructures and DSSCs. However, work on plasmon-enhanced DSSCs has reported improved dye absorption or photocurrent, while improved device performance was not observed. In addition, earlier plasmonic geometries contained metal nanoparticles in
5 direct contact with the dye and the electrolyte, resulting in recombination and back reaction of photo-generated carriers and corrosion of metal nanoparticles by electrolyte.

Recently, core-shell Au@SiO₂ nanoparticles have been used to enhance PCE by preventing carrier recombination and back reaction. However, by using an insulating shell, some of the photo-generated carriers from the most absorption-enhanced dye
10 molecules located on the surfaces of SiO₂ are lost, due to the difficulty in the injection to SiO₂.

When the oxide is a semiconducting oxide, carriers can be more readily transferred to the photoanode material than if the oxide is an insulator. This transfer can be particularly facilitated when both the semiconducting oxide and the photoanode
15 material include TiO₂.

Porous layer 150 can be made by first preparing a population of nanoparticles of a photoanode material, e.g., TiO₂, followed by a spin-casting procedure to deposit the nanoparticles over a current collector. For porous layers including nanoparticles 210, a population of plasmon-forming nanoparticles can be formed separately. The photoanode
20 nanoparticles and the plasmon-forming nanoparticles can be combined in a desired ratio prior to depositing over the current collector. The desired ratio can be measured with regard to wt% of the plasmon-forming nanoparticles in the total combined population of nanoparticles prior to depositing. Once the combined population has been formed, porous layer 150 can be made with the combined population according to conventional
25 procedures.

In conventional DSSCs, the dyes absorb incident light and generate electrons in excited states, which inject into the TiO₂ nanoparticles. The dye molecules are regenerated by electrons transferred from the electrolyte, which can be a solid or liquid electrolyte. For purposes of illustration only, and not by way of limitation, the following
30 discussion is made with reference to a liquid electrolyte including I⁻ and I₃⁻. The regenerative cycle is completed by reducing triiodide to iodide at the Pt cathode. The electrons in TiO₂ diffuse to the current collector (fluorine-doped tin oxide, FTO). In the plasmon-enhanced DSSCs, the LSP arising from plasmonic nanoparticles increases dye

absorption, allowing the thickness of photoanode to be decreased for a given level of light absorption. By decreasing the thickness of photoanode, less materials are required, and both recombination and back reaction of photo-carriers is reduced. Reducing recombination and back reactions in turn improved the electron collection efficiency and thus overall device performance. See, for example, U.S. Patent Application no. 13/560,422, which is incorporated by reference in its entirety.

EXAMPLES

Materials and methods

- 10 **Materials.** 50 wt.% glutaraldehyde solution, titanium (IV) chloride, hydrogen tetrachloroaurate (HAuCl_4), sodium citrate, acetonitrile, tert-butanol and phosphate buffered saline (PBS) buffer solution were purchased from Sigma Aldrich. Ammonium hexafluorotitanate ($(\text{NH}_4)_2\text{TiF}_6$) and boric acid ($\text{B}(\text{OH})_3$) were purchased from Alfa Aesar. Cis(diisothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II) bis(tetrabutylammonium) (also named N719) and TiO_2 NP paste (13/400 nm, Ti-Nanoxide D/SP) were purchased from Solaronix. N719 dye solution was prepared in acetonitrile and tert-butanol (volume ratio 1:1) mixture at 0.5 mM. All reagents were used as received and without further purification. All water was deionized (18.2 M Ω , mill-Q pore).
- 20 **M13 Virus Solution.** The stock solution, $\sim 10^{14}$ phage mL^{-1} , of E3M13 (AEEE expressed on the pVIII major coat protein) virus was diluted to 5×10^{13} phage mL^{-1} with PBS buffer.
- 25 **Synthesis of Au NPs.** The Au NP solution was prepared by the following procedure: 10 mg HAuCl_4 was initially dissolved in 100 mL water and the solution was heated to boil. 50 mg sodium citrate was dissolved in 5 mL water and the solution was then added into the boiling HAuCl_4 solution under vigorous stirring. The mixed solution was reacted in boiling for 30 minutes. The optical absorption spectroscopy measurements were performed using a Beckman Coulter DU800 UV-Vis spectrophotometer.
- 30 **Binding Au NPs on M13 Virus.** The different amount of phage solution was mixed with Au NP solution and then incubated in dark condition, and then stored at 4 °C for 12 hours. Then, Au NPs@virus was precipitated through the standard polyethylene glycol and NaCl solution to minimize the impurities. The final pellet was redissolved and diluted to 5×10^{13} phage mL^{-1} with PBS buffer. TEM observations of synthesized

nanostructures were performed using JEOL 200CX TEMs with an accelerating voltage of 120 kV.

M13 Virus Hydrogel. Glutaraldehyde solution was placed in a petri dish as a crosslinking reservoir. Virus or Au NPs@virus solution was pipetted onto a substrate.

5 Substrates were inverted and placed onto the reservoir surface. The phage solutions were allowed to remain in contact with the glutaraldehyde solution for 2 hours. After crosslinking, phage hydrogels were removed from the reservoir and transferred to PBS buffer for over 12 hours to remove excess glutaraldehyde.

TiO₂ Photoanode Generation. The prepared hydrogels were immersed in 0.2 M
10 TiCl₄ solution for ~6 hours and in a mixture of 30 mM (NH₄)₂TiF₆ and B(OH)₃ for 4 hours in 50 °C subsequently for nucleation. After the nucleation, the films were rinsed with water and then annealed at 500 °C for 30 minutes. The thicker films were achieved by repeating the process (crosslinking, nucleation and calcination). For the NP
photoanodes, layers of commercial NP TiO₂ paste (Solaronix) were doctor-bladed on the
15 substrates, and then annealed at 500 °C for 15 minutes. Film thickness was monitored using a surface profilometer (Veeco Dektak). SEM images were obtained using Helios Nanolab 600 Dual Beam Focused Ion Beam System.

Fabrication of DSSCs. After calcination, the photoanodes were cooled to 80 °C and immersed in the N719 solution, and kept at room temperature over 24 hours. The
20 counter-electrode was a 100-nm-thick platinum film sputtered on a FTO substrate. The electrolyte employed was a solution of 0.6 M 1-butyl-3-methylimidazolium iodide (Sigma Aldrich), 0.03 M I₂ (Sigma Aldrich), 0.10 M guanidinium thiocyanate (Sigma Aldrich) and 0.5 M 4-tert-butyl pyridine (Sigma Aldrich) in a mixture of acetonitrile and valeronitrile (volume ratio, 85:15). The dyed TiO₂ photoanodes and platinum counter-
25 electrodes were assembled into a sandwich-type cell and sealed with a hot-melt 25 µm Surlyn (Solaronix). The photoanode had dimensions of ~0.16 cm² (4 mm × 4 mm), further determined from a calibrated digital camera image.

Characterization of DSSCs. Photovoltaic measurements were performed using an AM 1.5 solar simulator (Photo Emission Tech.). The power of the simulated light was
30 calibrated to 100 mWcm⁻² by using a reference silicon photodiode with a power meter (1835-C, Newport) and a reference silicon solar cell to reduce the mismatch between the simulated light and AM 1.5. *J-V* curves were obtained by applying an external bias to the cell and measuring the generated photocurrent with a Keithley model 2400 digital source

meter. The voltage step and delay time of photocurrent were 10 mV and 40 ms, respectively. IPCE spectra were obtained with a computer-controlled system (Model QEX7, PV Measurements, Inc.) consisting of 150 W xenon lamp light source and a monochromator with two 1200 g/mm diffraction gratings. The incident photon flux was determined using a calibrated silicon photodiode (calibrated by PV Measurements, Inc.). Measurements were performed in a short-circuit condition, while the cell was under background illumination from a bias light of 50 mW cm^{-2} . EIS of DSSCs were measured using a Solartron 1260 frequency response analyzer. The obtained impedance spectra were fit to the transmission line model with Z-view software (v3.2b, Scribner Associates). The spectra were measured at various forward bias voltages (from 0.85 to 0.45 V) in the frequency range $\sim 0.1 \text{ Hz}$ to $\sim 1 \text{ MHz}$ with oscillation potential amplitudes of 10 mV at room temperature. The photoanode was connected to the working electrode. The platinum electrode was connected to the auxiliary electrode and reference electrodes. The impedance measurements were carried out at forward bias in dark conditions.

Results and discussion

First, a virus hydrogel network was formed on the substrate using a glutaraldehyde solution as the crosslinking agent (FIG. 4). A liquid-liquid interface was created after the substrate with the virus solution (specific gravity ~ 1) was placed upside down on the surface of the glutaraldehyde solution (specific gravity ~ 1.1). As the glutaraldehyde diffused across the interface and into the virus solution on the top, a virus hydrogel was spontaneously formed due to the covalent crosslinking between the amine groups on the virus coat proteins. After the virus hydrogel was achieved, the virus-templated TiO_2 nanowires were formed directly on the substrate by an aqueous phase nucleation method using solutions of TiO_2 precursors (*e.g.* TiCl_4 , $(\text{NH}_4)_2\text{TiF}_6$) which deposited a conformal TiO_2 thin layer on the virus template. The sacrificial virus scaffolds were then removed by a final calcination step. The calcination also converted the 3-D porous TiO_2 film was crystalized to the anatase phase (FIG. 5A).

It was observed that the virus-templated photoanode was composed of tightly packed TiO_2 crystallites forming interconnected nanowires (FIGS. 5B-5C). Compared to the size of individual viral particles, the virus-templated TiO_2 nanowires were approximately 100 nm in diameter and 2-3 μm in length (FIGS. 5C-5D), which suggested that each nanowire in the photoanode was templated by a bundle of viruses. In addition,

the mesoporous structure of the interconnected nanowire network persisted throughout the thin film, which could provide a directional electron pathway for electron transport (FIG. 5E). Moreover, the permeable matrix with interconnected pores can increase the interfacial contact with the electrolyte and the mobility of redox couples, which also reduces back recombination.

To demonstrate the improved electron diffusion length (L_n) and carrier collection of the 3-D virus-templated TiO_2 photoanode, the electrochemical impedance spectra were measured (FIG. 6A) after the photoanodes were assembled with the electrolyte and counter electrodes. The DSSC with the virus-templated photoanode showed longer L_n and thus better electron collection than the commonly used TiO_2 nanoparticle-based DSSC. Furthermore, the device performance of the DSSC with virus-templated TiO_2 photoanode was characterized (FIG. 6B and Table 1), which showed a PCE of 6.03% and a J_{SC} of 10.97 mA cm^{-2} . Despite the improved electron collection for the virus-templated TiO_2 photoanode, the J_{SC} and PCE were both lower than those of TiO_2 nanoparticle-based DSSC (6.63% and 12.31 mA cm^{-2}). Since the charge separation efficiency approached unity when N719 dye and TiO_2 are used, the decreased overall performance results from the reduced surface area, dye adsorption, and thus light harvesting of the 1-D structure of the virus-templated TiO_2 nanowires. In fact, the virus-templated device showed ~89.1% of J_{SC} with only ~73.5% of the adsorbed dye compared to the nanoparticle-based solar cell. Therefore, the virus-templated photoanodes composed of interconnected nanowires exhibited efficient electron collection, while the randomly packed nanoparticle photoanode was advantageous for light harvesting.

LSPs are the elementary electronic excited states in the metal nanoparticles. By utilizing LSPs generated surrounding Au or Ag nanoparticles, the light harvesting in various photovoltaic technologies has been improved. The ability of M13 virus to bind with these noble metal nanoparticles was utilized to improve the optical absorption of virus-templated photoanode in DSSCs. Once the viruses (FIG. 7A) and Au nanoparticles (20 nm, TEM images in FIG. 7B) were bound together (FIG. 7C), the same film fabrication process mentioned above was performed with the Au nanoparticle-virus complex. The morphology of virus-templated Au@TiO_2 structure was similar to that of the virus-templated TiO_2 films (FIG. 8). After the calcination of the virus-templated Au@TiO_2 photoanode, both Au and anatase TiO_2 were observed in the XRD pattern (FIG. 7D). In addition, it was observed in the TEM image (FIG. 7E) that the ~8 nm TiO_2

crystallites were densely packed around the Au nanoparticles. This could prevent the Au NPs from promoting electron recombination and also to prevent etching of Au NPs by the electrolyte.

5 **Table 1**

Type	Thickness (μm)	V_{OC} (mV)	FF (%)	J_{SC} (mA cm^{-2})	PCE (%)	Dye Loading ($\mu\text{mole cm}^{-3}$)
Virus-templated TiO_2	18.1	801.8	68.6	10.97	6.03	70.92
Virus-templated Au@TiO_2	15.1	832.7	74.0	13.72	8.46	68.22
Nanoparticle	17.7	781.1	68.8	12.31	6.63	96.87

The effect of Au nanoparticles on the optical absorption of dye-molecules in the solutions and thin films were investigated. The effect of LSP in the solution simulated the situation in the plasmon-enhanced DSSCs, since the concentrations of Au nanoparticles and dyes in solution can be easily controlled and the contribution from light scattering was minimized. The light absorption of dye-molecules increased with the presence of Au nanoparticles in the wavelength range of 450-530 nm with maximum relative enhancement 45% (FIGS. 9A-9C), which suggested that the increase in photo-absorption mainly arose from the interaction between dye-molecular dipoles and LSPs from Au nanoparticles. Similarly, the light absorption of dye-molecules in the virus-templated TiO_2 thin films was increased to a maximum 21% at 540 nm (FIGS. 9D-9F), which can be attributed to the enhanced near field electromagnetic intensity and scattering cross-section of Au nanoparticles. In addition, the shift of the absorption peak from the Au nanoparticle solution to a longer wavelength resulted from the high dielectric constant of TiO_2 thin layer surrounding the Au nanoparticles, which was also observed in previous reports.

To investigate the effect of LSPs on the spectral response of the solar cells, the IPCE of virus-templated TiO_2 -only and Au@TiO_2 photoanodes were compared (FIGS. 10A-10C). The IPCE of the plasmon-enhanced DSSC was increased over the entire wavelength range compared to the TiO_2 -only DSSC (FIG. 10A), indicating that the Au@TiO_2 structures improved light harvesting of the dye and thus the solar cell. Moreover, the most significant enhancement was in the range of 500-600 nm with a peak around 530 nm (FIGS. 10B-10C), in agreement with the absorption enhancement of the thin films.

The device performance of the virus-templated Au@TiO₂ photoanodes was optimized by the adjusting the concentration of the Au nanoparticles (~0.24 to ~2.40 wt.%) and the thickness of the photoanodes (~0.5 to ~18.1 μm) (FIGS. 11A-11B). In general, thicker photoanodes tend to absorb more light, and have higher PCEs and J_{SC}.

5 The virus-templated Au@TiO₂ DSSCs (concentrations of Au NPs, ~0.24 wt.% and ~0.8 wt.%) showed higher PCE and J_{SC} than the virus-templated TiO₂-only DSSCs with similar thicknesses of the photoanodes. In other words, to achieve the same PCE (*e.g.*, ~6%), the photoanode of the plasmon-enhanced DSSC (6.6 μm) was much thinner than that of the TiO₂-only DSSC (18.1 μm), reducing 63.5% of the photoactive materials used.

10 In addition, both PCE and J_{SC} increased monotonically with the concentration of Au nanoparticles from 0 to 0.8 wt.%. PCE and J_{SC} decreased when the concentration of Au nanoparticles was increased to 2.4 wt.%, probably due to the increased trapping of photo-excited electrons by Au nanoparticles and competing light absorption of Au nanoparticles with dye-molecules, which transformed part of the incident light into heat.

15 FIG. 11C and Table 1 show the *J-V* characteristics of a virus-templated plasmon-enhanced (Au 0.8 wt. %) DSSC and virus-templated TiO₂-only DSSC. The plasmon-enhanced DSSC achieved the J_{SC} of 13.72 mA cm⁻², a 25.1% increase compared to that of the TiO₂-only DSSC, 10.97 mA cm⁻². Also, the plasmon-enhanced DSSC showed higher V_{OC} than the TiO₂-only DSSC, which probably resulted from the reduced charge

20 recombination because of thinner optimized photoanodes and the lifted quasi-Fermi level due to the equilibrium between quasi-Fermi level of TiO₂ and the LSP energy level of Au NPs. In addition, the optimized thickness for the LSP-enhanced photoanode (15.1 μm) was thinner than that for the TiO₂-only photoanode (18.1 μm). As a result, by introducing Au@TiO₂ nanostructures into the virus-templated photoanode, the PCE (8.46%) of the

25 plasmon-enhanced DSSC was improved by 40.3% compared to that of the virus-templated TiO₂-only DSSC, 6.03%, while the photoanode thickness was decreased by 19.9%. The LSP from Au nanoparticles in nanowire-based photoanodes has the ability to increase the light harvesting without affecting the high L_n and thus maintain the efficient electron collection.

30 Other embodiments are within the scope of the following claims.

WHAT IS CLAIMED IS:

1. A method of making a photoanode for a dye-sensitized solar cell comprising:
 - 5 forming a network of metal-binding viruses; and
nucleating TiO₂ nanoparticles on the metal-binding viruses.
 2. The method of claim 1, wherein forming the network includes crosslinking the metal-binding viruses.
 - 10 3. The method of claim 1, further comprising annealing the TiO₂ nanoparticles.
 4. The method of claim 1, further comprising binding metal nanoparticles to
15 the viruses.
 5. The method of claim 4, wherein the metal nanoparticles include Au or Ag.
 6. A dye-sensitized solar cell comprising a photoanode including a three-
20 dimensional scaffold of TiO₂ nanowires.
 7. The dye-sensitized solar cell of claim 6, wherein the TiO₂ nanowires are interconnected.
 - 25 8. The dye-sensitized solar cell of claim 6, wherein the photoanode further comprises a plurality of a plasmon-forming nanostructures, wherein each plasmon-forming nanostructure includes a metal nanoparticle and a semiconducting oxide on a surface of the metal nanoparticle.
 - 30 9. The dye-sensitized solar cell of claim 6, wherein the TiO₂ nanowires have the dimensions of a virus template.

10. The dye-sensitized solar cell of claim 6, wherein the TiO₂ nanowires are formed by nucleation on a virus template.

5 11. A method of generating solar power, comprising illuminating a dye-sensitized solar cell including a photoanode including a three-dimensional scaffold of TiO₂ nanowires.

12. The method of claim 11, wherein the TiO₂ nanowires are interconnected.

10 13. The method of claim 11, wherein the photoanode further comprises a plurality of a plasmon-forming nanostructures, wherein each plasmon-forming nanostructure includes a metal nanoparticle and a semiconducting oxide on a surface of the metal nanoparticle.

15 14. The method of claim 11, wherein the TiO₂ nanowires have the dimensions of a virus template.

15 15. The method of claim 11, wherein the TiO₂ nanowires are formed by nucleation on a virus template.

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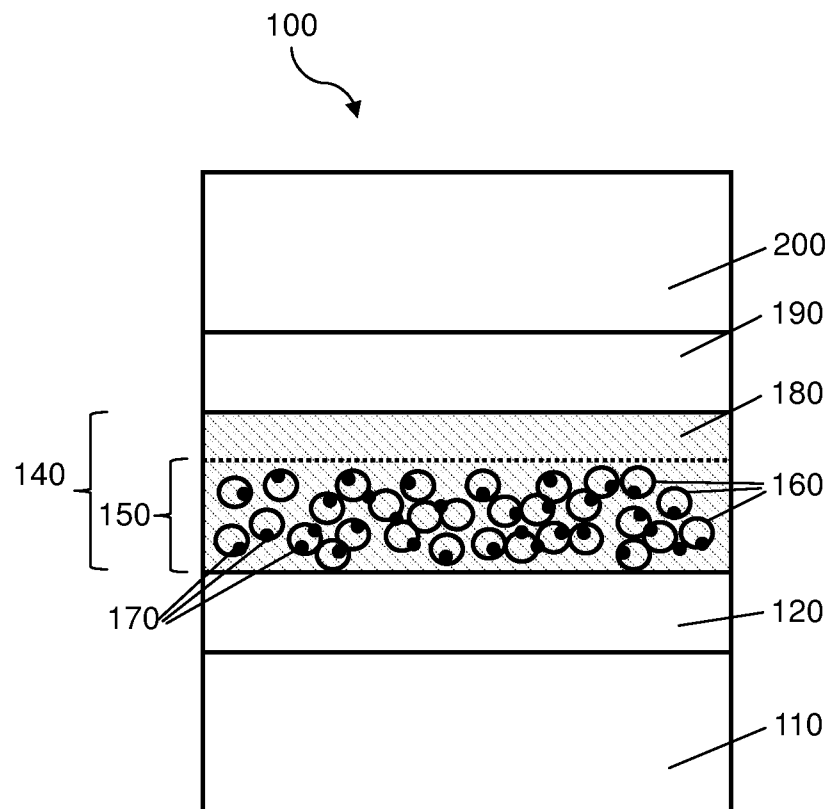


FIG. 1

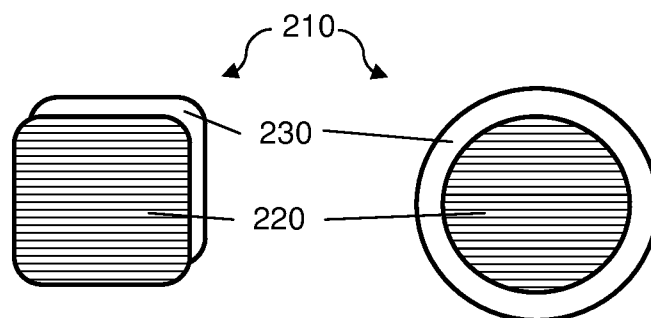


FIG. 2

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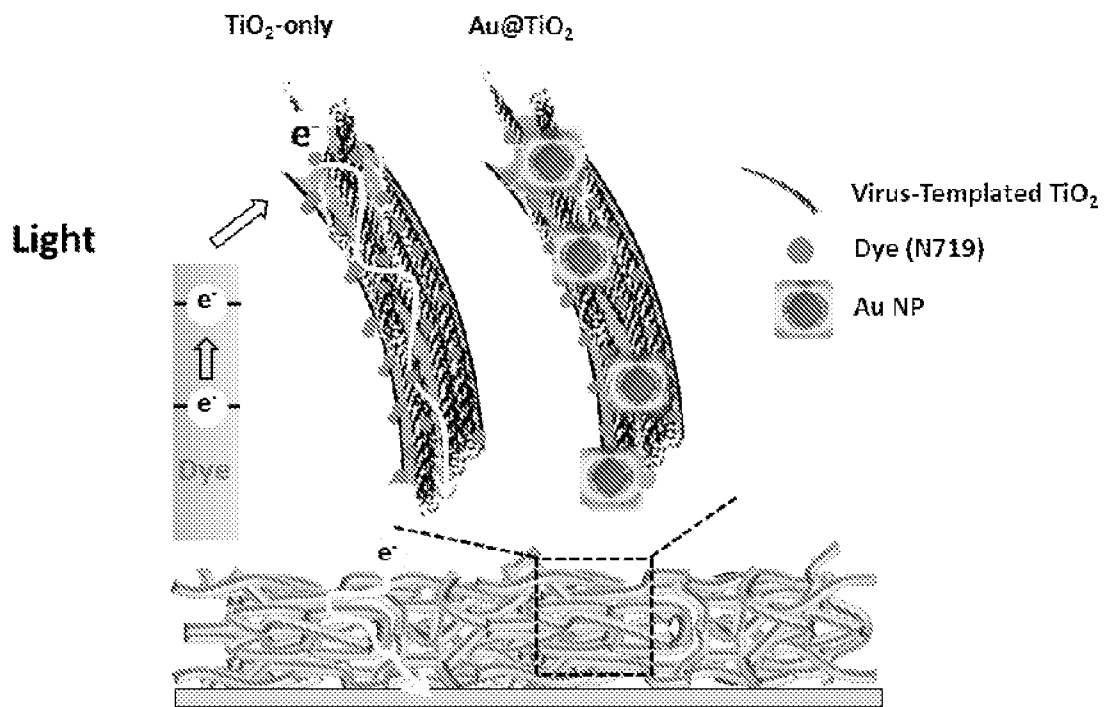


FIG. 3

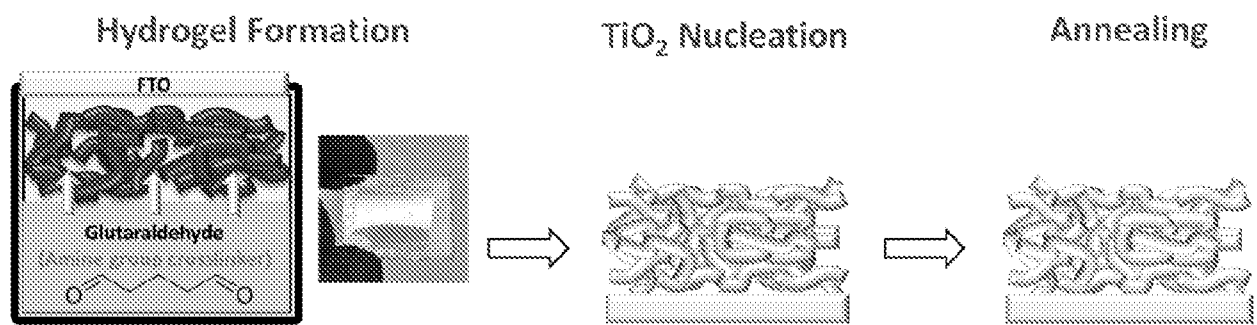


FIG. 4

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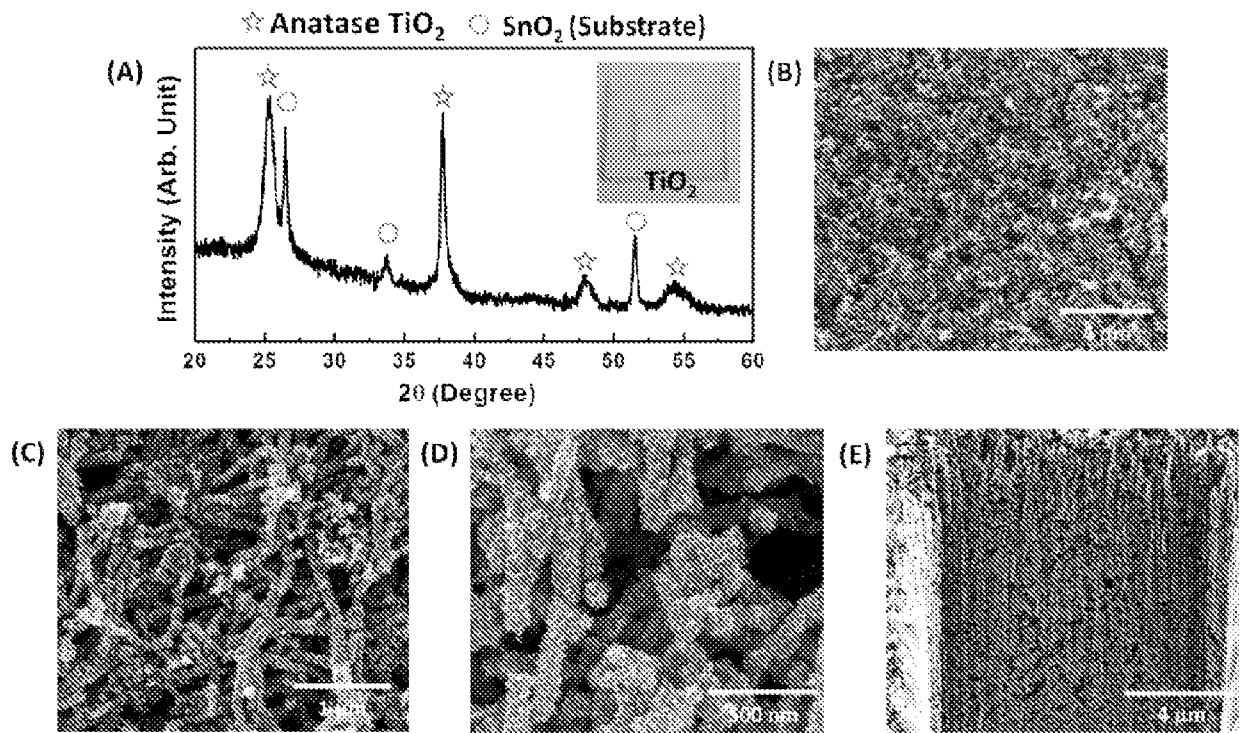


FIG. 5

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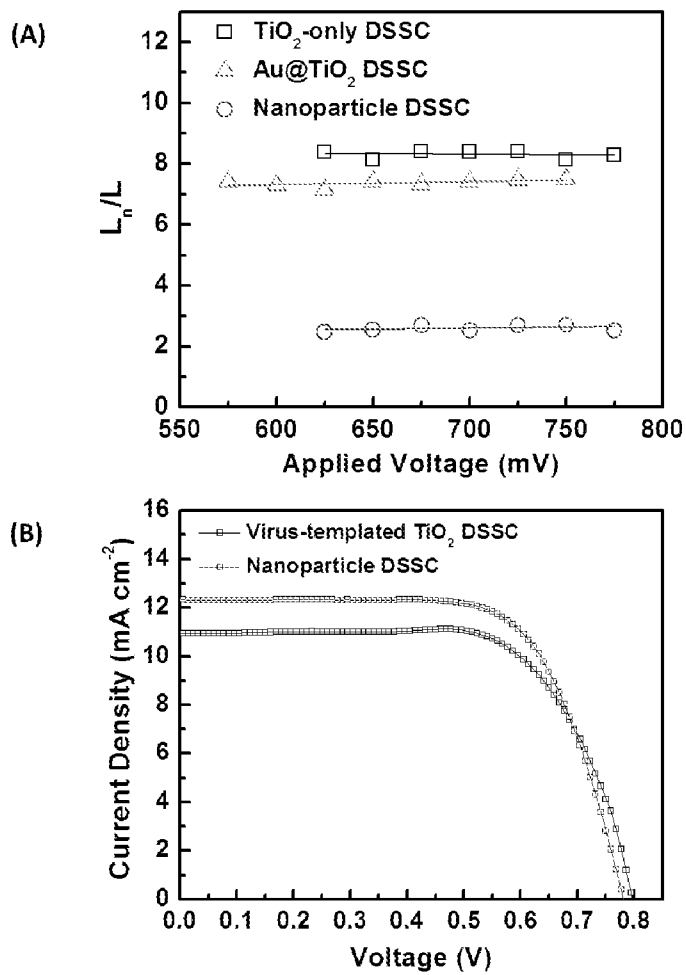


FIG. 6

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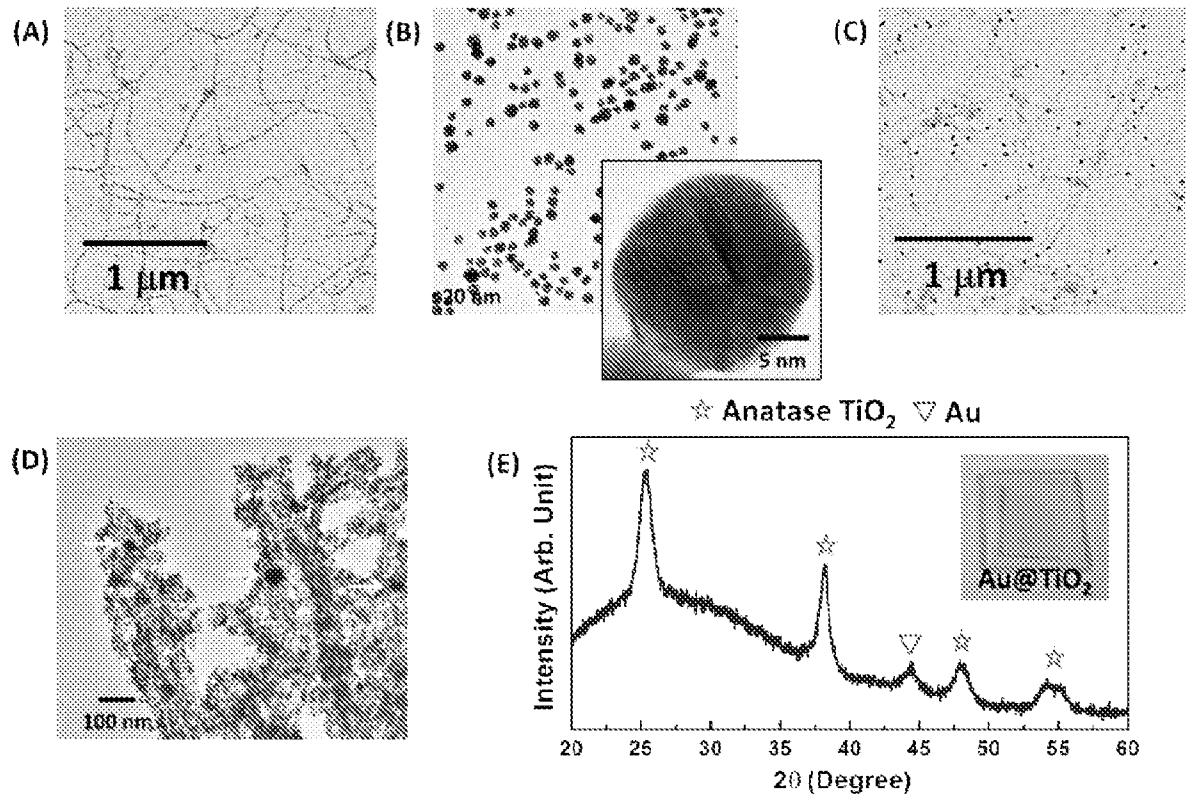


FIG. 7

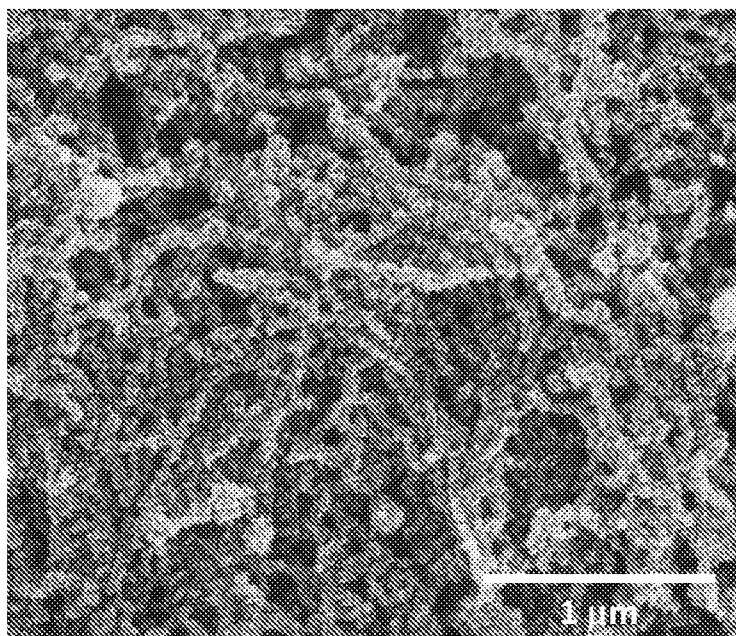


FIG. 8

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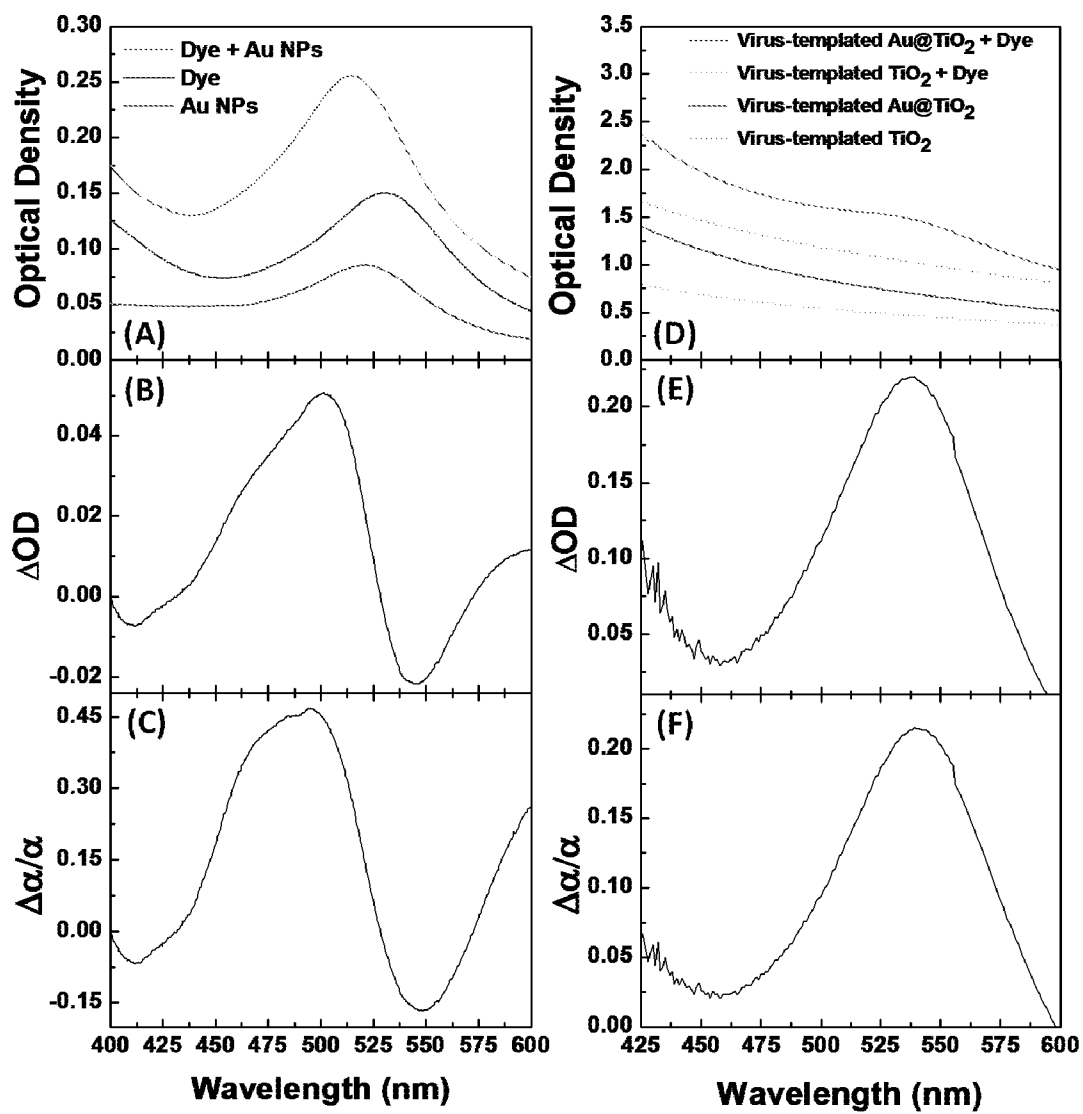


FIG. 9

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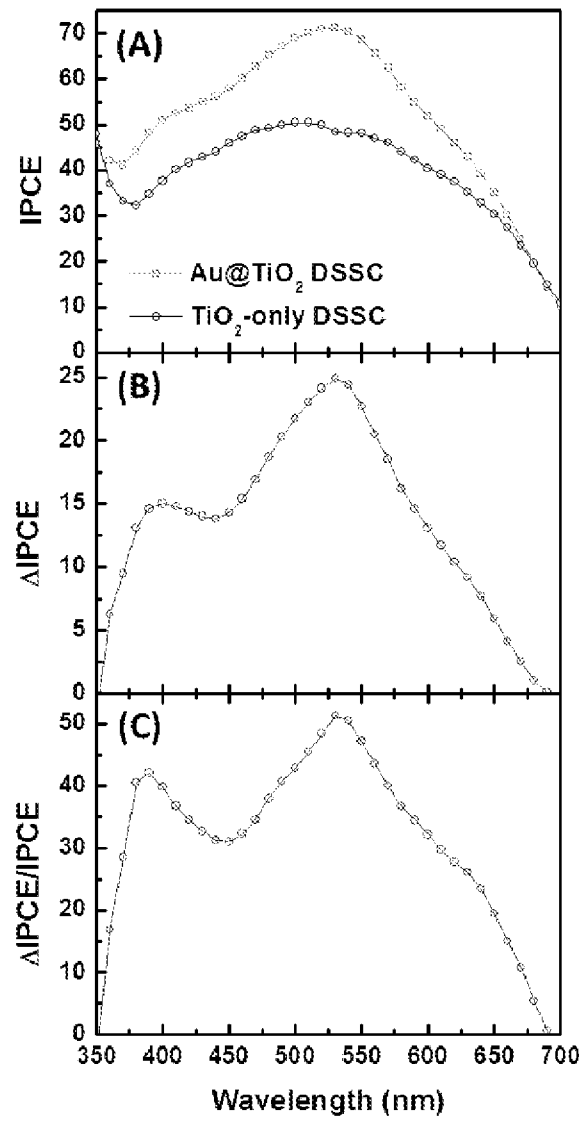


FIG. 10

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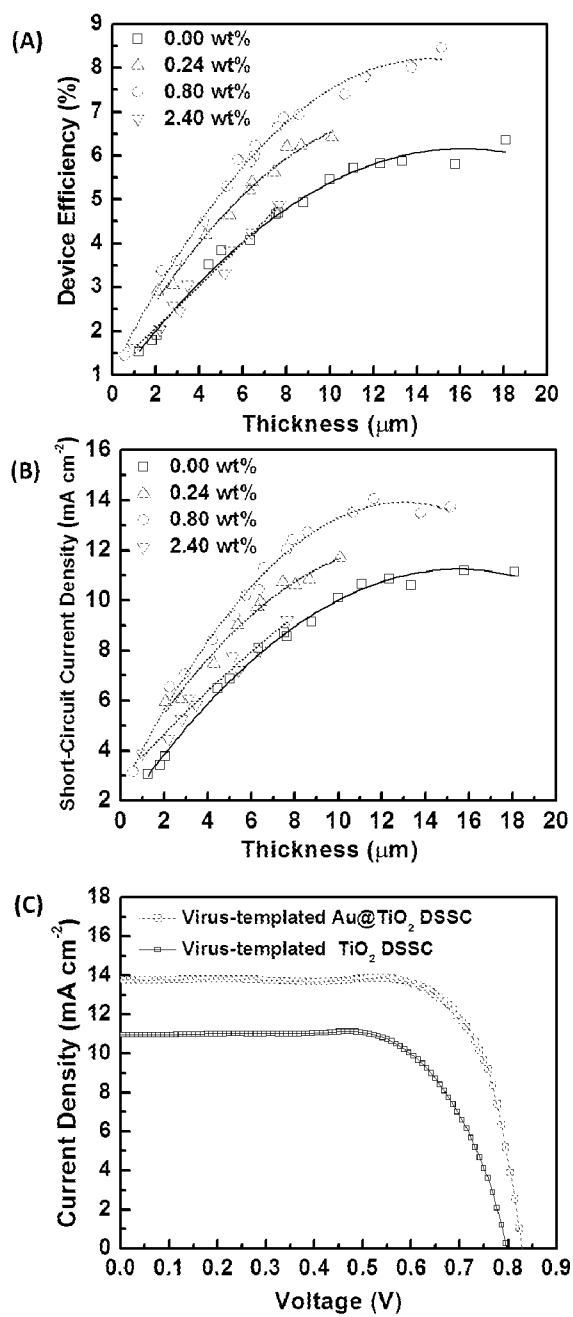


FIG. 11

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US13/70074

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - H01L 31/0224 (2014.01)

USPC - 136/250; 435/235.1; 438/1

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)

IPC(8) - H01L 31/0224 (2014.01)

USPC - 136/250, 255, 256, 258; 435/235.1; 438/1; 977/882

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)

MicroPatent (US Granted, US Applications, EP-A, EP-B, WO, JP, DE-G, DE-A, DE-T, DE-U, GB-A, FR-A); Google Patents; Google Scholar; IP.COM, IEEE Xplore; Search Terms Used: solar cells, photovoltaic cells, dye sensitized solar cells, DSSC, titanium dioxide, titania, metal oxide, metal, nanoparticle*, gold, Au, silver, Ag, core, shell, virus, M13, bacteriophage, illumination, self-assembly, nucleat*.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ----- Y	US 2012/0227800 A1 (DANG X et al.) September 13, 2012, Figures 1a, 1b, paragraphs [0050], [0056], [0059] - [0061], [0066], [0075].	1, 3-7, 9-12, 14, 15 ----- 2, 8, 13
Y	LEE, S et al, "Virus-Based Fabrication of Micro- and Nanofibers Using Electrospinning", Nano Lett., Vol. 4, No. 3, March 2004, Downloaded from the Internet: < http://pubs.acs.org/doi/abs/10.1021/nl034911t>, Abstract.	2
Y	QI, J et al. "Highly Efficient Plasmon-Enhanced Dye-Sensitized Solar Cells through Metal@Oxide Core-Shell Nanostructure", ACS NANO, VOL. 5 ' NO.9, 7108-7116, August 4, 2011, Downloaded from the Internet: < http://pubs.acs.org/doi/abs/10.1021/nn201808g>, Abstract, Page 7109, paragraph 1.	8, 13
A	US 2011/0114244 A1 (YOO P et al.) May 19, 2011, Abstract.	1-15

☐ Further documents are listed in the continuation of Box C.

* Special categories of cited documents:	"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
"A" document defining the general state of the art which is not considered to be of particular relevance	"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
"E" earlier application or patent but published on or after the international filing date	"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
"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)	"&" document member of the same patent family
"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	

Date of the actual completion of the international search

28 February 2014 (28.02.2014)

Date of mailing of the international search report

19 MAR 2014

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