

INORGANIC NANORODS AND A METHOD OF FORMING THE SAME, AND A
PHOTOELECTRODE AND A PHOTOVOLTAIC DEVICE COMPRISING THE
INORGANIC NANORODS

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Technical Field

[0001] Various embodiments relate to inorganic nanorods on an inorganic metal oxide substrate and a method of forming inorganic nanorods on an inorganic metal oxide substrate. Various embodiments relate to a device, for example an electrode or a
10 photoelectrode, comprising the inorganic nanorods on the inorganic metal oxide substrate. Various embodiments relate to a photovoltaic device, for example a solar cell, comprising the electrode or photoelectrode comprising the inorganic nanorods on the inorganic metal oxide substrate. Various embodiments further relate to tin oxide nanorods on an inorganic metal oxide substrate and a method of forming tin oxide nanorods on an
15 inorganic metal oxide substrate.

Background

[0002] With increasing attention towards carbon-neutral energy production, global
20 warming and fossil fuel depletion, solar electricity is receiving heightened attention as a potentially widespread approach to sustainable energy production (N. S. Lewis, *Science*, 315: 798, 2007; M. Grätzel, *Nature*, 414: 338, 2001). In general, transparent conductive oxides (TCO) such as indium tin oxide ($\text{Sn:In}_2\text{O}_3$ or generally known by its acronym ITO) and fluorine-doped tin oxide (F:SnO_2 or generally known by its acronym FTO)
25 films coated on glass are commonly used as transparent conductive oxide electrode (TCOE) for solar cells.

[0003] The improvement of solar energy conversion efficiency requires low resistance electrical connection to the electrodes which collect the charges generated by the absorption of sunlight. However, the use of 2-dimensional (2D) flat TCO film electrode
30 (2D-TCOE) on glass is far from being effective for charge collection. For example, dye-sensitized solar cells (DSCs) based on mesoporous titanium dioxide (TiO_2) film have

been intensively studied as a practical, more economic alternative to conventional silicon-based p-n junction cells in the market (B. O'Regan, M. Grätzel, *Nature*, 353: 737, 1991). The thick mesoporous TiO₂ film in the DSCs provides a large surface area for anchoring the light-harvesting dye molecules. However, the structural disorder at the contact
5 between two crystalline nanoparticles, the presence of oxygen defects, and the TiO₂ amorphous layer lead to enhanced scattering of free electrons, thus reducing diffusion coefficients of electrons in the mesoporous TiO₂ film and the efficiency of the DSCs. Therefore, electron transport presents a limiting factor in the performance of these nanocrystalline electrodes, hindering progress in achieving higher efficiencies.

10 [0004] In DSCs, ITO glass (ie. ITO-coated glass) and FTO glass (ie. FTO-coated glass) are commonly used as TCOE as the electron collecting electrode (cathode) while a TiO₂ mesoporous film is generally used as the working electrode. However, 2-dimensional (2D) flat ITO and FTO films have limited contact area with the TiO₂ mesoporous film working electrode coated on it, such that the electron collection efficiency of the 2D ITO
15 and FTO films as the TCOE is low. Doped zinc oxide (ZnO) and Nb₂O₅ are also possible candidates as the working electrode, since they have a more negative conduction band edge than TiO₂. However, they suffer from chemical instability (M. Grätzel, *Nature*, 414: 338, 2001).

[0005] SnO₂ has also been used as it is a wide band gap oxide material because of its
20 relatively higher electron conductivity and relatively higher electron mobility compared to TiO₂ and ZnO (Xinjian Feng et al., WO2010/024896). In addition, SnO₂ is relatively cheaper and more abundant compared to indium (In), which is rare and expensive. There are a number of conventional methods for synthesizing SnO₂ nanorod/nanowire arrays on substrates. These include thermal evaporation (L.A. Ma, *Physica B*, 403, p. 3410, 2008),
25 combustion chemical vapor deposition (CVD) process (Y. Liu, J. Dong and M.L. Liu, *Adv. Mater.*, 16, p. 353, 2004) and hydrothermal method (L. Vayssieres, *Angew. Chem. Int. Ed.*, 43, p. 3666, 2004; Yali Wang, et al., *Scripta Materialia*, 61(3): 234-236, 2009). For the thermal evaporation and combustion CVD technology (L.A. Ma, *Physica B*, 403, p. 3410, 2008; Y. Liu, J. Dong and M.L. Liu, *Adv. Mater.*, 16, p. 353, 2004), the substrate
30 temperature is at least 700°C, which is too high for FTO/ITO glass. The growth

temperature of hydrothermal method is lower ($<200^{\circ}\text{C}$), but the glass may be corrosive in the basic hydrothermal solution.

[0006] One of the methods used to overcome the temperature restriction on the substrates requiring processing at low temperatures is the transfer printing approach (Yi-Kuei Chang and Franklin Chau-Nan Hong, *Nanotechnology*, 20, 195302, 2009; Chi Hwan Lee et al., *PNAS*, 107(22), 9950-9955, 2010). This approach generally involves relocating or transferring structures or fully fabricated devices from donor substrates to receiver substrates using poly(dimethylsiloxane) (PDMS) stamps, tapes or soluble glues. The resulting transferred structures are generally oriented horizontally on the received substrates, approximating to 2D structures.

[0007] Recent developments have included using nanorods in dye-sensitised solar cells (DSCs) to enhance the electron transport efficiency. The mesoporous TiO_2 nanoparticle film working electrode in DSCs have a high surface area for better dye loading and light absorbance but suffers from serious electron combination among the nanoparticle boundaries. Therefore, developments have included replacing the mesoporous TiO_2 nanoparticle film working electrode with an oxide nanorod array working electrode for the DSCs to provide a straightforward electron path to the electrode, for example the FTO electrode. (Seo-Yong Cho, US2010/0051932; Xinjian Feng et al., WO2010/024896). However, this replacement has not been favorable because the efficiency of the DSCs with the nanorod array working electrode is much lower than that of DSCs with a nanocrystalline working electrode due to a decrease in the surface area. Furthermore, dense and long nanorods up to tens of microns are provided to provide a high surface area for more dye loading. However, growing long and densely packed array of nanorods on the substrate glasses may result in the substrate glasses becoming translucent or opaque. Furthermore, the growth conditions used may be corrosive to SnO_2 -based glass substrates such that the transmittance and conductivity of the glass substrates may deteriorate.

[0008] Generally, it is a challenge to provide solid dye-sensitised solar cells (SDSCs) with good performance as it is a challenge to fully fill in the gaps and pores of the electrodes of the solar cells with the solid, semisolid or gel electrolytes to provide good contact with the electrodes. There have been plenty of works carried out on solid electrolytes in terms of the solubility and stability, control of the crystal growth,

increasing the pore filling ratio, conductivity, and providing good contact with counter electrodes.

Summary

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[0009] According to an embodiment, a method of forming inorganic nanorods on an inorganic metal oxide substrate is provided. The method includes exposing the inorganic metal oxide substrate to a plasma. The plasma may include one or more precursor materials suitable for forming the inorganic nanorods on the inorganic metal oxide substrate.

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[0010] According to an embodiment, a method of forming inorganic nanorods on an inorganic metal oxide substrate is provided. The method may include: exposing the inorganic metal oxide substrate to a plasma at suitable conditions, wherein the plasma includes one or more precursor materials suitable for forming the inorganic nanorods on the inorganic metal oxide substrate at the given reaction conditions.

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[0011] According to an embodiment, inorganic nanorods on an inorganic metal oxide substrate are provided. The inorganic nanorods on the inorganic metal oxide substrate may be obtainable by the methods as described above.

[0012] According to an embodiment, a method of forming tin oxide nanorods on an inorganic metal oxide substrate is provided. The method includes exposing the inorganic metal oxide substrate to a plasma. The plasma may include one or more tin precursor materials suitable for forming the tin oxide nanorods on the inorganic metal oxide substrate.

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[0013] According to an embodiment, a method of forming tin oxide nanorods on an inorganic metal oxide substrate is provided. The method may include: exposing the inorganic metal oxide substrate to a plasma at suitable conditions, wherein the plasma includes one or more tin precursor materials suitable for forming the tin oxide nanorods on the inorganic metal oxide substrate at the given reaction conditions.

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[0014] According to an embodiment, tin oxide nanorods on an inorganic metal oxide substrate are provided. The tin oxide nanorods on the inorganic metal oxide substrate may be obtainable by the methods as described above.

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[0015] According to an embodiment, a device including inorganic nanorods on an inorganic metal oxide substrate is provided. The inorganic nanorods on the inorganic metal oxide substrate may be obtainable by the methods as described above.

5 [0016] According to an embodiment, a photovoltaic device including a photoelectrode is provided. The photoelectrode may include inorganic nanorods on an inorganic metal oxide substrate. The inorganic nanorods on the inorganic metal oxide substrate may be obtainable by the methods as described above.

Brief Description of the Drawings

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[0017] In the drawings, like reference characters generally refer to the same parts throughout the different views. The drawings are not necessarily to scale, emphasis instead generally being placed upon illustrating the principles of the invention. In the following description, various embodiments of the invention are described with reference to the following drawings, in which:

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[0018] Figure 1 shows a perspective view of an inductively coupled plasma-enhanced chemical vapor deposition (ICP-CVD) system, according to one embodiment.

[0019] Figure 2 shows a schematic representative block diagram of the ICP-CVD system of the embodiment of Figure 1.

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[0020] Figures 3(a)-3(f) show SEM images of SnO₂ nanorods grown on various substrates (3D-TCOEs) by ICP-CVD, according to various embodiments. The scale bar in Figure 3(a) represents 200 nm, the scale bars in Figures 3(b) to 3(d) represent 100 nm while the scale bars in Figures 3(e) and 3(f) represent 20 nm.

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[0021] Figures 4(a)-4(f) show SEM images of SnO₂ nanorods grown at different densities on various substrates by ICP-CVD, according to various embodiments. The scale bars in Figures 4(a) to 4(c) and 4(e) represent 100 nm while the scale bars in Figures 4(d) and 4(f) represent 200 nm.

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[0022] Figures 4(g) and 4(h) show SEM images of SnO₂ nanorods grown on patterned FTO glass substrates by ICP-CVD, according to various embodiments. The scale bar in Figure 4(g) represents 100 nm while the scale bar in Figure 4(h) represents 1 μ m.

[0023] Figures 5(a) and 5(b) show UV-Vis spectra of the 3D-TCOE on an ITO glass and an FTO glass, respectively, according to various embodiments.

[0024] Figures 6(a)-6(f) show schematic diagrams illustrating dye-sensitized solar cells (DSCs) with 3D-TCOE, according to various embodiments.

5 [0025] Figures 7(a) and 7(b) show SEM images of tin oxide nanoflowers and nanobrushes respectively, according to various embodiments. The scale bar in Figure 7(a) represents 200 nm while the scale bar in Figure 7(b) represents 100 nm.

[0026] Figure 8(a) shows an SEM image of SnO_2 - SrTiO_3 core-sheath nanorods, according to various embodiments. The scale bar represents 10 nm.

10 [0027] Figures 8(b) and 8(c) show an SEM image and a TEM image of SnO_2 - TiO_2 core-sheath nanorods respectively, according to various embodiments. The scale bar in Figure 8(b) represents 10 nm while the scale bar in Figure 8(c) represents 20 nm.

[0028] Figures 9(a), 9(b) and 9(c) show SEM images of composite electrodes comprising TiO_2 nanocrystals and TiO_2 powder paste embedded in the 3D-TCOE, TiO_2 nanocrystals and CuI embedded in the 3D-TCOE and TiO_2 nanocrystals embedded in the 3D-TCOE, respectively, according to various embodiments. The scale bar in Figure 9(a) represents 10 nm, the scale bar in Figure 9(b) represents 100 nm while the scale bar in Figure 9(c) represents 20 nm.

20 [0029] Figures 10(a) and 10(b) show a TEM image of a ZnSe quantum dot and an SEM image of the CIS film respectively, according to various embodiments. The scale bars in Figures 10(a) and 10(b) represent 2 nm and 5 μm respectively.

[0030] Figure 11(a) shows an SEM image of TiO_2 nanocrystals-modified SnO_2 nanorods. Figures 11(b) and 11(c) show TEM images of a ZnO nanocrystals-modified SnO_2 nanorod and a Pd nanocrystals-modified SnO_2 nanorod, respectively. The scale bar in Figure 11(a) represents 20 nm while the scale bars in Figure 11(b) and 11(c) represent 5 nm.

[0031] Figure 12(a) shows a plot of photovoltaic responses of solid state sensitized solar cells using CuSCN and NMO1 as light sensitizer, according to various embodiments.

30 [0032] Figure 12(b) shows a plot of photovoltaic responses of solid state sensitized solar cells using CuSCN and NMO2 as light sensitizer, according to various embodiments.

[0033] Figure 13 shows a plot of photocurrent density-voltage curves of standard SDSCs, flat 2D SDSCs and 3D-TCOE SDSCs, according to various embodiments.

[0034] Figure 14 shows a plot of photocurrent density-voltage curves of a standard 2D-TCOE LDSC, a 2D-TCOE LDSC, and a 3D-TCOE LDSC, according to various
5 embodiments.

Detailed Description

[0035] The following detailed description refers to the accompanying drawings that
10 show, by way of illustration, specific details and embodiments in which the invention may be practiced. These embodiments are described in sufficient detail to enable those skilled in the art to practice the invention. Other embodiments may be utilized and structural, logical, and electrical changes may be made without departing from the scope of the invention. The various embodiments are not necessarily mutually exclusive, as
15 some embodiments can be combined with one or more other embodiments to form new embodiments.

[0036] Various embodiments may provide a transparent conducting oxide electrode (TCOE) which may have high transmittance for visible light or solar light, good conductivity for electrons and chemical stability. Various embodiments may provide a
20 device including the TCOE of various embodiments, without or with reduced at least some of the associated disadvantages of conventional devices.

[0037] In various embodiments, the TCOE may include an array of inorganic nanorods on an inorganic metal oxide substrate. In various embodiments, for example, tin oxide (SnO_2) is used as the material for the nanorod array of the TCOE.

[0038] According to various embodiments, a method of forming inorganic nanorods on
25 an inorganic metal oxide substrate is provided. The method includes exposing the inorganic metal oxide substrate to a plasma. The plasma may include one or more precursor materials suitable for forming the inorganic nanorods on the inorganic metal oxide substrate.

[0039] According to various embodiments, a method of forming inorganic nanorods on
30 an inorganic metal oxide substrate is provided. The method may include: exposing the

inorganic metal oxide substrate to a plasma at suitable conditions, wherein the plasma includes one or more precursor materials suitable for forming the inorganic nanorods on the inorganic metal oxide substrate at the given reaction conditions.

[0040] According to various embodiments, a method of forming tin oxide nanorods on an inorganic metal oxide substrate is provided. The method includes exposing the inorganic metal oxide substrate to a plasma. The plasma may include a tin precursor material suitable for forming the tin oxide nanorods on the inorganic metal oxide substrate.

[0041] According to various embodiments, a method of forming tin oxide nanorods on an inorganic metal oxide substrate is provided. The method includes exposing the inorganic metal oxide substrate to a plasma at suitable conditions. The plasma may include a tin precursor material suitable for forming the tin oxide nanorods on the inorganic metal oxide substrate at the given reaction conditions.

[0042] In various embodiments, the method of forming inorganic nanorods or tin oxide nanorods on an inorganic metal oxide substrate may be a one-step or a multi-step process to grow the nanorods or a nanorod array on the substrate.

[0043] According to various embodiments, inorganic nanorods on an inorganic metal oxide substrate is provided. The inorganic nanorods on the inorganic metal oxide substrate may be obtainable, for example, by exposing the inorganic metal oxide substrate to a plasma at suitable conditions. The plasma may include one or more precursor materials suitable for forming the inorganic nanorods on the substrate at the given reaction conditions.

[0044] According to various embodiments, tin oxide nanorods on an inorganic metal oxide substrate are provided. The tin oxide nanorods on the inorganic metal oxide substrate may be obtainable, for example, by exposing the inorganic metal oxide substrate to a plasma at suitable conditions. The plasma may include one or more tin precursor materials suitable for forming the tin oxide nanorods on the substrate at the given reaction conditions.

[0045] According to various embodiments, a device including inorganic nanorods on an inorganic metal oxide substrate is provided. The inorganic nanorods on the inorganic metal oxide substrate may be obtainable, for example, by exposing the inorganic metal oxide substrate to a plasma at suitable conditions. The plasma may include one or more

precursor materials suitable for forming the inorganic nanorods on the substrate at the given reaction conditions. In various embodiments, the device may be an electrode or a photoelectrode. The electrode or the photoelectrode may be a transparent electrode.

[0046] According to various embodiments, a photoelectrode including inorganic nanorods on an inorganic metal oxide substrate is provided. The inorganic nanorods on the inorganic metal oxide substrate may be obtainable, for example, by exposing the inorganic metal oxide substrate to a plasma at suitable conditions. The plasma may include one or more precursor materials suitable for forming the inorganic nanorods on the substrate at the given reaction conditions.

[0047] According to various embodiments, a photovoltaic device comprising a photoelectrode is provided. The photoelectrode may include inorganic nanorods on an inorganic metal oxide substrate. The inorganic nanorods on the inorganic metal oxide substrate may be obtainable, for example, by exposing the inorganic metal oxide substrate to a plasma at suitable conditions. The plasma may include one or more precursor materials suitable for forming the inorganic nanorods on the substrate at the given reaction conditions. In various embodiments, the photovoltaic device may be a solar cell.

[0048] Various embodiments may provide an array of inorganic nanorods, for example tin oxide (SnO_2) nanorods, on a transparent conductive oxide electrode (TCOE) and a method of growing or forming the array of inorganic nanorods on a TCOE. The TCOE may be an indium tin-oxide glass (ie. ITO glass or ITO-coated glass) or a fluorine-doped tin oxide glass (ie. FTO glass or FTO-coated glass). The ITO or FTO coating on the glass substrates acts as an electrode. Accordingly, various embodiments may provide a 3-dimensional TCOE (3D-TCOE) and a method of forming the same. Further embodiments may provide solid dye-sensitized solar cells (SDSCs) and liquid dye-sensitized solar cells (LDSCs) with the 3D-TCOE of various embodiments.

[0049] By growing inorganic nanorods on the TCOE, the 2D film-type ITO TCOE or FTO TCOE is extended spatially to three dimension to form 3D-TCOE. In various embodiments, the inorganic nanorods grown on the substrates may have good conductivity. In various embodiments, the inorganic nanorods grown on the substrates may be at least substantially vertically or perpendicular aligned to the substrates.

However, it should be appreciated that the inorganic nanorods may also be grown at an angle (eg. tilted) to the substrates.

[0050] In various embodiments, using SnO₂ nanorods as an example and not limitations, growing an array of SnO₂ nanorods on an ITO film (tin doped In₂O₃) glass and an FTO film (fluorine doped SnO₂) glass widely used as the TCOE, the SnO₂ nanorods have the same composition or matrix material as that of the ITO film or the FTO film. The incorporation of SnO₂ nanorods in the 3D-TCOE is advantageous in terms of compatibility and cost as SnO₂ is also the matrix materials of the ITO or FTO electrode on the glass substrates of the TCOE. Accordingly, the direct growth of SnO₂ nanorods on the ITO glass or FTO glass substrates by ICP-CVD provides lattice matching between the SnO₂ nanorods and the ITO or FTO electrode, thereby minimizing or preventing the formation of a Schottky barrier between the SnO₂ nanorods and the ITO or FTO electrode. This may help to provide relatively fast electron transport between the SnO₂ nanorods and the ITO or FTO electrode.

[0051] Various embodiments may provide a method of growing inorganic nanorods, for example SnO₂ nanorods, at relatively low deposition temperatures by inductively coupled plasma-enhanced chemical vapor deposition (ICP-CVD) directly on the TCOE, such as a glass, an ITO glass or an FTO glass substrate, to form 3D-TCOE. The ICP-CVD process is a form of plasma enhanced chemical vapor deposition (PECVD). In various embodiments, the ICP-CVD method may directly grow an array of uniform inorganic nanorods on large area glass substrates.

[0052] The incorporation of 3D-TCOE of various embodiments into solar cells is advantageous. The 3D-TCOE may provide a direct and short conduction pathway from the point of electron-hole pair generation to the collecting electrode and may improve the electron transport efficiency. By improving the electron transport efficiency, the conversion efficiency of solar cells may be improved. Therefore, the 3D-TCOE of various embodiments may be developed for high efficiency or high conversion efficiency solar cells, which may further lower the cost of solar electricity. In addition, the 3D-TCOE with nanorods of various embodiments may provide an increased surface area or contact area in direct contact with the active working electrode in the solar cells that may

shorten the charge collection distance and thereby improve the charge collection efficiency and the overall efficiency of the solar cells.

[0053] In addition, solar cells incorporating the 3D-TCOE of various embodiments may show enhanced current density or photocurrent density and higher conversion efficiency.

5 [0054] For example, SnO_2 is a promising wide band gap oxide material because of its relatively higher electron conductivity and relatively higher electron mobility, and therefore may provide low resistance contact of the light absorbing region of the solar cells to the electrodes.

[0055] Various embodiments may provide for the growth of inorganic nanorods, for example SnO_2 nanorods, with relatively small gaps in between the inorganic nanorods, thereby enabling the development of photovoltaic or solar cells with relatively higher solar light absorption efficiency and conversion efficiency. The 3D-TCOE of various
10 embodiments may also be used for other applications such as display, photochemical, photocatalyst, lithium-ion battery, supercapacitors, energy-efficient windows, field emission electrode, transparent EMC shielding glass, sensor, circuit substrate.

[0056] In various embodiments, the inorganic metal oxide substrate for the growth of inorganic nanorods, for example SnO_2 nanorods, may include, but is not limited to, glass (for example soda-lime glass, silica glass, borate glass and phosphate glass), quartz (for example crystalline quartz and fused quartz), crystals (for example silicon crystals and
20 sapphire crystals), ceramics (for example porcelain, tiles, alumina, ceria and zirconia), and composites (for example cermet, woven glass fiber, fiber-enhanced composites and a combination of glass and crystal).

[0057] In further embodiments, other substrates may be used, such as gold, platinum, titanium foil, stainless steel, metal, metal foil, metal-coated substrates and silicon wafer
25 (Si wafer). The Si wafer may further include a layer of silicon dioxide (SiO_2/Si wafer), a layer of silicon nitride ($\text{Si}_3\text{N}_4/\text{Si}$ wafer) or layers of platinum and silicon dioxide ($\text{Pt}/\text{SiO}_2/\text{Si}$ wafer). The Si wafer may include metal-coated SiO_2/Si substrate. It should be appreciated that other non-metal substrates and metal substrates may also be used for the growth of inorganic nanorods, such as SnO_2 nanorods. Accordingly, while examples or
30 embodiments have been described with reference to inorganic metal oxide substrates, the examples and embodiments as described may be similarly applicable for other substrates.

[0058] In various embodiments, the inorganic metal oxide substrate may be coated with at least a layer of coating material, including but not limited to, SnO_2 , SnO , In_2O_3 , ZnO , TiO_2 , TiN , Fe_2O_3 , CuO , Cu_2O , VO_2 , V_2O_5 , Nb_2O_5 , WO_3 , CdO , F-doped SnO_2 , Sb-doped SnO_2 , Sn-doped In_2O_3 , F-doped In_2O_3 , ZnO-doped In_2O_3 (ZIO), Al-doped ZnO (AZO),
5 F-doped ZnO , Ga-doped ZnO (GZO), Nb-doped TiO_2 , Nb-doped SrTiO_3 , (La, Sr) CoO_3 , (La, Sr) MnO_3 , SrRuO_3 , CuAlO_2 , CuInO_2 or any combination thereof. In various embodiments, (La, Sr) CoO_3 may mean La-doped SrCoO_3 or Sr-doped LaCoO_3 , depending on whether the composition is Sr-rich or La-rich. Similarly, (La, Sr) MnO_3 may mean La-doped SrMnO_3 or Sr-doped LaMnO_3 .

[0059] In various embodiments, the thickness of the coating layer may be approximately 5 nm to 10 μm , for example approximately 5 nm to 5 μm , approximately 5 nm to 1 μm , approximately 5 nm to 500 nm, approximately 500 nm to 10 μm or approximately 1 μm to 10 μm , such that the thickness of the coating layer may be about 5 nm, about 10 nm, about 50 nm, about 100 nm, about 500 nm, about 1 μm , about 5 μm or about 10 μm .

[0060] In various embodiments, the inorganic metal oxide substrate may be transparent. In various embodiments, the inorganic metal oxide substrate may be conductive or semiconductive. In various embodiments, the inorganic metal oxide substrate may be conductive or semiconductive as a result of the inorganic metal oxide substrate being coated with at least a layer of coating material.

[0061] In various embodiments, the inorganic metal oxide substrate, for example glass, may be coated with tin oxide, titanium dioxide, indium tin oxide, fluorine-doped tin oxide or aluminium-doped zinc oxide (AZO) to provide tin oxide-coated glass ($\text{SnO}_2/\text{glass}$), titanium dioxide-coated glass ($\text{TiO}_2/\text{glass}$), indium tin oxide-coated glass ($\text{Sn:In}_2\text{O}_3/\text{glass}$ or ITO glass), fluorine-doped tin oxide-coated glass ($\text{F:SnO}_2/\text{glass}$ or FTO glass) and
25 aluminium-doped zinc oxide-coated glass ($\text{Al:ZnO}/\text{glass}$), respectively.

[0062] In further embodiments, the layer of coating may include a combination of different coating materials. In further embodiments, a plurality of coating layers may be provided, where each layer may have a different coating material or a combination of coating materials, such that two layers, three layers or four layers of coatings may be
30 provided on the glass or inorganic metal oxide substrate.

[0063] In various embodiments, the at least one layer of coating material on the inorganic metal oxide substrate may act as a transparent conductive oxide electrode (TCOE), or a seeding layer, or a protective layer, or a combination thereof. A TCOE may provide a collection and conduction path for electrons. A seeding layer may be provided to promote the growth of inorganic nanorods, for example SnO₂ nanorods, on the inorganic metal oxide substrate or the coated inorganic metal oxide substrate. A protective layer may be provided as an intermediate layer between the plasma during the growth process and the inorganic metal oxide substrate or the coated inorganic metal oxide substrate to minimize any effect that may inhibit the growth of inorganic nanorods on the substrate as a result of the direct contact of the plasma with the inorganic metal oxide substrate or the coated inorganic metal oxide substrate. Therefore, the protective layer helps to promote the growth of inorganic nanorods by minimizing any adverse effects. Accordingly, surface modification of the substrates, for example glass and FTO glass substrates, by providing a thin seeding and/or protective layer on the substrates may promote the growth of inorganic nanorods for the 3D-TCOE of various embodiments. In various embodiments, the seeding layer and the protective layer may be a layer of SnO₂.

[0064] In various embodiments, a protective layer may be provided on an FTO glass. The protective layer may be a layer of SnO₂, which is also the matrix material of the TCOE. In further embodiments, the protective layer may be a layer of TiO₂ or other conductive materials or semiconductive materials.

[0065] Thin film deposition processes as known in the art may be used to deposit the layer or layers of coatings. These may include but not limited to, sol-gel spin/dip coating, CVD, sputtering and physical evaporation. The sol-gel spin/dip coating process provides a cost-effective process for large area deposition of thin film, such as a SnO₂ thin film.

[0066] In various embodiments, the sol-gel spin/dip coating process was used to deposit the layer of SnO₂ thin film. By way of example to illustrate the process and not limitation, about 0.01-0.2 M SnCl₂, or SnCl₄ or dibutyltin diacetate was dissolved in ethanol and the solution was used as precursor. The precursor solution was then coated on an FTO glass substrate by spin coating. After spin coating, the coated FTO glass was annealed at approximately 400-500°C for about 0.5-1 hour to crystallize the SnO₂ layer. The SnO₂ layer may act as a protective layer on the FTO glass.

[0067] In various embodiments, the 3D-TCOE incorporating an array of inorganic nanorods, for example SnO₂ nanorods, may have a high transmittance due to optical coupling, good conductivity and high electron mobility, and in particular when compared to 2D ITO glass or 2D FTO glass. Accordingly, the 3D-TCOE of various embodiments are transparent and conductive and include an array of 3D nanorods. The 3D-TCOE of various embodiments may include short nanorods and sparsely distributed nanorods to allow the filling of nanocrystals (eg. TiO₂ nanoparticles), for example in between the nanorods, and for enhanced electric contact interface. In various embodiments, the morphology of the nanorods and patterning of the nanorods may be controlled. In various embodiments, at least one portion of the inorganic metal oxide substrate may be patterned. For example, patterning may be carried out at one or more portions of the inorganic metal oxide substrate, to deposit the nanorods in certain portions of the substrates to provide different surface morphologies.

[0068] In various embodiments, in order to provide a 3D-TCOE with inorganic nanorods, for example SnO₂ nanorods, with high transmittance, for example in the visible light region, and good conductivity (ie. electron conductivity), one or more of the following non-limiting requirements may be controlled during the deposition process, for example in order to control the microstructures of the nanorods:

- The deposited inorganic nanorods may have small dimensions, for example a diameter of less than 30 nm, which is much smaller than ½ wavelength of the light, in order to reduce the scattering and reflection effect of the light and increase the surface light coupling. In various embodiments, the diameter of the nanorods may be about 5 nm to about 100 nm, eg. about 5 nm, about 10 nm, about 20 nm, about 50 nm, about 80 nm or about 100 nm, and the length is up to tens of micrometer, depending on the growth time, eg. a length of about 10 μm, about 20 μm, about 30 μm, about 50 μm, about 70 μm or about 100 μm. As an example and not limitation, the typical dimension for the nanorods grown for about 2 h is approximately 5 nm to 15 nm in diameter and about 300 nm in length.
- The ICP-CVD deposition process may be free or have minimal corrosive effect on the substrates, in order to minimize any adverse effects on the optical and electrical properties of the substrates.

- The seed layer (eg. a SnO₂ seed layer) on the substrates (eg. an FTO glass) may be dense and/or thin. A porous and/or thick seed layer may result in large nanorod sizes, low transmittance and high resistance of the 3D-TCOE.

- The inorganic nanorods, for example SnO₂ nanorods, grown on the substrates may be at least substantially vertically or perpendicularly aligned to the substrates. Alternatively, the inorganic nanorods, for example SnO₂ nanorods, may also be grown at an angle to the substrates or tilted on the substrates, for improved light capturing.

- The compact density and length of the inorganic nanorods may be controlled by the seed layers and deposition time. In various embodiments, providing sparsely distributed nanorods may be advantageous for gap filling by TiO₂ nanoparticles in between the nanorods.

- Doping by, for example but not limited to, F, Sb, In, Zn or any combination thereof, may be carried out to increase the conductivity of the inorganic nanorods.

- The array of inorganic nanorods of various embodiments may be used as both the collecting electrode and the working electrode. In various embodiments, a thin insulate layer such as a layer of TiO₂ may be coated on the inorganic nanorods to form TiO₂-inorganic core-sheath nanorods or structures. Furthermore, in various embodiments, branched structures and surface modifications may be provided to the array of inorganic nanorods or the 3D-TCOE to increase the light absorbance.

[0069] The 3D-TCOE of various embodiments may be used in photovoltaic cells, including solar cells. The cells may be, but not limited to thin film photovoltaic cells, thin film solar cells, organic solar cells and dye-sensitised solar cells (DSCs).

[0070] In various embodiments, the DSCs, including the SDSCs and LDSCs exhibit enhanced efficiency. This may be due to a decrease in the electron-hole recombination as a result of the use of the 3D-TCOE of various embodiments.

[0071] Various embodiments advantageously provide a large volume of free space in the array of inorganic nanorods, for example SnO₂ nanorods, for coating an active oxide layer, for example TiO₂, on the surface of the nanorods, for use in solar cells.

[0072] Various embodiments advantageously use SnO₂ as the material in the 3D-TCOE of various embodiments, which is cheap and abundant in the Earth. Together with the

increase in the efficiency of solar cells employing the 3D-TCOE of various embodiments, the solar cells of various embodiments may lower the cost of solar electricity.

[0073] In addition to solar cells, the 3D-TCOE of various embodiments may be used in a variety of applications including display technology, energy-efficient windows, field emission electrodes, transparent electromagnetic compatibility (EMC) shielding glass, photocatalysts, sensors, supercapacitors, lithium batteries and fuel cells.

[0074] In the context of various embodiments, the inorganic nanorods may include a material selected from the group consisting of SnO_2 , SnO , In_2O_3 , ZnO , TiO_2 , TiN , Fe_2O_3 , CuO , Cu_2O , VO_2 , V_2O_5 , Nb_2O_5 , WO_3 , CdO , F-doped SnO_2 , Sb-doped SnO_2 , Sn-doped In_2O_3 , F-doped In_2O_3 , ZnO-doped In_2O_3 (ZIO), Al-doped ZnO (AZO), F-doped ZnO , Ga-doped ZnO (GZO), Nb-doped TiO_2 , Nb-doped SrTiO_3 , (La, Sr) CoO_3 , (La, Sr) MnO_3 , SrRuO_3 , CuAlO_2 , CuInO_2 and any combination thereof. In the context of various embodiments, (La, Sr) CoO_3 may mean La-doped SrCoO_3 or Sr-doped LaCoO_3 , depending on whether the composition is Sr-rich or La-rich. Similarly, (La, Sr) MnO_3 may mean La-doped SrMnO_3 or Sr-doped LaMnO_3 . In the context of various embodiments, any reference to the term 'inorganic nanorods' may refer to nanorods comprising any one or more of these materials.

[0075] In the context of various embodiments, the term 'tin oxide' may include SnO and SnO_2 .

[0076] In the context of various embodiments, the term "nanorod" may mean a nanostructure extending, for example in a longitudinal direction, with dimensions in the order of nanometers and the term "nanorods" may mean an array of such nanostructures. The term "nanorod" may be used to refer to a nanostructure of any nanometer dimensions (eg. length, width, diameter or cross-section) and therefore may be used with the same meaning as the terms "nanowire", "nanopillar", "nanocolumn", "nanotube" and the likes. In further embodiments, the term "nanorod" may include a microstructure extending, for example in a longitudinal direction, with dimensions in the order of micrometers (microns).

[0077] In the context of various embodiments, the term "inorganic metal oxide" may include inorganic metalloid oxides.

[0078] In various embodiments, the inorganic metal oxide substrate may include, but is not limited to, material that comprises a metal or metalloid oxide, such as silica or silicates. Generally, the term "metal oxide", as used herein, comprises also oxides of metalloids, such as silicon oxides, as well as composites or mixtures that include a metal/metalloid oxide. Specific examples for suitable materials include, but are not limited to glass (for example soda-lime glass, silica glass, borate glass and phosphate glass), quartz (for example crystalline quartz and fused quartz), crystals (for example silicon crystals and sapphire crystals), ceramics (for example porcelain, tiles, alumina, ceria and zirconia) and composites (for example cermet, woven glass fiber, fiber-enhanced composites and a combination of glass and crystal). In various embodiments, the inorganic metal oxide substrate may be transparent and/or conductive.

[0079] In various embodiments, the inorganic metal oxide substrate may be coated with at least one layer of coating material, wherein the coating material may include, but not limited to SnO_2 , SnO , In_2O_3 , ZnO , TiO_2 , TiN , Fe_2O_3 , CuO , Cu_2O , VO_2 , V_2O_5 , Nb_2O_5 , WO_3 , CdO , F-doped SnO_2 , Sb-doped SnO_2 , Sn-doped In_2O_3 , F-doped In_2O_3 , ZnO-doped In_2O_3 (ZIO), Al-doped ZnO (AZO), F-doped ZnO , Ga-doped ZnO (GZO), Nb-doped TiO_2 , Nb-doped SrTiO_3 , (La, Sr) CoO_3 , (La, Sr) MnO_3 , SrRuO_3 , CuAlO_2 , CuInO_2 or any combination thereof to provide coated inorganic metal oxide substrates. In various embodiments, (La, Sr) CoO_3 may mean La-doped SrCoO_3 or Sr-doped LaCoO_3 , depending on whether the composition is Sr-rich or La-rich. Similarly, (La, Sr) MnO_3 may mean La-doped SrMnO_3 or Sr-doped LaMnO_3 . In various embodiments, using tin oxide as an example, the direct growth of SnO_2 nanorods on coated inorganic metal oxide substrates such as the ITO glass or FTO glass substrates provides lattice matching between the SnO_2 nanorods and the ITO or FTO electrode as the SnO_2 nanorods have the same composition or matrix material as that of the ITO film or the FTO film. This may minimize or prevent the formation of a Schottky barrier between the SnO_2 nanorods and the ITO or FTO electrode, which may help to provide relatively fast electron transport between the SnO_2 nanorods and the ITO or FTO electrode.

[0080] In the context of various embodiments, the term "transparent" as used in for example a transparent substrate, may mean that the substrate is transmissible to light (ie. optically transparent) such that light, for example visible light, may at least substantially

pass through the substrate. In the context of various embodiments, the term “conductive” or ‘semiconductive’ as used in for example a conductive substrate, may mean that the substrate has the property of conductivity such that electrically charged particles, for example electrons, may at least substantially travel through the conductive substrate.

5 [0081] In various embodiments, the inorganic metal oxide substrate may be a thin film or in the form of a bulk substrate.

[0082] In various embodiments, the plasma used for exposing to the inorganic metal oxide substrate may be an inductively coupled plasma. The plasma may include one or more precursor materials suitable for forming inorganic nanorods on the inorganic metal oxide substrate. The one or more precursor materials may be in the form of a vapour. In
10 various embodiments, the plasma may further include gaseous argon and gaseous oxygen. The gaseous argon (Ar) acts as a carrier gas while the gaseous oxygen (O₂) acts as a reaction gas for the oxidation of the one or more precursor materials for forming the inorganic nanorods.

15 [0083] In the context of various embodiments, the terms “suitable conditions” or “reaction conditions” may refer to the growth conditions of the inorganic nanorods, for example tin oxide nanorods, on the inorganic metal oxide substrate.

[0084] In various embodiments, the suitable conditions or the reaction conditions for the growth of the inorganic nanorods, for example tin oxide nanorods, on the inorganic metal oxide substrate may include the power used to generate the inductively coupled plasma,
20 the flow rate of the gaseous argon, the flow rate of the gaseous oxygen, the combined flow rate or sum of the flow rates of the gaseous argon and the gaseous oxygen, the ratio of the flow rate of the gaseous argon to the flow rate of the gaseous oxygen and the substrate temperature.

25 [0085] In various embodiments, the plasma or the inductively coupled plasma may be generated at a power of about 200 W. In preferred embodiments, a power of 400 W or more (ie. a power of ≥ 400 W) for the growth of the inorganic nanorods, for example SnO₂ nanorods, on the inorganic metal oxide substrate may be provided. In further preferred embodiments, a power of 800 W or more (ie. a power of ≥ 800 W) may be
30 provided, for example in a range of about 800 W to about 2000 W (2 kW), a range of about 800 W to about 1600 W, a range of about 800 W to about 1200 W or a range of

about 1200 W to about 2000 W, such that the power used to generate the inductively coupled plasma may be about 800 W, about 1000 W, about 1200 W, 1400 W, about 1600 W or about 2000 W. However, it should be appreciated that a higher power may be used, limited only by the power specification of the ICP generator used to generate the plasma.

[0086] In various embodiments, the plasma or the inductively coupled plasma generated at a power of about 200 – 400 W may deposit one or more layers of inorganic films on the inorganic metal oxide substrate. In various embodiments, the plasma or the inductively coupled plasma generated at a power of about 400 W or more may grow inorganic nanorods on the inorganic metal oxide substrate. In the range of about 400-800W, the inorganic nanorods grown may be relatively short and/or sparsely distributed on the inorganic metal oxide substrate. At a power of about 800 W or more (ie. a power of ≥ 800 W), the inorganic nanorods grown may be relatively long, uniformly grown and/or densely packed on the inorganic metal oxide substrate.

[0087] In various embodiments, the flow rate of the gaseous argon (Ar) may be about 1000 sccm (standard cubic centimeters per minute) or lower for the growth of the inorganic nanorods on the inorganic metal oxide substrate (ie. a flow rate of ≤ 1000 sccm or equivalently $\leq 1.67 \times 10^{-5} \text{ m}^3/\text{s}$). Accordingly, the gaseous Ar may be provided at a flow rate of ≤ 1000 sccm, for example in a range of about 0 sccm to about 1000 sccm, about 0 sccm to about 500 sccm, or about 0 sccm to about 300 sccm, or about 0 sccm to about 100 sccm, and preferably in a range of about 50 sccm to about 100 sccm (or equivalently about $8.33 \times 10^{-7} \text{ m}^3/\text{s}$ to about $1.67 \times 10^{-6} \text{ m}^3/\text{s}$).

[0088] In various embodiments, the flow rate of the gaseous oxygen (O_2) may be in a range of about 0.1 sccm to about 1000 sccm (or equivalently about $1.67 \times 10^{-9} \text{ m}^3/\text{s}$ to about $1.67 \times 10^{-5} \text{ m}^3/\text{s}$), for example in a range of about 0.1 sccm to about 500 sccm, or about 0.1 sccm to about 300 sccm or about 0.1 sccm to about 100 sccm. Accordingly, the gaseous O_2 may be provided at a flow rate of ≤ 1000 sccm (or equivalently $\leq 1.67 \times 10^{-5} \text{ m}^3/\text{s}$). However, it should be appreciated that a flow rate lower than 0.1 sccm, for example 0.01 sccm, may also be used, to provide gaseous oxygen (O_2) for oxidation of the one or more precursor materials. In various embodiments, the flow rate of the gaseous oxygen (O_2) may be zero (ie. 0 sccm).

[0089] In various embodiments, the flow rate of the gaseous Ar and the flow rate of the gaseous O₂ may be provided such that the total or sum of the flow rates of the gaseous Ar and the gaseous O₂ may be between about 10 sccm to about 1000 sccm. Accordingly, the gaseous argon and the gaseous oxygen may be provided at a combined flow rate of
5 between about 10 sccm to about 1000 sccm (or equivalently between about 1.67×10^{-7} m³/s to about 1.67×10^{-5} m³/s), for example in a range of about 10 sccm to about 500 sccm, about 10 sccm to about 100 sccm or about 100 sccm to about 1000 sccm.

[0090] In various embodiments, the flow rate of the gaseous Ar and the flow rate of the gaseous O₂ may be provided such that the ratio of the flow rate of the gaseous Ar to the
10 flow rate of the gaseous O₂ may be between about 0 to about 50, for example in a range of about 0 to about 30, a range of about 0 to about 10, a range of about 10 to about 50 or a range of about 20 to about 50, such that the ratio may be about 0, about 0.5, about 1.0, about 5, about 10, about 30 or about 50.

[0091] In various embodiments, the substrate temperature may be about 400°C or lower
15 (ie. a temperature of $\leq 400^\circ\text{C}$) for the growth of the inorganic nanorods, for example SnO₂ nanorods, on the inorganic metal oxide substrate.

[0092] In the context of various embodiments, the term “precursor material” may mean a precursor source used to form the inorganic nanorods. The precursor material may react with oxygen to form the inorganic materials which may be deposited on the inorganic
20 metal oxide substrate to grow the inorganic nanorods. In various embodiments, one or more precursor materials may be provided to grow the inorganic nanorods. In various embodiments, for example, the tin precursor material for SnO₂ nanorods may include, but not limited to dibutyltin diacetate, monobutyltin chloride, monobutyltin trichloride, monomethyltin trichloride, dimethyltin chloride, dimethyltin dichloride, trimethyltin
25 chloride, tetramethyltin, tin tetrachloride, tin tert-butoxide, tin acetate, tin bis(acetylacetonate), tin 2-ethylhexanoate, tin oxalate and tin phthalocyanine.

[0093] In the context of various embodiments, a “photoelectrode” may include an array of inorganic nanorods on an inorganic metal oxide substrate (ie. 3D-TCOE) of various
30 embodiments, and including a film, for example for use in photovoltaic cells. The photovoltaic device may be a solar cell. In various embodiments, the film may include a material of TiO₂, ZnO, SnO₂, TiN, SrTiO₃ or Nb₂O₅. The film may be mesoporous.

[0094] In various embodiments, the film may include nanostructures. The nanostructures may include a material selected from the group consisting of TiO_2 , ZnO , SnO_2 , SrTiO_3 , Nb_2O_5 and any combination thereof. In various embodiments, the nanostructures may be selected from a group consisting of nanoparticles, nanorods, nanowires, nanotubes, nanosheets, nanospheres and any combination thereof.

[0095] In various embodiments, the photoelectrode may include, but not limited to a nanoparticle, a nanorod, a nanowire, a nanotube, a nanoflower, a nanobrush, a nanocrystal, a nanocrystalline film, or any combination thereof.

[0096] In various embodiments, the photoelectrode may include a sensitizer. The sensitizer may include, but not limited to a dye, a quantum dot, a nanocrystal, a nanocrystalline film, a photonic crystal, or any combination thereof.

[0097] In various embodiments, the dye may include but not limited to N719, N749, Z907 and N3. In various embodiments, the quantum dot, the nanocrystal, the nanocrystalline film and the photonic crystal may include a compound including but not limited to ZnS , ZnSe , CdS , CdSe , CdTe , PbS , PbSe , InAs , InP , NiO , SnS , SnS_2 , Cu_2O , Si , Se , In_2S_3 , AgS_2 , Sb_2S_3 , CuS_2 , CuInS_2 , $\text{CuIn}(\text{S},\text{Se})_2$, $\text{Cu}(\text{In},\text{Ga})\text{Se}_2$, $\text{Cu}(\text{In},\text{Ga})(\text{S},\text{Se})_2$, $\text{Cu}_2\text{ZnSnS}_4$, $\text{Cu}_2\text{ZnSnSe}_4$ and $\text{Cu}_2\text{CdSnSe}_4$.

[0098] In various embodiments, for example when the photoelectrode of various embodiments is used in a photovoltaic cell, the photovoltaic cell or the photoelectrode may include a working electrode, for example in the form of a film deposited on the photoelectrode. In various embodiments, the film may include a material of TiO_2 , ZnO , SnO_2 , TiN , SrTiO_3 or Nb_2O_5 . In various embodiments, the working electrode may be configured to at least substantially contact the photoelectrode. In various embodiments, the film may include nanostructures of a material of TiO_2 , ZnO , SnO_2 , TiN , SrTiO_3 , Nb_2O_5 or any combination thereof. The nanostructures may be nanoparticles, nanorods, nanowires, nanotubes, nanosheets, nanospheres or any combination thereof. In various embodiments, the film may be mesoporous. In various embodiments, the photoelectrode on its own may also be configured to function as a working electrode.

[0099] In various embodiments, the inorganic nanorods, for example SnO_2 nanorods, may be directly grown on the inorganic metal oxide substrate. As an example and not limitation, the direct growth of SnO_2 nanorods on inorganic metal oxide substrates or

coated inorganic metal oxide substrates such as the ITO glass or FTO glass substrates provides lattice matching between the SnO₂ nanorods and the ITO or FTO electrode as the SnO₂ nanorods have the same composition or matrix material as that of the ITO film or the FTO film. This may minimize or prevent the formation of a Schottky barrier between the SnO₂ nanorods and the ITO or FTO electrode, which may help to provide relatively fast electron transport between the SnO₂ nanorods and the ITO or FTO electrode.

[00100] Various embodiments may provide an ICP-CVD system for forming inorganic nanorods on an inorganic metal oxide substrate. The ICP-CVD system may include a chamber for exposing the inorganic metal oxide substrate to a plasma at suitable conditions. The plasma may include one or more precursor materials suitable for forming the inorganic nanorods on the inorganic metal oxide substrate at the given reaction conditions.

[00101] In various embodiments, the one or more precursor materials may be vaporised and the vapor carried into the chamber by flowing gaseous argon (Ar) acting as the carrier gas. Gaseous oxygen (O₂) may be flown into the chamber as the reaction gas. An inductively coupled plasma may be generated, comprising the vapor of the one or more precursor materials, the gaseous Ar and the gaseous O₂. Subsequently, the plasma may come into contact with the inorganic metal oxide substrate positioned in the chamber and inorganic nanorods may be formed on the inorganic metal oxide substrate by chemical vapor deposition (CVD). Accordingly, exposing the inorganic metal oxide substrate to the plasma is part of a process of chemical vapor deposition (CVD) to form the inorganic nanorods on the inorganic metal oxide substrate.

[00102] In various embodiments where one or more inorganic films are deposited or coated on the inorganic metal oxide substrate, a plasma treatment may be carried out without any additional precursor material to grow inorganic nanorods from the one or more inorganic films due to the sputtering-regrowth effect in the plasma.

[00103] The use of inductively coupled plasma (ICP) is advantageous compared to capacitively coupled plasma (CCP) that is commonly used, as the ICP plasma or discharges are of relatively high electron density and are free of contamination because the electrodes used to generate the ICP discharges are completely outside the reaction

chamber of the ICP discharges. In contrast, in a CCP system, the electrodes to generate the CCP discharges are generally placed inside the reactor or deposition chamber and are thus exposed to the plasma or discharges and the subsequent reactive chemical species that may be formed.

5 [00104] In order that the invention may be readily understood and put into practical effect, particular embodiments will now be described by way of examples and not limitations, and with reference to the figures.

[00105] Various embodiments may provide an ICP-CVD system for forming tin oxide (SnO_2) nanorods on an inorganic metal oxide substrate. The ICP-CVD system may include a chamber for exposing the inorganic metal oxide substrate to a plasma at suitable conditions. The plasma may include one or more tin precursor materials suitable for forming the tin oxide nanorods on the inorganic metal oxide substrate at the given reaction conditions. The tin precursor material may include dibutyltin diacetate (DBTD). In various embodiments, DBTD may be vaporised and the vapor carried into the chamber
15 (eg. deposition chamber) by flowing gaseous argon (Ar) acting as the carrier gas. Gaseous oxygen (O_2) may be flown into the chamber as the reaction gas. An inductively coupled plasma may be generated, comprising the vapor of DBTD, the gaseous Ar and the gaseous O_2 . Subsequently, the plasma may come into contact with the inorganic metal oxide substrate positioned in the chamber and SnO_2 nanorods may be formed on the
20 inorganic metal oxide substrate by chemical vapor deposition (CVD). Accordingly, exposing the inorganic metal oxide substrate to the plasma is part of a process of chemical vapor deposition (CVD) to form the SnO_2 nanorods on the inorganic metal oxide substrate.

[00106] Figure 1 shows a perspective view of an inductively coupled plasma-enhanced chemical vapor deposition (ICP-CVD) system 100, according to one embodiment.
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[00107] The ICP-CVD system 100 is custom-designed and custom-built and may be used to directly grow SnO_2 nanorods or a nanorod array on a substrate, including an inorganic metal oxide substrate. In various embodiments, the ICP-CVD system 100 may be a custom-designed cold wall, horizontal ICP-CVD system.

30 [00108] In various embodiments, the ICP-CVD system 100 may be used to grow SnO_2 nanorods at a growth temperature of 300°C or lower (ie. a temperature of $\leq 300^\circ\text{C}$), when

exposing the inorganic metal oxide substrate to the inductively coupled plasma during SnO₂ nanorod growth. Therefore various substrates, such as glass, ITO glass, FTO glass, quartz, crystal, ceramic, metal foil and polymer, for example polytetrafluoroethylene (PTFE), may be used for the direct growth of SnO₂ nanorods on the substrates, to form three-dimensional transparent conductive oxide electrode (3D-TCOE)., Furthermore, the ICP-CVD system 100 may provide large area deposition and quantity deposition. In other words, the ICP-CVD system 100 may allow deposition over large area substrates and may also enable deposition on a large number of substrates over a certain period of time, thereby increasing the efficiency of the deposition process.

[00109] The ICP-CVD system 100 comprises four modules for performing different functions. Figure 2 shows a schematic representative block diagram 200 of the ICP-CVD system 100 of Figure 1 to illustrate the different modules. As shown in Figure 2, the modules include a reactive source delivery module 202, a deposition chamber and pressure control module 204, a plasma generation module 206, and a software integration module in the form of a processing unit or computer 208. The reactive source delivery module 202 includes separately a bubbler delivery module 210 and a direct liquid injection module 212 together with their respective gas handling manifolds that act to regulate and direct the flow of reactants into the deposition chamber 214 of the deposition chamber and pressure control module 204. The various functional modules 202, 204, 206, of the ICP-CVD system are interfaced to the computer 208 with an integrated custom-designed Graphical User Interface (GUI).

[00110] The deposition chamber 214 may be a quartz cylinder with a diameter of about 150 mm and may be wound with copper band (not shown) connected to a radio frequency (RF) generator 216 for ICP plasma generation. The RF generator 216 operates at 13.56 MHz and is capable of delivering an RF power of up to 2000 W (2 kW). A matching network 218 may be placed between the RF generator 216 and the glow discharge or plasma in the deposition chamber 214 in order to provide impedance matching between the RF generator 216 and the plasma. This may help to maximize the power transfer from the RF generator 216 to the plasma and minimize reflections back to the RF generator 216.

[00111] Some of the advantages and differences of the custom-designed ICP-CVD system 100 (Figure 1) and as represented by the schematic representative block diagram 200 (Figure 2) compared to conventional CVD systems are as follows.

5 Precursor delivery methods

[00112] Conventional CVD systems are equipped with a gas delivery module and/or a bubbler delivery module to deliver the gaseous precursor and/or the liquid/solid precursor vapor to the deposition chamber. For multicomponent materials, one individual delivery channel is required for each component, and therefore it may be challenging to control
10 the flow rate of each delivery channel in order to obtain the required stoichiometric composition of the as-deposited materials. For the ICP-CVD system 100 (Figure 1), a direct liquid injection module 212 (Figure 2) is also equipped, where a mixture of liquid cocktail precursor with the necessary chemicals may be used as the precursor, thereby providing relatively more control over the composition of the materials by changing the
15 ratio of the chemicals in the liquid cocktail precursor.

Deposition mode

[00113] Using the ICP-CVD system 100 (Figure 1), both substrate heating-assisted CVD (namely metal-organic chemical vapor deposition or MOCVD) and plasma-enhanced
20 CVD (PECVD) may be achieved. Coupled with three precursor delivery ways to deliver gaseous precursor, liquid/solid precursor vapor and liquid precursor, six deposition modes may be achieved. These deposition modes include MOCVD with bubbler delivery assisted by electrical heating, MOCVD with liquid injection delivery assisted by electrical heating, MOCVD with both bubbler delivery and liquid injection delivery
25 assisted by electrical heating, PECVD with bubbler delivery assisted by plasma, PECVD with liquid injection delivery assisted by plasma and PECVD with both bubbler delivery and liquid injection delivery assisted by plasma. In contrast, for conventional CVD system, only one or two of these modes may be achieved in one system.

Plasma type

[00114] The type of plasma used may affect the growth of nanorods and the 3D-TCOE of various embodiments. Conventionally, the most common plasma used in commercial CVD systems is capacitively coupled plasma (CCP), generated by two parallel plate electrodes powered by a single radio-frequency (RF) power supply, typically at 13.56 MHz. These electrodes are generally placed inside the reactor or deposition chamber and are thus exposed to the plasma or discharges and the subsequent resulting reactive chemical species, possibly causing contamination. In the ICP-CVD system 100 (Figure 1), inductively coupled plasma (ICP) is used, where the ICP is generated by a copper tape electrode rounded outside of and surrounding the deposition chamber 214. The copper electrode is connected to a 2 kW RF power supply. In the ICP-CVD system 100, the ICP discharges generated are of relatively high electron density and are free of contamination because the electrodes are completely outside the reaction chamber.

[00115] As an example of carrying out the method of growing SnO₂ nanorods of the invention, the exemplary growth parameters of the 3D-TCOE of various embodiments are illustrated in Table 1.

Table 1: Growth parameters of SnO₂ nanorods by ICP-CVD

Parameters	
RF power (kW)	1.2
RF Tune	34
Reflected power (kW)	0.03
Precursor temperature (°C)	90
Gas line temperature (°C)	100
Ar carrier gas (sccm)	50
O ₂ (sccm)	50
Pressure in chamber (mTorr)	90
Deposition time (min)	120
Substrate	TCO (ITO or FTO) glass
Substrate-nozzle distance (D _{sn}) (cm)	10 (Funnel type nozzle)

[00116] Dibutyltin diacetate (DBTD) was used as the tin precursor material. The DBTD precursor was soaked at about 90°C and its vapor was carried into the deposition chamber by gaseous argon (Ar) as the carrier gas, provided at a flow rate of about 50 sccm (or equivalently $8.33 \times 10^{-7} \text{ m}^3/\text{s}$). Gaseous oxygen (O_2) was used as the reaction gas and was provided into the deposition chamber at a flow rate of about 50 sccm (or equivalently $8.33 \times 10^{-7} \text{ m}^3/\text{s}$). The substrates were inserted into a quartz boat and then the quartz boat was placed in the plasma zone of the quartz deposition chamber. Subsequently, the Ar/ O_2 plasma, including the DBTD vapor, was generated by a 0.4-1.2 kW ICP generator to deposit or grow SnO_2 nanorods on the substrates. After deposition for a period of about 0.5 hour to about 4 hours, the substrates with SnO_2 nanorods, in other words the 3D-TCOE, were taken out and ready for use.

[00117] During deposition, there was no additional heating, such as electrical heating, of the substrate. In addition, no post-annealing was performed. The substrate temperature measured after deposition in 1.2 kW plasma for about 2 hours was below 300°C (ie. $\leq 300^\circ\text{C}$). As a result of the heating effect of the ICP plasma, the substrate temperature increases with an increase in the deposition time. Therefore, the temperature of the substrate shortly after the deposition process indicates the highest temperature of the substrate. Accordingly, the substrate temperature shortly after deposition was measured to indicate the highest substrate temperature which was observed to be below 300°C after deposition in 1.2 kW plasma for about 2 hours. Therefore, the ICP-CVD process may be used to grow the SnO_2 nanorods at relatively low deposition temperatures.

[00118] No temperature measurements had been taken during the growth of the nanorods as it is a challenge to either measure the substrate temperature in real time by a thermal couple due to the electromagnetic annoy noise of the ICP or to open the metal shield of the ICP-CVD system to measure the temperature by an IR sensor due to the harmful effects of the radio frequency (rf) radiation.

[00119] The growth parameters of ICP-CVD may affect the growth of SnO_2 nanorods on the substrates and therefore the resulting 3D-TCOE. There is a certain threshold for some of the growth parameters where any value above or below the threshold may affect the deposition of SnO_2 and growth into either SnO_2 nanorods or granular SnO_2 thin films. Some of the growth parameters are as follows.

Plasma type

[00120] The ICP discharge has a relatively higher electron density compared to the CCP discharge of a similar power and therefore the ICP discharge provides a relatively stronger sputtering effect. During deposition, the sputtering effect of the ICP discharge etches the loose particles of SnO₂ deposited on the substrate, which then promotes the preferential growth of SnO₂ nanorods. The SnO₂ nanorods grown are shown, for example, in Figures 3(a)-3(f). In contrast, CVD system employing CCP discharges may only deposit SnO₂ thin films.

ICP power

[00121] The RF power of the ICP discharge may affect the growth of the nanorods and consequently the 3D-TCOE. It was observed that SnO₂ nanorods may be obtained at ICP power of about 400 W or more (ie. ≥ 400 W), and preferably a power of 800 W or more (ie. ≥ 800 W). ICP power lower than 400 W (ie. < 400 W) produced SnO₂ granular thin films. In various embodiments, the use of ICP power beyond 800 W (ie. ≥ 800 W) promotes the growth of relatively sharper and longer SnO₂ nanorods. The higher the ICP power, the sharper and longer are the SnO₂ nanorods. Therefore, the relatively strong sputtering effect induced by the relatively high electron density of the ICP discharge at relatively high RF power (ie. ≥ 800 W) is one of the factors promoting the growth of SnO₂ nanorods.

Plasma gas ratio and flow rate

[00122] For the growth of SnO₂ nanorods, gaseous argon (Ar) is used as the carrier gas to carry the vapour of the tin precursor material into the deposition chamber while gaseous oxygen (O₂) is used as the reaction gas. In various embodiments, both the gaseous Ar and the gaseous O₂ are provided at a flow rate of about 50 sccm. Within the ICP plasma or discharge containing the mixture of Ar and O₂, the O₂ species oxidise the precursor vapour into metal oxides (ie. oxidises the tin precursor vapour into tin oxide).

[00123] In various embodiments, the SnO₂ nanorods may be grown when the ratio of the flow rate of the gaseous Ar to the flow rate of the gaseous O₂ is in the range of between

about 0 to about 50, and preferably about 0.5 to about 1.5, and when the combined flow rate of the gaseous Ar and the gaseous O₂ is in the range of between about 10 sccm to about 1000 sccm (or equivalently between about 1.67×10^{-7} m³/s to about 1.67×10^{-5} m³/s), and preferably about 50 sccm to about 150 sccm (or equivalently between about 8.33×10^{-7} m³/s to about 2.50×10^{-6} m³/s).

[00124] A relatively higher amount of tin precursor vapour may be provided into the deposition chamber by flowing the gaseous Ar at a relatively higher flow rate of Ar of 500 sccm or more. However, the higher amount of tin precursor vapour may result in the growth of granular thin films rather than nanorods, due to the relatively higher deposition rate of tin precursor material on the substrate.

[00125] Deposition was also carried out with an ICP discharge where gaseous Ar is not flown into the deposition chamber. For example, based on the process parameters of 0 sccm Ar and 100 sccm O₂, a deposition time of about 2 hours and a plasma power of about 1.2 kW, short nanorod-like particles were observed. Therefore, it is expected that longer nanorods may be grown with increasing deposition time. In addition, deposition was carried out with an ICP discharge without flowing in gaseous O₂ into the deposition chamber and no obvious nanorods may be observed.

Substrate treatment

[00126] In various embodiments, inorganic metal oxide substrates such as quartz, glass, indium tin oxide coated glass (ITO glass) and fluorine-doped tin oxide coated glass (FTO glass) may be used for the growth of SnO₂ nanorods to form 3D-TCOE. The substrates may be used directly for the growth of the nanorods. A thin seed layer such as SnO₂ and TiO₂ may be coated on the substrate to promote the growth of the nanorods.

[00127] The morphology of the SnO₂ nanorods on the substrates or the 3D-TCOEs of various embodiments was observed using scanning electron microscopy (SEM). Figures 3(a)-3(f) show scanning electron microscopy (SEM) images of SnO₂ nanorods grown on various substrates (3D-TCOEs) by ICP-CVD, according to various embodiments.

[00128] Figure 3(a) shows an SEM image 300 of the top view of the SnO₂ nanorods, for example 302, grown on a glass substrate.

[00129] Figure 3(b) shows an SEM image 304 of the top view of the SnO₂ nanorods, for example 306, grown on an FTO glass.

[00130] Figure 3(c) shows an SEM image 308 of the top view of the SnO₂ nanorods, for example 310, grown on an ITO glass. Figure 3(d) shows an SEM image 312 of the side view of the SnO₂ nanorods, for example 310, grown on an ITO glass (ie. a glass substrate 314 with a layer of ITO 316) for the embodiment of Figure 3(c).

[00131] In the embodiments of Figures 3(a)-3(d), the SnO₂ nanorods grown are about 5 nm in diameter at the tip of the nanorods and about 16 nm in diameter at the base of the nanorods. The SnO₂ nanorods grown may have a length of about 700 nm. In various embodiments, longer nanorods up to several micrometers may be obtained by increasing the deposition time.

[00132] In various embodiments, the array of SnO₂ nanorods may have high spatial distribution density. Based on Figures 3(a)-3(d), the spatial distribution density is calculated or estimated to be about $2.78 \times 10^{14} \text{ m}^{-2}$, the surface area of the array of SnO₂ nanorods is about $3.5 \text{ } \mu\text{m}^2$ and the substrate area is about $1 \text{ } \mu\text{m}^2$, which are about 2.5 times larger than flat thin films.

[00133] Figure 3(e) shows an SEM image 318 of the top view of the SnO₂ nanorods, for example 320, grown on an ITO glass. As shown in Figure 3(e), the SnO₂ nanorods, for example 320, are grown at an angle to the ITO glass. In other words, the SnO₂ nanorods, for example 320, are tilted SnO₂ nanorods. In various embodiments, the SnO₂ nanorods may be tilted at least substantially in one direction.

[00134] In various embodiments, the SnO₂ nanorods grown may be substantially cylindrical, for example the embodiments as shown in Figures 3(a)-3(e).

[00135] In various embodiments, the SnO₂ nanorods grown may be substantially rectangular. Figure 3(f) shows an SEM image 322 of the top view of rectangular SnO₂ nanorods, for example 324, grown on an ITO glass.

[00136] In various embodiments, the density of the SnO₂ nanorods grown on various substrates for the 3D-TCOEs may be controlled. Figures 4(a)-4(c) show SEM images of SnO₂ nanorods grown at different densities on an ITO glass while Figures 4(d)-4(f) show SEM images of SnO₂ nanorods grown at different densities on an FTO glass. In 3D-TCOEs of various embodiments, an array of SnO₂ nanorods may be provided at a

relatively low density such that relatively large gaps may be provided in between the nanorods so that nanoparticles, for example TiO_2 nanoparticles, may fill the gaps between the nanorods for applications, for example in solar cells.

[00137] In various embodiments, the growth of SnO_2 nanorods on various substrates may be patterned by, for example using substrates with patterned areas of seed layer, thereby leading to patterned 3D-TCOE. Therefore, different surface morphologies may be achieved using patterned substrates. In various embodiments, one or more portions of the inorganic metal oxide substrate may be patterned to provide different surface morphologies.

[00138] Figures 4(g) and 4(h) show SEM images of SnO_2 nanorods grown on patterned FTO glass substrates by ICP-CVD, according to various embodiments. The SEM image 400 of Figure 4(g) shows that the density of the SnO_2 nanorods is relatively higher in the region 402, compared to the density of the SnO_2 nanorods in the region 404. This is because the region 402 has been patterned with TiO_2 , which promotes the growth of SnO_2 nanorods.

[00139] The substrate may also be randomly patterned. Figure 4(h) shows an SEM image 406 of SnO_2 nanorods grown in a network-like pattern 408 on the surface of the FTO glass substrate. The network-like pattern 408 may help in providing a relatively faster electron transport.

[00140] The optical properties of the 3D-TCOE formed using the ICP-CVD process of various embodiments were measured. Figure 5(a) shows a plot 500 of the UV-Vis spectra of the 3D-TCOE on an ITO glass. The plot 500 of Figure 5(a) shows the UV-Vis spectrum for an ITO glass 502, the UV-Vis spectrum for a 2D TCOE 504 (ie. SnO_2 granular thin film on the ITO glass) and the UV-Vis spectrum for a 3D-TCOE 506 (ie. SnO_2 nanorods on the ITO glass). The results show that the transmittance of the ITO glass incorporating the 3D TCOE in respect of visible light in the wavelength range of about 378-678 nm is relatively enhanced compared to that of the 2D-TCOE.

[00141] Figure 5(b) shows a plot 508 of the UV-Vis spectra of the 3D-TCOE on an FTO glass. The plot 508 of Figure 5(b) shows the UV-Vis spectrum for an FTO glass 510, the UV-Vis spectrum for a 2D-TCOE 512 (ie. SnO_2 granular thin film on the FTO glass) and the UV-Vis spectrum for a 3D-TCOE 514 (ie. SnO_2 nanorods on the FTO glass). Similar

to the results for the ITO glass as shown in Figure 5(a), the 3D-TCOE, or in other words, the FTO glass deposited with the SnO₂ nanorods, shows relatively improved transmittance in the visible wavelength range compared to that for the 2D-TCOE.

[00142] The results of Figures 5(a) and 5(b) show that 3D-TCOEs show relatively higher transmittance in the visible wavelength range compared to the 2D-TCOEs and are therefore suitable as transparent conductive electrodes.

[00143] Table 2 shows the carrier mobility (ie. the Hall mobility) and the carrier concentration for different electrodes based on the FTO glass. The carrier mobility and the carrier concentration of the FTO glass, the 2D-TCOE (ie. SnO₂ film on FTO glass) and the 3D-TCOE (ie. SnO₂ nanorods on FTO glass) in Table 2 were measured based on the Hall Effect. Generally as known in the art, the transparent conductive oxides (TCOs) used as the thin film electrodes in solar cells should have a minimum carrier concentration on the order of approximately 10^{20} cm^{-3} for low resistivity. Table 2 show that the results for the Hall mobility measured for the 2D-TCOE and the 3D-TCOE are relatively close and the carrier concentration for the 3D-TCOE is maintained at the same order of approximately 10^{20} cm^{-3} .

Table 2 : Carrier mobility and carrier concentration for electrodes of FTO glass

	FTO glass	SnO ₂ film/ FTO glass	SnO ₂ nanorods/ FTO glass
Hall mobility (cm ² /V-s)	34.4	20	12.3
Carrier concentration (/cm ³)	-4.57×10^{20}	-4.58×10^{20}	-7.81×10^{20}

Dye-sensitised solar cells (DSCs) with 3D-TCOE

[00144] Figures 6(a) to 6(f) show schematic diagrams illustrating dye-sensitized solar cells (DSCs) with 3D-TCOEs, according to various embodiments. The 3D-TCOEs may be the SnO₂ nanorod 3D-TCOEs of various embodiments, which may be used directly as the 3D-TCOEs or modified. Figures 6(a) to 6(f) show DSCs based on FTO glasses or ITO glasses as illustrative examples and not limitations. In various embodiments, the

array of SnO₂ nanorods of the 3D-TCOE of various embodiments may provide a high surface area platform for surface modification.

[00145] In various embodiments, the electrolyte in the DSCs may be a solid, a semisolid, a liquid or a gel or a gel-like material. The electrolyte may include hole conductors including iodine, iodides, copper iodide (CuI), copper thiocyanate (CuSCN), other n-type conductors or p-type conductors, solutions and composites or any combination thereof.

[00146] Figure 6(a) shows a DSC 600a including a three dimensional transparent conducting oxide electrode (3D-TCOE) 602. The 3D-TCOE 602 includes an FTO glass (ie. a layer of FTO 604a coated on a glass substrate 606a), a layer of SnO₂ 608 and an array of SnO₂ nanorods 610. The layer of SnO₂ 608 may act as the seeding and/or protective layer to promote the growth of the SnO₂ nanorods 610.

[00147] The DSC 600a further comprises an electrolyte 612, a platinum (Pt) counter electrode 614, a second FTO glass 616a for sealing the DSC 600a and an electrical interconnection 618 for the flow of electricity or electrons between the 3D-TCOE 602 and the Pt counter electrode 614. The electrical interconnection 618 may be a wire. In addition, the DSC 600a may include a dye 620 provided on the surface of the nanorods 610 of the 3D-TCOE 602 as a sensitizer.

[00148] For Figures 6(b) to 6(f), like references as that provided for Figure 6(a) are used to denote the substantially similar part or components of the DSCs of Figures 6(b) to 6(f) with respect to Figure 6(a) and explanation regarding the corresponding similar components of the DSCs of Figures 6(b) to 6(f) with respect to the DSC of Figure 6(a) will not be presented here as the explanation with regard to the like components of the DSC of Figure 6(a) may be similarly applicable here for the like components of the DSCs of Figures 6(b) to 6(f).

[00149] For the embodiment as shown in Figure 6(b), the DSC 600b includes a 3D-TCOE 602 modified to include nanoflower-like structures or nanoflowers 622. Such a modification by including nanoflowers 622 in the 3D-TCOE 602 may help to increase the surface area, thereby increasing the light absorption efficiency and also the loading amount of sensitizer, such as a dye. The nanoflowers 622 may further include a dye 620 provided on the surface of the nanoflowers 622. In various embodiments, the dye 620 may also be provided on the nanorods 610. In further embodiments, other structures such

as nanobrushes or branched structures may be provided instead of or in addition to the nanoflowers 622.

[00150] Figure 7(a) shows an SEM image 700 of tin oxide (SnO_2) nanoflower-like structures or nanoflowers 702 provided or embedded with SnO_2 nanorods 704 of the 3D-TCOE while Figure 7(b) shows an SEM image 706 of tin oxide (SnO_2) nanobrushes 708 provided or embedded with SnO_2 nanorods 710 of the 3D-TCOE. The 3D-TCOEs with nanoflowers 702 or nanobrushes 708 have a relatively larger surface area which may provide relatively higher light absorption and relatively higher dye loading. In various embodiments, the nanoflowers 702 or nanobrushes 708 were deposited by the PECVD process, followed by a post-plasma treatment in 1.2 kW Ar and O_2 plasma in the ICP-CVD system of various embodiments.

[00151] For the embodiment as shown in Figure 6(c), the DSC 600c includes a 3D-TCOE 602 modified to include a layer of coating 624, in addition to a dye 620, deposited on a surface of the nanorods 610 to substantially and uniformly surround the nanorods 610 to form core-sheath nanorods. The core-sheath nanorod structures may help to increase the contact area of the 3D-TCOE 602. The layer of coating 624 may be a layer of strontium titanate (SrTiO_3) or titanium dioxide (TiO_2). In further embodiments, the layer of coating 624 may be a layer of zinc oxide (ZnO), magnesium oxide (MgO), aluminium oxide (Al_2O_3) or niobium oxide (Nb_2O_5). Figure 8(a) shows an SEM image 800 of tin oxide-strontium titanate (SnO_2 - SrTiO_3) core-sheath nanorods 802. Figure 8(b) shows an SEM image 804 of tin oxide-titanium dioxide (SnO_2 - TiO_2) core-sheath nanorods 806 while Figure 8(c) shows a TEM image 808 of tin oxide-titanium dioxide (SnO_2 - TiO_2) core-sheath nanorods 810. As can be seen in Figure 8(c), two distinct crystal regions may be observed, namely the SnO_2 core 812 and the TiO_2 sheath 814.

[00152] For the embodiment as shown in Figure 6(d), the DSC 600d includes a 3D-TCOE 602 modified to include nanoparticles or nanocrystals 626 to form a composite electrode. The nanoparticles or nanocrystals 626 may further include a dye 620 provided on the surface of the nanoparticles or nanocrystals 626. In various embodiments, the dye 620 may also be provided on the nanorods 610. The nanoparticles or nanocrystals 626 may be embedded with the 3D-TCOE 602. For example, the nanoparticles or nanocrystals 626 may be provided in spaces in between the nanorods 610. In further

embodiments, nanocrystalline films may be provided or embedded with the 3D-TCOE 602 to form a composite electrode, instead of or in addition to the nanoparticles or nanocrystals 626. For the purpose of illustration and not limitation, the DSC 600d includes a 3D-TCOE 602 on an ITO glass (ie. a layer of ITO 604b coated on a glass substrate 606b) and a second ITO glass 616b, instead of FTO glasses as illustrated for the
5 embodiments shown in Figures 6(a)-6(c) and 6(e)-6(f).

[00153] For the embodiment as shown in Figure 6(e), the DSC 600e includes a 3D-TCOE 602 modified to include quantum dots (QDs) 626 as an inorganic sensitizer. In further
10 embodiments, other structures such as nanocrystals or photonic crystals may be provided instead of or in addition to the QDs 626 as the inorganic sensitizer.

[00154] For the embodiment as shown in Figure 6(f), the DSC 600f includes a 3D-TCOE 602 modified to include quantum dots (QDs) 630 as an inorganic sensitizer and a porous
15 nanocrystal film provided or embedded with the 3D-TCOE 602 to form a composite electrode. In further embodiments, other structures such as nanocrystals or photonic crystals may be provided instead of or in addition to the QDs 630 as the inorganic sensitizer.

[00155] In various embodiments, the composite electrode including nanocrystalline films, for example in the embodiments of Figures 6(d) and 6(f), may help to increase the surface
20 area, thereby increasing the light absorption efficiency and also the loading amount of sensitizer, such as a dye.

[00156] Figure 9(a) shows an SEM image 900 of a composite electrode including TiO_2 nanocrystals 902 and TiO_2 powder paste 904 embedded in a 3D-TCOE (not shown). The
 TiO_2 nanocrystals 902 may be obtained using hydrothermal synthesis.

[00157] Figure 9(b) shows an SEM image 906 of a composite electrode including TiO_2 nanocrystals 908 embedded with the 3D-TCOE 910. The 3D-TCOE 910 includes an
25 array of SnO_2 nanorods 912, with CuI, for example as represented by 913, on a glass substrate 914 coated with a layer of FTO 916 (ie. an FTO glass). The CuI 913 fills the gaps of the TiO_2 nanocrystals 908. The SEM image 906 shows a solid DSC.

[00158] Figure 9(c) shows an SEM image 918 of a composite electrode including TiO_2 nanocrystals 920 embedded with the 3D-TCOE 922. The 3D-TCOE 922 includes an
30

array of SnO₂ nanorods 924, on a glass substrate 926 coated with a layer of FTO 928 (ie. an FTO glass).

[00159] In various embodiments, hybrids DSCs based on any two or more embodiments of Figures 6(a) to 6(e) may be provided.

5 [00160] In various embodiments, the QDs 626, 630, may include one or more of cadmium selenide (CdSe), zinc selenide (ZnSe), lead sulfide (PbS), tin sulfide (SnS), copper indium disulphide (CuInS₂), copper indium diselenide (CuInSe₂ or known by its acronym CIS) and copper indium gallium diselenide (or known by its acronym CIGS) as the inorganic sensitizers. In various embodiments, the QDs 626, 630 may be provided
10 instead of organic dyes in order to increase the chemical stability of the solar cells.

[00161] Figures 10(a) and 10(b) show a TEM image 1000 of a ZnSe quantum dot 1002 and an SEM image 1004 of the CIS film respectively, according to various embodiments. The ZnSe quantum dot 1002 was synthesised by a hydrothermal method. The CIS quantum dots were synthesised using an electrodeposition method.

15 [00162] In various embodiments, the inorganic nanorods of various embodiments may provide a high surface area platform for surface modification for various applications. Figure 11(a) shows an SEM image 1100 of SnO₂ nanorods 1102 modified with TiO₂ nanocrystals 1104, Figure 11(b) shows a TEM image 1106 of a SnO₂ nanorod 1108 modified with zinc oxide (ZnO) nanocrystals 1110 while Figure 11(c) shows a TEM
20 image 1112 of a SnO₂ nanorod 1114 modified with palladium (Pd) nanocrystals 1116. As examples, the embodiment of Figure 11(a) may find applications in the fields of photocatalysis, photovoltaic and photochemical, the embodiment of Figure 11(b) may find applications in the fields of photoelectrodes and photocatalysis while the embodiment of Figure 11(c) may find applications as catalysts and electrodes in the fields
25 of supercapacitors, lithium batteries and fuel cells.

Fabrication of solid dye-sensitised solar cells (SDSCs) with 3D-TCOE

[00163] The fabrication of solid dye-sensitised solar cells (SDSCs) of various
30 embodiments will now be described by way of the following non-limiting examples. In various embodiments, the embodiments illustrated in Figures 6(a) to 6(f) with 3D-TCOE of various embodiments may be used for the fabrication of SDSCs.

[00164] A TiO_2 thick paste or thick film was prepared using hydrothermally grown TiO_2 and subsequently deposited, using the doctor blade method, screen printing, spin coating or spray coating, on the 3D-TCOE of various embodiments on an FTO glass to form a photoelectrode. The TiO_2 thick paste may be mesoporous. The FTO glass was pre-coated with a layer of TiO_2 thin film.

[00165] The TiO_2 thick paste or thick film on the 3D-TCOE on the FTO glass (ie. the photoelectrode) was then annealed at about 450°C for about 1 hour and cooled down naturally to room temperature. In various embodiments, the temperature was increased from room temperature to about 450°C at a slow ramp rate of about $10^\circ\text{C}/\text{minute}$. Multiple TiO_2 layers may be deposited to obtain the desired thickness of the TiO_2 film after the annealing of each layer.

[00166] The light sensitizer Ruthenium dye N719 was dissolved in approximately 200 ml pure ethanol. The annealed photoelectrode was subsequently dipped into the light sensitizer Ruthenium dye N719, overnight at room temperature, to achieve better dye loading. The photoelectrode was subsequently rinsed with ethanol so that, preferably, only a monolayer of dye was anchored on the TiO_2 layer. The photoelectrode may then be used as a working electrode in a SDSC.

Example 1: Copper thiocyanate (CuSCN) hole conductor

[00167] Copper thiocyanate (CuSCN) was used as the inorganic hole conductor in solid state SDSCs.

[00168] Approximately 0.2 g of CuSCN was added to approximately 10 ml of propyl sulfide to form a solution A. The resulting solution A was stirred overnight and allowed to settle down for about 1 day. Subsequently, approximately 2 ml was taken out from the supernatant portion of the solution A (ie. the upper portion of the 10 ml solution), which was then further diluted with approximately 150 μl of propyl sulfide to form a solution B, which may then be used for deposition.

[00169] The photoelectrode including the 3D-TCOE of various embodiments was used as the working electrode in the SDSCs. The working photoelectrode was placed on a hot plate at a temperature of approximately 80°C . A thermoplastic was then used to define an active area on the working electrode. In various embodiments, the thermoplastic may be

the 25-micro thick SX-1170 spacer from Solaronix Inc. (Switzerland). The solution B obtained was then manually dripped onto the active area using a pipette, and dried for about 20 seconds. This process of dripping and drying the solution B onto the active area was repeated, until approximately 1 μm thickness of dried solution B is obtained. It should be appreciated that the process may be repeated for any number of times depending on the thickness required. For example, the process may be repeated 5 times, 10 times, 20 times, 80 times, 100 times or more.

[00170] A gold-coated or Pt-coated counter electrode was then clamped with the working photoelectrode using binder clips to form a device for measurement purposes.

Example 2: STF sensitizer

[00171] $\text{Sr}(\text{Ti}, \text{Fe})\text{O}_3$ (STF in short) material or sensitizer, such as STF particles (hereinafter referred as NMO1) and STF nanoparticles (hereinafter referred as NMO2), were also used as light sensitizers in the SDSCs. STF is a p-type inorganic semiconductor, and acts as the photosensitizer as well as the inorganic hole conductor.

[00172] The feasibility of using the NMO1 and NMO2 material as light sensitizer (ie. for light absorption) in solid sensitized solar cells was investigated. The device was fabricated in a way similar to the solid-state SDSCs, except the substitution of N719 Ru-dye with NMO1 or NMO2. The NMO1 or NMO2 material was deposited in a colloidal form, where about 1 g of as received NMO1 or NMO2 nanoparticles was dispersed in approximately 20 ml ethanol using ultrasonic bath. Then, the colloidal was spin-coated at about 480 rpm for about 20 seconds on a Degussa P25- TiO_2 -coated photoelectrode, followed by baking at about 100°C . The sample was kept overnight before the inorganic hole conductor CnSCN was deposited to form a solid state sensitized solar cell.

[00173] Figure 12(a) shows a plot 1200 of photovoltaic responses of solid state sensitized solar cells using CuSCN 1202 and CuSCN with NMO1 as light sensitizer 1204, according to various embodiments. The plot 1200 is shown in terms of the current density 1206 against the applied bias voltage 1208 of the SDSCs, under 1 sun. ($100 \text{ mW}/\text{cm}^2$) light illumination conditions.

[00174] Figure 12(a) shows that the open circuit voltages for the solid state sensitized solar cells using CuSCN 1202 and the solid-state NMO1-sensitized solar cells with

CuSCN 1204 are approximately 0.32 V and 0.23 V respectively. In addition, the solid state sensitized solar cells using CuSCN 1202 and the solid-state NMO1-sensitized solar cells with CuSCN 1204 exhibit a similar short circuit current density of about $28 \mu\text{A}/\text{cm}^2$.

[00175] Figure 12(b) shows a plot 1210 of photovoltaic responses of solid state sensitized solar cells using CuSCN with NMO2 as light sensitizer under dark condition 1212 and under 1 sun ($100 \text{ mW}/\text{cm}^2$) light illumination 1214, according to various embodiments. The plot 1210 is shown in terms of the current density 1216 against the applied bias voltage 1218 of the SDSCs.

[00176] Figure 12(b) shows that the open circuit voltage of the solid-state NMO2-sensitized solar cells is about 0.53 V, which is comparable to that for N719 dye-sensitized solid state solar cells. For the solid-state NMO2-sensitized solar cells under light illumination 1214, the short circuit current density is about $2.75 \mu\text{A}/\text{cm}^2$.

Example 3: Copper(I) iodide (CuI) hole conductor

[00177] Approximately 0.3 g of CuI powders and approximately 0.02 g of 1-methyl-3-ethylimidazolium thiocyanate (MEISCN) were dissolved in approximately 10 ml of acetonitrile to form a CuI solution (ie. CuI sol). Then, the CuI sol was maintained under stirring in a condition of non-illumination (eg. in the dark) for about 3 hours until completely dissolved.

[00178] Dye-coated TiO_2 films were provided to the 3D-TCOE of various embodiments to form a working electrode. The working electrode was then placed on a hot plate (with the surface temperature of the hot plate at about $80\text{-}100^\circ\text{C}$). While on the hot plate, the working electrode was moistened with the CuI-acetonitrile solution prepared earlier, and repeated until the active region TiO_2 film pores were filled with the CuI/molten salt material from the CuI-acetonitrile solution.

[00179] Figure 13 shows a plot 1300 of photocurrent density-voltage curves (I-V characterization results) of standard SDSCs 1302, flat 2D SDSCs 1304 with a SnO_2 film on FTO glass, and 3D SDSCs 1306, with CuI as the hole conductor, according to various embodiments. The plot 1300 is shown in terms of the current density 1308 against the biased voltage 1310 of the SDSCs.

[00180] Both the standard SDSCs 1302 and the flat SDSCs 1304 include a 2D-TCOE while the 3D SDSCs 1306 include a 3D-TCOE. The results shown in Figure 13 indicates that the SDSCs with 3D-TCOE (ie. the 3D SDSCs 1306) show much higher current intensity and thus higher efficiency, η , of 0.87 % compared to the standard SDSCs 1302 and the flat SDSCs 1304.

[00181] The results shown in Figure 13 also indicates that the 3D SDSCs 1306 show a much higher fill factor (FF) of 0.49 compared to 0.29 for the standard SDSCs 1302 and 0.33 for the flat SDSCs 1304. The fill factor (FF), as generally known in the context of solar cell technology, is defined as the ratio of the actual maximum obtainable power, to the theoretical power and is used as one of the parameters to evaluate the performance and the energy yield of photovoltaic or solar cells.

Fabrication of liquid dye-sensitised solar cells (LDSCs) with 3D-TCOE

[00182] In various embodiments, the embodiments illustrated in Figures 6(a) to 6(f) with 3D-TCOE of various embodiments may be used for the fabrication of liquid dye-sensitised solar cells (LDSCs). In various embodiments, the electrolyte in the LDSCs may be in the form of a liquid, a jelly-like liquid or a gel. In various embodiments, these electrolytes may be commercially obtained from Dyesol. In various embodiments, liquid electrolyte may be advantageous in providing good contact with the electrodes of the LDSCs as the liquid electrolyte may fill in the gaps and pores in the electrodes.

[00183] The fabrication of LDSCs of various embodiments will now be described by way of the following non-limiting examples.

[00184] A TiO_2 thick paste was prepared using hydrothermally grown TiO_2 and subsequently deposited on the 3D-TCOE of various embodiments on an FTO glass to form a photoelectrode. The TiO_2 layer may be mesoporous. In various embodiments, the TiO_2 layer may be deposited using the doctor blade method, screen printing, spin coating or spray coating. The FTO glass was pre-coated with a layer of compact or dense TiO_2 thin film.

[00185] The photoelectrode was then annealed at about 450°C for about 1 hour. In various embodiments, the temperature was increased from room temperature to about 450°C at a slow ramp rate of about $10^\circ\text{C}/\text{minute}$. Subsequently, the photoelectrode was

cooled down naturally to room temperature. Multiple TiO_2 layers may be deposited to obtain the desired thickness of the TiO_2 film after the annealing of each layer.

[00186] The light sensitizer Ruthenium dye N719 was dissolved in approximately 200 ml pure ethanol. The annealed photoelectrode of the 3D-TCOE with the layer of TiO_2 , was subsequently dipped into the Ruthenium dye N719, overnight at room temperature, in an impregnation process to achieve better dye loading.

[00187] In the following day, the photoelectrode impregnated with the Ruthenium dye N719 was rinsed with pure ethanol to wash away any excess Ruthenium dye N719 sensitizer. The photoelectrode may then be used as a working electrode in a LDSC.

[00188] A thermoplastic with a thickness of approximately $25\text{ }\mu\text{m}$ was used to define an active area on the working electrode. The thermoplastic may also serve as a spacer between the working electrode and a counter electrode (eg. a gold-coated or Pt-coated counter electrode). The working photoelectrode with the thermoplastic was placed on a hot plate and heated to a temperature of approximately 100°C to allow the thermoplastic to stick firmly on the working electrode.

[00189] Subsequently, an iodide-based electrolyte was dripped onto the active area and a platinum-coated counter electrode was then clamped with the working photoelectrode using binder clips to form a device for measurement purposes. In various embodiments, the iodide-based electrolyte may be the electrolyte Iodolyte from Solaronix Inc. (Switzerland). In various embodiments, the counter electrode was prepared using a fine coater where platinum was sputtered onto transparent conducting oxide (TCO) glasses. The thickness of the platinum coating is approximately $5\text{ nm} - 20\text{ nm}$.

[00190] The 3D-TCOE LDSCs of various embodiments were observed to show high visible light transmittance and good conductance, which provide advantageous properties for the LDSCs.

[00191] Standard Grätzel-type LDSCs using flat FTO glass and LDSCs with 2D-TCOE incorporating SnO_2 film were also prepared for comparison measurement purposes against the LDSCs with 3D-TCOE incorporating SnO_2 nanorods of various embodiments. For measurement purposes and not limitation, the LDSC with 3D-TCOE used was based on the embodiment illustrated in Figure 6(d).

[00192] Figure 14 shows a plot 1400 of photocurrent density-voltage curves (I-V characterization results) of a standard 2D-TCOE LDSC 1402, a 2D-TCOE LDSC (with SnO₂ film) 1404, and a 3D-TCOE LDSC (with SnO₂ nanorods) 1406, according to various embodiments. The plot 1400 is shown in terms of the current density 1408
5 against the voltage 1410 of the LDSCs.

[00193] The results in Figure 14 shows that while the open circuit voltage, V_{OC} , for the standard 2D-TCOE LDSC 1402, the 2D-TCOE LDSC 1404 and the 3D-TCOE LDSC 1406 are substantially similar at about 0.75 V, there is an increase in the short circuit current density, J_{SC} , for the 3D-TCOE LDSC 1406. In comparison to the standard 2D-
10 TCOE LDSC 1402 with J_{SC} of about 8.36 mA/cm², there is an enhancement of about 63.5% to about 13.67 mA/cm² for the J_{SC} of the 3D-TCOE LDSC 1406.

[00194] In addition, it was observed that the energy conversion efficiencies of the 3D-TCOE LDSC 1406, at about 6.17%, are about 52.0% more, compared to about 4.06% for the standard 2D-TCOE LDSC 1402 and about double, when compared to about 2.97%
15 for the 2D-TCOE LDSC 1404. This may imply that a better charge separation in the SnO₂/TiO₂ coupled photoelectrode system may be enhanced by fast electron transfer processes between two semiconductors with different energy levels.

[00195] In addition to providing a high surface-to-volume aspect ratio on the substrate, the 3D-TCOE of various embodiments may assist the charge transport along the length
20 (ie. the longitudinal direction) of the nanorods towards the electrode, thereby lowering the chance of random charge hopping across and trapping at the TiO₂ nanoparticles grain boundaries.

[00196] While the invention has been particularly shown and described with reference to specific embodiments, it should be understood by those skilled in the art that various
25 changes in form and detail may be made therein without departing from the spirit and scope of the invention as defined by the appended claims. The scope of the invention is thus indicated by the appended claims and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced.

CLAIMS

What is claimed is:

- 5 1. A photovoltaic device comprising:
a photoelectrode comprising inorganic nanorods on an inorganic metal oxide
substrate; and
a mesoporous film configured to at least substantially contact the photoelectrode.
- 10 2. The photovoltaic device as claimed in claim 1, wherein the inorganic nanorods
comprise a material selected from the group consisting of SnO₂, SnO, In₂O₃, ZnO, TiO₂,
TiN, Fe₂O₃, CuO, Cu₂O, VO₂, V₂O₅, Nb₂O₅, WO₃, CdO, F-doped SnO₂, Sb-doped SnO₂,
Sn-doped In₂O₃, F-doped In₂O₃, ZnO-doped In₂O₃ (ZIO), Al-doped ZnO (AZO), F-doped
15 ZnO, Ga-doped ZnO (GZO), Nb-doped TiO₂, Nb-doped SrTiO₃, (La, Sr)CoO₃, (La,
Sr)MnO₃, SrRuO₃, CuAlO₂, CuInO₂ and any combination thereof.
3. The photovoltaic device as claimed in claim 1 or 2, wherein the inorganic metal
oxide substrate is selected from the group consisting of glass, quartz, crystal and ceramic.
- 20 4. The photovoltaic device as claimed in any one of claims 1 to 3, wherein the
inorganic metal oxide substrate is coated with at least one layer of coating material,
wherein the coating material is selected from the group consisting of SnO₂, SnO, In₂O₃,
ZnO, TiO₂, TiN, Fe₂O₃, CuO, Cu₂O, VO₂, V₂O₅, Nb₂O₅, WO₃, CdO, F-doped SnO₂, Sb-
doped SnO₂, Sn-doped In₂O₃, F-doped In₂O₃, ZnO-doped In₂O₃ (ZIO), Al-doped ZnO
25 (AZO), F-doped ZnO, Ga-doped ZnO (GZO), Nb-doped TiO₂, Nb-doped SrTiO₃, (La,
Sr)CoO₃, (La, Sr)MnO₃, SrRuO₃, CuAlO₂, CuInO₂ and any combination thereof.
5. The photovoltaic device as claimed in any one of claims 1 to 4, wherein the
mesoporous film comprises a material selected from the group consisting of TiO₂, ZnO,
30 SnO₂, TiN, SrTiO₃ and Nb₂O₅.

6. The photovoltaic device as claimed in any one of claims 1 to 5, wherein the mesoporous film comprises nanostructures comprising a material selected from the group consisting of TiO_2 , ZnO , SnO_2 , SrTiO_3 , Nb_2O_5 and any combination thereof.

5 7. The photovoltaic device as claimed in claim 6, wherein the nanostructures are selected from a group consisting of nanoparticles, nanorods, nanowires, nanotubes, nanosheets, nanospheres and any combination thereof.

8. The photovoltaic device as claimed in any one of claims 1 to 7, wherein at least
10 one portion of the inorganic metal oxide substrate is patterned.

9. The photovoltaic device as claimed in any one of claims 1 to 8, wherein the inorganic metal oxide substrate is transparent.

15 10. The photovoltaic device as claimed in any one of claims 1 to 9, wherein the inorganic metal oxide substrate is conductive or semiconductive.

11. The photovoltaic device as claimed in any one of claims 1 to 10, wherein the inorganic nanorods are at least substantially perpendicular to the inorganic metal oxide
20 substrate.

12. The photovoltaic device as claimed in any one of claims 1 to 11, wherein the inorganic nanorods are doped with a material selected from the group consisting of F, Sb, In, Zn and any combination thereof.

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13. The photovoltaic device as claimed in any one of claims 1 to 12, wherein the inorganic nanorods further comprise a layer of coating on a surface of the inorganic nanorods to form core-sheath nanorods.

14. The photovoltaic device as claimed in claim 13, wherein the layer of coating comprises a material selected from the group consisting of titanium dioxide, zinc oxide, magnesium oxide, aluminium oxide, niobium oxide and strontium titanate.
- 5 15. The photovoltaic device as claimed in any one of claims 1 to 14, wherein the photoelectrode further comprises a nanoparticle, or a nanorod, or a nanowire, or a nanotube, or a nanoflower, or a nanobrush, or a nanocrystal, or a nanocrystalline film, or any combination thereof.
- 10 16. The photovoltaic device as claimed in any one of claims 1 to 15, wherein the photoelectrode further comprises a sensitizer.
17. The photovoltaic device as claimed in claim 16, wherein the sensitizer comprises a dye, or a quantum dot, or a nanocrystal, or a nanocrystalline film, or a photonic crystal,
15 or any combination thereof.
18. The photovoltaic device as claimed in claim 17, wherein the dye is selected from a group consisting of N719, N749, Z907 and N3.
- 20 19. The photovoltaic device as claimed in claim 17, wherein the sensitizer selected from a group consisting of the quantum dot, the nanocrystal, the nanocrystalline film and the photonic crystal comprises a compound selected from the group consisting of ZnS, ZnSe, CdS, CdSe, CdTe, PbS, PbSe, InAs, InP, NiO, SnS, SnS₂, Cu₂O, Si, Se, In₂S₃, AgS₂, Sb₂S₃, CuS₂, CuInS₂, CuIn(S,Se)₂, Cu(In,Ga)Se₂, Cu(In,Ga)(S,Se)₂, Cu₂ZnSnS₄,
25 Cu₂ZnSnSe₄ and Cu₂CdSnSe₄.
20. The photovoltaic device as claimed in any one of claims 1 to 19, further comprising an electrolyte.
- 30 21. The photovoltaic device as claimed in claim 20, wherein the electrolyte comprises a solid, or a semisolid, or a gel, or a liquid.

22. The photovoltaic device as claimed in claim 20 or 21, wherein the electrolyte comprises iodine, or iodide, or copper iodide, or copper thiocyanate or any combination thereof.

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23. The photovoltaic device as claimed in any one of claims 1 to 22, further comprising a counter electrode.

24. The photovoltaic device as claimed in any one of claims 1 to 23, wherein the
10 photovoltaic device is a solar cell.