

COMPOSITE PASTE, METHOD OF MANUFACTURING THEREOF, AND USE THEREOF IN PHOTOELECTRODES

CROSS-REFERENCE TO RELATED APPLICATION

5 [0001] This application claims the benefit of priority of Singapore patent application No. 201303600-9 filed on 9 May 2013, the content of which is incorporated herein by reference in its entirety for all purposes.

TECHNICAL FIELD

10 [0002] The invention relates to a composite paste, method of manufacturing the composite paste, as well as its use in photoelectrodes and photoelectrochemical cells.

BACKGROUND

[0003] Photoelectrochemical (PEC) cell is promising as a cheap and efficient technology
15 for converting light or solar energy into electricity and/or fuel. The cell typically comprises a light-sensitive semiconductor electrode (or photoelectrode) and a metallic counter electrode, both of which are immersed in an electrolyte solution.

[0004] Upon irradiance by light, photons striking a photoactive material of the photoelectrode can release photoelectrons from the material. The photoelectrons or electrons
20 generated on the photoelectrode are transported through the semiconductor bulk to the counter electrode via the external circuit. At the same time, the electrolyte serves as a medium for transporting holes to the counter electrode.

[0005] PEC cells based on this model may generally be classified into two types: regenerative and non-regenerative (photosynthetic) cell. The regenerative cell type is
25 epitomized by the Dye-Sensitized Solar Cell (DSSC), wherein the electrolyte is constantly rejuvenated back to its original state by electrons flowing through the closed-loop system of the cell. The electrolyte rejuvenation is assisted by redox agents in the electrolyte, which donate electrons to the photoelectrode and receive electrons from the counter electrode. In this regard, the loss of electrons in the oxidised photoactive material is replenished by the
30 redox couple in the electrolyte.

[0006] On the other hand, the non-regenerative cell type is typical of direct photolysis cells for water-splitting, wherein the electrolyte (water) is not rejuvenated but cleaved into hydrogen and oxygen.

[0007] Even though PEC cells appear to operate on seemingly sustainable mechanisms of charge generation, separation, and transportation, the technology is hindered by limited operational lifetime of the cells. The short lifetime of PEC cells may largely be attributed to photocorrosion of the photoelectrode in the electrolyte solution. The problem of corrosion has been perpetuated by nature paradox, in that narrow band-gap semiconductors sensitive to visible light are usually chemically unstable, while wide band-gap semiconductors, such as titanium oxide (TiO_2), which are chemically stable, usually possess selective photoresponses that are shifted towards the ultraviolet range.

[0008] Although dye-sensitizers have been used in place of semiconductors as the source of photoelectrons as exemplified in the DSSC to resolve this dilemma, the approach is hampered by the ease in which dye desorbs and dissolves in ionic and organic solutions. The problem of desorption and dissolution arises from weak anchorage of dye molecules on the underlying metal-oxide, and relates to the process by which dye is loaded into the mesopores of the metal-oxide layer, whereby mesoporous metal-oxide layers are immersed into dye solutions such that the dye may be absorbed into the metal-oxide layer.

[0009] Furthermore, conventional methods to fabricate dye-sensitized photoelectrodes may involve formation of metal-oxide nanorods on a transparent conducting substrate using hydrothermal or sol-gel crystal growth processes, which typically requires long processing times and are therefore not process efficient. In addition, high temperature annealing is required to form a conductive mesoporous layer capable of functioning as a photoelectrode, that allows anchoring of photoactive organic dyes and transporting of photoelectrons to the underlying contact electrode.

[0010] In view of the above, there exists a need for an improved method to manufacture photoelectrodes that overcomes or at least alleviates one or more of the above-mentioned problems.

SUMMARY

[0011] In a first aspect, the invention refers to sensitized aqueous composite paste comprising metal oxide particles, photosensitizer, and optionally carbon nanotubes.

[0012] In a second aspect, the invention refers to a method for manufacturing a sensitized aqueous composite paste according to the first aspect. The method comprises

- a) providing metal oxide particles, optionally grinding the metal oxide particles;
- b) mixing the metal oxide particles with an aqueous solution, preferably deionized water, to form a paste-like mixture;
- c) adding a photosensitizer to the paste-like mixture in the dark;
- d) optionally adding carbon nanotubes to the paste-like mixture; and
- e) mixing evenly to form the sensitized aqueous composite paste.

[0013] In a third aspect, the invention refers to a method for manufacturing a photoelectrode. The method comprises

- a) providing a sensitized aqueous composite paste according to the first aspect or a sensitized aqueous composite paste manufactured by a method according to the second aspect;
- b) depositing the sensitized aqueous composite paste on an electrically conducting substrate to form a sensitized aqueous composite paste layer; and
- c) drying the sensitized aqueous composite paste layer to form a photoelectrode.

[0014] In a third aspect, the invention refers to a photoelectrode manufactured by a method according to the second aspect.

[0015] In a fourth aspect, the invention refers to a photochemical cell comprising a photoelectrode manufactured by a method according to the second aspect.

[0016] In a fifth aspect, the invention refers to a method for manufacturing a photochemical cell. The method comprises

- a) providing a photoelectrode manufactured by a method according to the second aspect; and
- b) encapsulating the photoelectrode with an electrolyte and a counter electrode to form the photochemical cell.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] The invention will be better understood with reference to the detailed description when considered in conjunction with the non-limiting examples and the accompanying drawings, in which:

[0018] **FIG. 1** shows a scanning electron microscopy (SEM) image of zinc oxide (ZnO) mesoporous surface fabricated on glass substrate (x 20,000). Scale bar in the figure denotes a length of 1 μm .

[0019] **FIG. 2** is a graph showing photocurrent-voltage characteristics of the photoelectrode with different dye concentrations of 0 ml, 0.125 ml, 0.175 ml, 0.250 ml, and 0.375 ml, without annealing. Y-axis: current density (mA/cm^2); x-axis: voltage (V vs AgCl).

[0020] **FIG. 3** is a graph showing photo-conversion efficiency of photoelectrode samples with different dye concentrations of 0 ml, 0.125 ml, 0.175 ml, 0.250 ml, and 0.375 ml. Y-axis: photoconversion efficiency (%); x-axis: voltage (V vs AgCl).

[0021] **FIG. 4** is a graph comparing the operational lifetime of a photoelectrode sample disclosed herein without carbon nanotubes (CNT) ("ZnO Photoelectrode (without CNT)") as compared to that of the conventional sample ("Conventional ZnO Photoelectrode"). Half-life of the photoelectrode sample disclosed herein is 107 minutes, which compares favorably with the half-life of 7 min for the conventional sample. Y-axis: normalized photocurrent; x-axis: time (min).

[0022] **FIG. 5** is a graph comparing the photocurrent-voltage characteristics of the photoelectrodes fabricated using a method disclosed herein with ("ZnO Photoelectrode (with CNT)") and without CNT ("ZnO Photoelectrode (without CNT)"). The photocurrent-voltage characteristic of the conventional photoelectrode ("Conventional ZnO Photoelectrode") was also acquired and plotted for comparison. Y-axis: photocurrent (mA/cm^2); x-axis: voltage (V vs Ag/AgCl).

[0023] **FIG. 6** is a graph comparing the photoconversion efficiency (PCE) of the photoelectrodes fabricated using a method disclosed herein with ("ZnO Photoelectrode (with CNT)") and without CNT ("ZnO Photoelectrode (without CNT)"). The PCE of the conventional photoelectrode ("ZnO Conventional Photoelectrode") was also computed and plotted for comparison. Y-axis: photoconversion efficiency (%); x-axis: voltage (V vs AgCl).

[0024] **FIG. 7** is a graph comparing the lifetime of the photoelectrode disclosed herein with ("ZnO Photoelectrode (with CNT)") and without CNT ("ZnO Photoelectrode (without CNT)"). The lifetime of the conventional photoelectrode ("Conventional ZnO Photoelectrode") was acquired and plotted for comparison. As indicated, half-life of the photoelectrode sample with CNT is 370 min. Y-axis: normalized photocurrent; x-axis: time (min).

[0025] **FIG. 8** is a graph showing effects of annealing on ZnO. ZnO, which is annealed at 500 °C (“ZnO 500 °C Annealing”), is compared with ZnO with dye coated thereon and annealed at 200 °C using a method disclosed herein (“ZnO + dye 200 °C Annealing”). Y-axis: photocurrent density j_p (mA/cm²); x-axis: voltage (V vs AgCl). As shown in the figure, using a method disclosed herein, anatase phase nano zinc oxide particles with improved photocurrent density may be synthesized without requiring high-temperature heat treatment. This is surprising as a person skilled in the art understands that ZnO requires high temperature annealing to suppress its defect level. By adding dye into the ZnO paste and using only a low temperature annealing, overall light absorption and conversion efficiency may be improved. This translates into a stable photocatalyst product with visible light activity. Dispersion degree of the obtained sol is good, and visible light activity as well as sterilization performance may be greatly improved through dye sensitization and precious metal surface deposition technology.

DETAILED DESCRIPTION

[0026] As disclosed herein, a photosensitizer such as organic dye is mixed with metal oxide particles in aqueous solution to form a sensitized aqueous composite paste. Carbon nanotubes may be added to the composite paste to improve electrical conductivity and mechanical strength of the composite paste. A photoelectrode may be fabricated using the sensitized aqueous composite paste by depositing the composite paste on an electrically conducting substrate, followed by drying of the composite paste. Advantageously, high temperature annealing used in conventional methods are not required, which translates into processing efficiency and cost savings. By mixing the photosensitizer with the metal oxide particles in forming the composite paste, the photosensitizer may be loaded more efficiently in the composite paste, such that the photosensitizer is present at least substantially throughout the photoelectrode thus formed. Furthermore, the process of direct mixing allows addition of the photosensitizer to be effectively controlled. Due to improved contact between the photosensitizer and the metal oxide particles, stronger bonds may be formed between the photosensitizer and the metal oxide particles, such that in use, molecules of the photosensitizer are prevented from desorbing from the photoelectrode into an electrolyte solution in a photochemical cell. This translates in improved durability of the photochemical cell. Advantageously, the synthesis procedure is simple, and raw materials may be obtained

easily. This translates into lower costs of production, and in turn, device costs, rendering the method suitable for mass production in industry.

[0027] With the above in mind, the present invention refers in a first aspect to a sensitized aqueous composite paste.

5 [0028] As used herein, the term "aqueous composite paste" refers to a viscous dispersion of solid particles in an aqueous medium. The viscous dispersion of solid particles may be described as a semi-liquid or a semi-solid, and may be in a slurry-like form. The term "sensitized aqueous composite paste" as used herein refers to an aqueous composite paste that has been modified with a light absorbing material that is capable of fluorescence,
10 otherwise termed herein as a photosensitizer.

[0029] The sensitized aqueous composite paste comprises metal oxide particles. The metal oxide particles comprise oxide of a metal selected from Group 4 to Group 14 of the Periodic Table of Elements. In various embodiments, the metal oxide particles comprise oxide of a metal selected from the group consisting of titanium, zinc, tin, iron, tungsten, and
15 combinations thereof. For example, the metal oxide particles may be selected from the group consisting of ZnO, TiO₂, Fe₂O₃, WO₃, and combinations thereof. In specific embodiments, the metal oxide particles comprise or consist of ZnO.

[0030] The term "particle" as used herein refers to microstructures, nanostructures, and combinations thereof. The term "microstructures" refers to materials with at least one
20 dimension in the micrometer range. The term "nanostructures" refers to materials with at least one dimension in the nanometer range.

[0031] The metal oxide particles may be metal oxide microstructures. For example, the metal oxide microstructures may be microparticles, microrods, and the like. At least one dimension of the metal oxide microstructures may be less than 100 μm , such as a length in
25 the range from about 1 μm to about 100 μm , about 1 μm to about 80 μm , about 1 nm to about 60 μm , about 1 μm to about 40 μm , about 10 μm to about 100 μm , about 10 μm to about 80 μm , about 10 μm to about 60 μm , about 10 μm to about 40 μm , about 20 μm to about 80 μm , or about 30 μm to about 60 μm .

[0032] The metal oxide particles may be metal oxide nanostructures. Examples of
30 nanostructures that may be used include nanoparticles, nanopowder, nanorods, nanowires, nanotubes, nanodiscs, nanoflowers, nanoflakes and nanofilms. In various embodiments, the metal oxide particles are metal oxide nanoparticles.

[0033] At least one dimension of the metal oxide nanostructures is less than 100 nm. For example, at least one dimension of each electrically conductive nanostructure may have a length in the range of about 1 nm to about 100 nm, about 1 nm to about 80 nm, about 1 nm to about 60 nm, about 1 nm to about 40 nm, about 10 nm to about 100 nm, about 10 nm to about 80 nm, about 10 nm to about 60 nm, about 10 nm to about 40 nm, about 20 nm to about 80 nm, or about 30 nm to about 60 nm.

[0034] The sensitized aqueous composite paste includes a photosensitizer. As mentioned above, the term "photosensitizer" as used herein refers to a light absorbing material that is capable of fluorescence, and is typically a photosensitive dye molecule.

[0035] The photosensitizer may be coated on the metal oxide particles, such that at least a portion of a surface of each metal oxide particle is coated with the photosensitizer. In various embodiments, a substantial portion of or an entire portion of a surface of each metal oxide particle is coated with the photosensitizer. In some embodiments, the metal oxide particles are porous such that the photosensitizer is also present within the pores of the metal oxide particles.

[0036] In various embodiments, the photosensitizer is selected from the group consisting of an organic dye, a metal complex dye, polymers capable of producing free electrons under light irradiance, chromophores, and combinations thereof.

[0037] The term "organic dye" as used herein refers to a dye compound that does not contain inorganic components. Examples of an organic dye include, but are not limited to, an azo dye, a quinine dye, a quinone imine dye, a quinacridone dye, a squarylium dye, a cyanine dye, a merocyanine dye, a triphenylmethane dye, a xanthene dye, a porphyrin dye, a perylene dye, an Indigo dye and a naphthalocyanine dye.

[0038] The term "metal complex dye" as used herein refers to a dye compound having coordination complex of a metal ion with one or more electron donors (ligands). Examples of a metal complex dye include, but are not limited to, a complex of Cu, Ni, Fe, Co, V, Sn, Si, Ti, Ge, Cr, Zn, Ru, Mg, Al, Pb, Mn, In, Mo, Y, Zr, Nb, Sb, La, W, Pt, Ta, Ir, Pd, Os, Ga, Tb, Eu, Rb, Bi, Se, As, Sc, Ag, Cd, Hf, Re, Au, Ac, Tc, Te and Rh. In various embodiments, the metal complex dye is an organometallic dye.

[0039] The term "chromophore" as used herein refers to a photoactive compound, and includes any electromagnetic radiation absorbing species such as fluorescent brighteners, ultraviolet absorbers, and infra-red absorbing dyes.

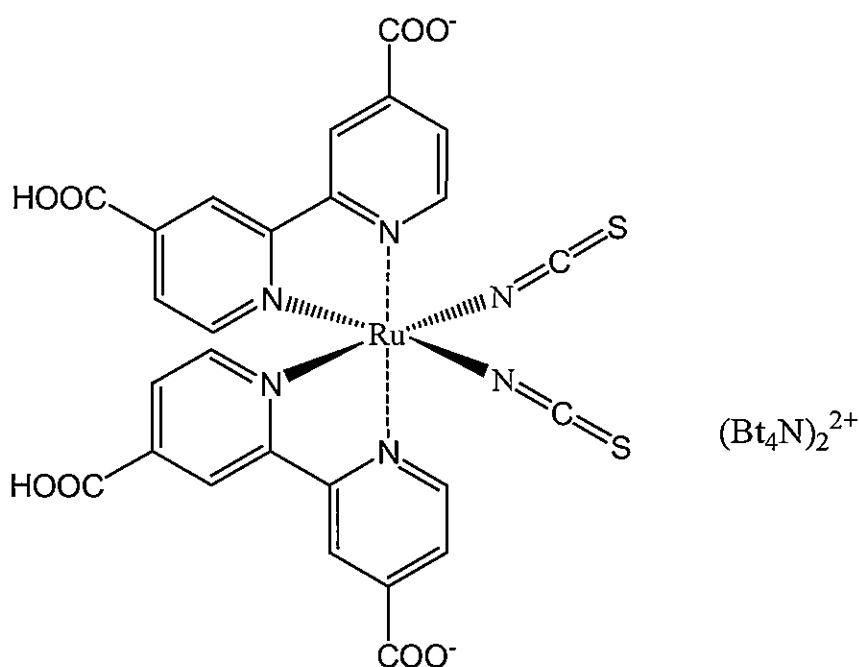
[0040] Further examples of photosensitizer include organometallic chelates, fluorescent and phosphorescent dyes, and conjugated dendrimers. Specific examples of photosensitizer include fluorescent dyes and compounds (organic, inorganic, and composite) such as perylene, rubrene, quinacridone, and their derivatives; BaTiO₃, and LiNbO₃,

- 5 [0041] In various embodiments, the photosensitizer comprises or consists of a metal-complex dye. An example of a metal complex that can be used as a dye is a ruthenium bipyridine or ruthenium tripyridine dye. Two or more different metal-complex dyes may be used as the photosensitizer. For example, the photosensitizer may include a ruthenium-, an osmium- or an iron-complex, or a combination of two or three transition metals in a
10 supramolecular complex.

[0042] In various embodiments, the metal-complex dye is a ruthenium-based dye.

[0043] In specific embodiments, the ruthenium-based dye has formula

[0044]



- 15 [0045] The sensitized aqueous composite paste optionally comprises carbon nanotubes. The carbon nanotubes may form a highly efficient electron transport network in the sensitized aqueous composite paste, and may accordingly be used to improve electron transfer efficiency of photoelectrodes formed using the sensitized aqueous composite paste. Further, the carbon nanotubes may enhance mechanical strength and stability of the composite paste.

- 20 [0046] A carbon nanotube refers generally to a cylinder of rolled up graphitic sheets, and may exist in different forms, such as single-walled carbon nanotubes (SWNT), double-walled

carbon nanotubes (DWNT), multi-walled carbon nanotubes (MWNT), or modified multi-walled carbon nanotubes.

[0047] Single-walled carbon nanotubes refer generally to seamless cylinders formed from one graphite layer. For example, carbon nanotubes may be described as a graphite plane (so called graphene) sheet rolled into a hollow cylindrical shape so that the structure is one-dimensional with axial symmetry, and in general exhibiting a spiral conformation, called chirality. A single-wall nanotube may be defined by a cylindrical sheet with a diameter of about 0.7 nm to about 20 nm, such as about 1 nm to about 20 nm.

[0048] Double-walled carbon nanotubes consist of two layers of graphite sheets rolled in on to form a tube shape. The two layers of graphite sheets may form a concentric cylinder. The nanotubes are considered as a cross between SWNT and MWNT, as they may have the electronic properties of the SWNT and the mechanical strength of MWNT.

[0049] Multi-walled carbon nanotubes consist of multiple layers of graphite rolled in on to form a tube shape. The nanotubes may also exist in forms in which they have hydrophilic groups such as hydroxyl group, pyrenes, esters, thiols, amines, a carboxyl group and mixtures thereof on their surface.

[0050] Single-, double- and multi-walled carbon nanotubes may equally be used in a composite paste disclosed herein. In various embodiments, the carbon nanotubes are single-walled carbon nanotubes. The carbon nanotubes may be of any desired length, such as in the range from about 0.1 nm to about 10 μm , such as about 1 nm to about 5 μm , or 10 nm to about 1 μm . In one embodiment, the carbon nanotubes may be at least 1 μm or at least 2 μm , or between about 0.5 μm and about 1.5 μm , or between about 1 μm and about 5 μm .

[0051] Depending on the intended application, the composite paste may comprise differing amounts of metal oxide, photosensitizer, carbon nanotubes, and water. Weight percentage of photosensitizer may be based on the intended application, and may vary depending on conductivity requirements and transparency requirements. Presence and/or amount of carbon nanotubes may be used to tune the working current. When carbon nanotubes are present, weight percentage of the carbon nanotubes may be based upon effects of improving the working condition of the photoelectrode. Weight percentage (wt%) is calculated based on total weight of the composite paste.

[0052] In a further aspect, a method for manufacturing a sensitized aqueous composite paste is provided. The method includes providing metal oxide particles. Examples of metal oxide particles that may be used have already been discussed above. In various embodiments, the metal oxide particles are metal oxide nanoparticles.

5 [0053] In various embodiments, providing metal oxide particles includes grinding the metal oxide particles. Advantageously, by grinding the metal oxide particles, size and surface roughness of the metal oxide particles, for example, may be adjusted to achieve or to improve surface mechanical activation effects of the metal oxide particles. This may also result in promotion of interfacial reaction between the metal oxide particles with other species present
10 in the composite paste. In particular, binding of the photosensitizer with the metal oxide particles may be improved.

[0054] The method includes mixing the metal oxide particles with an aqueous solution to form a paste-like mixture. In various embodiments, the aqueous solution comprises or consists of water. In preferred embodiments, the aqueous solution comprises or consists of
15 deionized water.

[0055] A photosensitizer is added to the paste-like mixture in the dark. Suitable photosensitizers have already been discussed above. In various embodiments, the photosensitizer is added in a drop-wise manner to the paste-like mixture. By adding the photosensitizer in a drop-wise manner to the paste-like mixture, quantity of the
20 photosensitizer added may be better controlled, as well as to facilitate uniform mixing of the photosensitizer with the other components in paste-like mixture.

[0056] Advantageously, addition of a photosensitizer such as organic dyes to the composite paste allows tailoring of the optical, thermal, mechanical, and/or dielectric properties of the composite paste, while maintaining stability, ease of processing, and flexible
25 chemistry provided by the organic components of the composition.

[0057] Carbon nanotubes are optionally added to the paste-like mixture. The carbon nanotubes may be added to the paste-like mixture before, after, or at the time of adding the photosensitizer. In various embodiments, the carbon nanotubes are added to the paste-like mixture after addition of the photosensitizer.

30 [0058] Presence of carbon nanotubes in the composite paste translates into formation of highly conductive paths for transporting photoelectrons. Furthermore, the carbon nanotubes also provide additional structural support for the sensitized aqueous composite paste to

reinforce bonds between the photosensitizer and the metal oxide, as well as adhesion of the sensitized aqueous composite paste to a surface onto which the composite paste is applied.

[0059] The method includes mixing evenly the photosensitizer, and optionally the carbon nanotubes, with the paste-like mixture to form the sensitized aqueous composite paste. The mixing may be carried out using any suitable method, such as stirring, shaking, blending, or vortexing. The mixing may be carried out such that the photosensitizer, the metal oxide particles, and when present, the carbon nanotubes, may be mixed in such a way that the composite paste is at least substantially homogeneous.

[0060] In a third aspect, a method for manufacturing a photoelectrode is provided. The method includes providing a sensitized aqueous composite paste according to the first aspect or a sensitized aqueous composite paste manufactured by a method according to the second aspect, and depositing the sensitized aqueous composite paste on an electrically conducting substrate to form a sensitized aqueous composite paste layer.

[0061] By mixing the photosensitizer with the metal oxide particles in forming the composite paste, the photosensitizer may be loaded more efficiently in the composite paste, such that the photosensitizer is present at least substantially throughout the photoelectrode. As mentioned above, even though an organic dye may be loaded on a mesoporous metal oxide layer by immersing the mesoporous metal oxide layer into a solution containing the organic dye in the dark for a length of time, the loading takes place via a passive diffusion mechanism, and the dye molecules are not able to travel deep within the interiors of the mesoporous layer. This results in an inefficient loading of the dye molecules on the metal oxide layer. Furthermore, infusion of the dye molecules from the solution into the mesoporous metal oxide layer may be blocked due to attachment of the dye molecules on the outer surface of the metal oxide layer. As a result, dye coverage on the metal oxide layer is often incomplete to the extent that the efficiency and durability of a photoelectrode are compromised. Since the dye molecules are not locked deeply within the mesopores, the dye molecules are only attached weakly on the outer surface of the metal-oxide layer and anchorage on the metal oxide is weak. The problem is accentuated by reduction in formation constant between the metal oxides and certain organic dyes in oxidized state during photo-excitation. A reduction in formation constant under electromagnetic irradiance further weakens the dye-metal oxide bond to accelerate desorption and dissolution, the process of which is known as photocorrosion.

[0062] The composite paste may be deposited by any suitable thin film formation methods, such as roller coating, air knife coating, blade coating, wire bar coating, slide hopper coating, extrusion, curtain coating, spin coating, spray coating, offset coating, gravure printing, screen printing, wet printing, or a combination of the aforementioned methods.

5 [0063] In various embodiments, the composite paste is deposited on the electrically conducting substrate by blade coating or screen printing. Blade printing, otherwise termed as “Doctor’s blade technique”, as well as screen printing, allows formation of the sensitized aqueous composite paste layer to be carried out in a rapid manner and at low costs, rendering the method highly suitable and adaptable for industrial application. This compares favorably
10 to state of the art hydrothermal and sol-gel techniques which involve crystal growth processes and are accordingly, slower and more cumbersome to be carried out on large surfaces.

[0064] The metal oxide particles present in the composite paste may form a network structure, and maintain stability and adhesion of the photoelectrode thus formed to the electrically conducting substrate. At the same time, the metal oxide particles, each having at
15 least a portion of a surface coated with a photosensitizer, may hold the photosensitizer in place such that lifetime of the photoelectrode is maintained for various applications, such as in photocatalysis.

[0065] Method of the third aspect includes drying the sensitized aqueous composite paste layer to form a photoelectrode. In various embodiments, drying the sensitized aqueous
20 composite paste layer is carried out at ambient conditions. For example, the sensitized aqueous composite paste layer may be dried in air at atmospheric pressure, and at ambient temperature in the range of about 15 °C to 40 °C.

[0066] Due to presence of the photosensitizer on the metal oxide particles, which are susceptible to damage at high temperatures, the substrate is not subjected to high temperature
25 annealing. Advantageously, this translates into processing efficiency and cost savings. The process to manufacture photoelectrode may be carried out at ambient or low temperatures. This distinguishes between methods involving high temperature annealing performed on the mesoporous metal oxide layer prior to dye-loading, so as to reduce defects in the crystalline nanorods to improve electron transfer efficiency. As disclosed herein, electron transfer
30 efficiency may be improved with use of carbon nanotubes. Therefore, carbon nanotubes may optionally be included into the composite paste to enhance electron transfer efficiency.

[0067] Even though annealing of the composite paste layer is not required, the composite paste may, in some embodiments, be annealed at a low temperature after drying. In various embodiments, anatase ZnO is used in the aqueous composite paste. In this way, high temperature processing requirements of forming anatase ZnO on-site are not necessary, since
5 anatase ZnO in the composite paste is generated off-site, and not formed while ZnO is present in the composite paste. In so doing, a much lower temperature is used for processing, thereby translating into processing efficiency as well as cost savings.

[0068] Furthermore, annealing of the composite paste layer may be carried out at a suitable temperature that does not significantly degrade the photosensitizer, such as organic
10 dyes, while being able to reduce at least some defects in the metal oxide particles. For example, annealing the composite paste layer may be carried out at a temperature that is less than 200 °C, such as a temperature in the range of about 100 °C to about 200 °C, about 150 °C to about 200 °C, or about 180 °C to about 200 °C.

[0069] The photoelectrode may be mesoporous. According to IUPAC definition,
15 mesopores have a size of between about 2 nm to about 50 nm. Due to the porous structure, the photoelectrode has a high surface area. Advantageously, this translates into improved anchoring ground for the photosensitizer molecules, as well as an enlarged photoactive surface and dye-electrolyte interface for a faster redox reaction.

[0070] The invention relates in further aspects to a photoelectrode manufactured by a
20 method according to the third aspect, and a photochemical cell comprising a photoelectrode manufactured by a method according to the third aspect.

[0071] The term “photoelectrode” as used herein refers generally to an electrode that is used in a photoelectrochemical cell for conversion of electromagnetic energy to another energy form or energy source, or to drive or facilitate a chemical reaction.

25 [0072] The photoelectrode may comprise metal oxide particles and a photosensitizer, and may be mesoporous. Carbon nanotubes may optionally be present. Examples of metal oxide particles and photosensitizers that may be used have already been mentioned above.

[0073] A method for manufacturing a photochemical cell is also provided. The method comprises providing a photoelectrode manufactured by a method according to the second
30 aspect, and encapsulating the photoelectrode with an electrolyte and a counter electrode to form the photochemical cell.

[0074] A photoelectrochemical cell that includes a photoelectrode according to the embodiments disclosed herein may be any photoelectrochemical cell, such as a photoelectrolytic cell, a photocatalytic cell, a light emitting cell or a dye-sensitized solar cell. In a photocatalytic cell, light serves in accelerating the rate of a reaction, whereas in a photoelectrolytic cell a reaction is driven by irradiation, for example light, in the contra-thermodynamic direction.

[0075] A photoelectrochemical cell, and in particular a photovoltaic cell, is often called a solar cell since the typical source of electromagnetic energy used is sunlight. Nevertheless, the use of visible light, corresponding to a wavelength range of about 400 nanometers to about 700 nanometers, is merely one embodiment of a use of a photoelectrode disclosed herein. Other application areas include use at electromagnetic radiation of any wavelength, including a distinct wavelength, a set of distinct wavelengths or any region of the electromagnetic spectrum. A further example of a region of the electromagnetic spectrum is ultraviolet light, corresponding to a wavelength range of about 30 nanometers to about 400 nanometers.

[0076] Besides the afore-mentioned, a photoelectrode comprising the sensitized aqueous composite paste may be applied to solar conversion reactions such as water splitting. Accordingly, a photoelectrode disclosed herein may for example be included in a water splitting photoelectrochemical cell.

[0077] Hereinafter, the present invention will be described more fully with reference to the accompanying drawings, in which exemplary embodiments of the invention are shown. This invention may, however, be embodied in many different forms and should not be construed as limited to the exemplary embodiments set forth herein. Rather, these embodiments are provided so that this disclosure will be thorough and complete, and will fully convey the scope of the invention to those skilled in the art. In the drawings, lengths and sizes of layers and regions may be exaggerated for clarity.

[0078] As used herein, the term "and/or" includes any and all combinations of one or more of the associated listed items. The terminology used herein is for the purpose of describing particular embodiments only and is not intended to be limiting of the invention. As used herein, the singular forms "a", "an" and "the" are intended to include the plural forms as well, unless the context clearly indicates otherwise. It will be further understood that the terms "comprises" and/or "comprising," when used in this specification, specify the presence of

stated features, integers, steps, operations, elements, and/or components, but do not preclude the presence or addition of one or more other features, integers, steps, operations, elements, components, and/or groups thereof.

[0079] Unless otherwise defined, all terms (including technical and scientific terms) used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. It will be further understood that terms, such as those defined in commonly used dictionaries, should be interpreted as having a meaning that is consistent with their meaning in the context of the relevant art and will not be interpreted in an idealized or overly formal sense unless expressly so defined herein.

[0080] The invention illustratively described herein may suitably be practiced in the absence of any element or elements, limitation or limitations, not specifically disclosed herein. Thus, for example, the terms "comprising", "including", "containing", etc. shall be read expansively and without limitation. Additionally, the terms and expressions employed herein have been used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed. Thus, it should be understood that although the present invention has been specifically disclosed by preferred embodiments and optional features, modification and variation of the inventions embodied therein herein disclosed may be resorted to by those skilled in the art, and that such modifications and variations are considered to be within the scope of this invention.

[0081] The invention has been described broadly and generically herein. Each of the narrower species and subgeneric groupings falling within the generic disclosure also form part of the invention. This includes the generic description of the invention with a proviso or negative limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically recited herein.

[0082] Other embodiments are within the following claims and non-limiting examples. In addition, where features or aspects of the invention are described in terms of Markush groups, those skilled in the art will recognize that the invention is also thereby described in terms of any individual member or subgroup of members of the Markush group.

EXPERIMENTAL SECTION

[0083] Method to fabricate photoelectrode that targets to address problem of dye desorption and dissolution is provided. In embodiments disclosed herein, dye is mixed directly into the metal oxide particles in aqueous solution to form a sensitized aqueous composite paste for making the mesoporous layer of the photoelectrode. This technique locks the dye molecules strongly into the mesoporous layer, and prevents them from desorbing into the electrolyte solution. Compared to methods using conventional absorption mechanism, the dye is less easily desorbed into the electrolyte solution. The process of direct mixing allows the addition of dye to be effectively controlled. The process to fabricate photoelectrode is also faster than conventional techniques using absorption.

[0084] Use of carbon nanotubes to form a highly efficient electron transport network in the photoactive bulk layer is also disclosed herein. By direct addition of carbon nanotube (CNT) into the composite paste comprising both the dye and aqueous metal oxide, electron transport efficiency and mechanical stability of the dye-sensitized layer may be enhanced. Furthermore, presence of CNT eliminates the need for high temperature annealing to create a layer of high quality crystalline metal-oxide for electron transport, as the CNT provides for efficient electron transport within the mesoporous layer. The removal of high temperature annealing reduces the cost of production.

[0085] In various embodiments, a composite paste comprising metal-oxides, organic dye, and carbon nanotubes capable of generating electrons under solar excitation and transporting these electrons efficiently within the conductive bulk of the paste is provided. The composite paste exhibits a significantly higher resistance against desorption and dissolution of dye in ionic and organic solution so as to mitigate problem of photocorrosion faced by the conventional dye sensitized photoelectrodes.

[0086] **Example 1: General procedure**

[0087] The metal-oxide comprised in the paste may be titanium oxide (TiO_2), zinc oxide (ZnO), tin oxide (SnO_2), or the like, and is responsible for anchoring the photoactive dye molecules, as well as transporting the photoelectrons to the contact layer. In the process of fabricating the paste, metal oxide in the form of nanoparticle powder is first grinded and mixed with de-ionized water evenly to form a paste-like mixture. The organic dye is then added in a drop-wise manner, and stirred evenly with the metal-oxide paste in the dark.

[0088] As disclosed herein, the organic dye may include ruthenium compounds, polymers or any other chromophores which is capable of producing free electrons under light irradiance. Small amount of carbon nanotubes (CNT) may also be added and mixed evenly with the dye-sensitized metal-oxide paste. The CNT serves to increase the electrical conductivity of the paste, and facilitate electron transport within the composite bulk to the contact electrode. At the same time, the CNT provides an additional physical support for reinforcing anchorage of dye on the metal-oxide, as well as that of the composite bulk on the substrate.

[0089] In fabricating the photoelectrode, the composite paste is dispensed evenly onto the transparent conducting oxide substrate (for example, FTO glass) and the excess paste is scraped off the surface with a flat knife, the technique of which is known as the Doctor's blade. Other fabrication techniques, such as screen printing is also highly favorited. The coated substrate is then air-dried in the dark at room temperature, and may be further annealed under low temperature before it is encapsulated with the electrolyte and counter electrode to complete the PEC cell.

[0090] **Example 2: Characterisation**

[0091] Photoelectrode prototypes have been developed, and characterized in experiments for proof of concept.

[0092] In the first part of development, the dye was mixed with the ZnO paste, the ratio of the dye and ZnO has been optimized to achieve higher efficiency of the system; in the second part of the development, the optimized dye and ZnO has been mixed with a small amount of CNT. The concentration of CNT has been optimized as well.

[0093] **Example 3: Surface Morphology**

[0094] Ideally, the surface of the photoelectrode should be highly mesoporous for three reasons: 1) to provide a strong anchoring ground for the dye molecules, 2) to enlarge photoactive surface and, 3) to enlarge dye-electrolyte interface for a faster redox reaction.

[0095] In order to investigate the surface morphology presented by the composite paste disclosed herein, a photoelectrode sample was fabricated.

[0096] In fabricating the sample, ZnO nanoparticles of 30mg was ground into fine powder and mixed evenly with 0.25 ml of deionized water by stirring to form ZnO paste. The resulting paste was dispensed onto a glass substrate using a flat knife, and the excess paste

was scrapped off (Doctor's blade technique). The resulting layer was air-dried and examined with Scanning Electron Microscope (SEM) (image shown in **FIG. 1**).

[0097] It could be observed from the SEM image that the surface presented by the ZnO layer was highly mesoporous and randomly orientated. Such morphology helped to lock the dye molecules into the mesopores and prevent them from desorbing into the electrolyte solution. The high mesoporosity also increased the area for solar exposure while enlarging the interactive surface between the dye and redox couples in the electrolyte.

[0098] **Example 4: Efficiency Analysis (without CNT)**

[0099] In order to investigate the efficiency of the photoelectrode fabricated with the invention, the same paste was formed by mixing 30 mg of grinded ZnO nanoparticle powder in 0.25 ml of deionized water.

[00100] The paste was then sensitized with N719 dye of different quantities: 0, 0.125, 0.175, 0.250 and 0.375 ml respectively. In the process of sensitizing, the dye was added in a drop-wise manner, while the paste was constantly stirred to ensure homogeneous mixture of the composite. The paste containing different dye quantities were then dispensed on the FTO glass substrate with doctor's blade technique and air-dried in the dark. The photoelectrodes were then immersed into 0.1 M/L Na_2SO_4 electrolytic solution together with a Pt counter electrode and Ag/AgCl reference electrode.

[00101] The setup, thus, formed a typical three-arm electrolytic system for water-splitting. In characterizing the system, the photoelectrode was subjected to white light of 100 mW/cm^2 . The potential of the photoelectrode with respect to the reference electrode was controlled by the potentiostat (263A, Princeton Applied Research) while the photocurrent was acquired on the source-meter.

[00102] The photocurrent-voltage characteristics of the photoelectrode samples were plotted in **FIG. 2**, and it was observed that the photocurrent generally increased with the dye quantity until the maximum current was achieved at the dye quantity of 0.250 ml. Further dye-loading beyond this optimum point reduced the photocurrent, and the phenomenon was attributed to effect of excess dye which was not attached directly to the ZnO. The excess dye shielded the underlying dye molecules directly anchored onto the metal oxides, and these attached dyes were the main contributors to the injected photocurrent. The shielding effects from the excess dye reduced the effective exposure of the photocurrent contributing dye to solar irradiance such that the photoconversion efficiency was compromised. The results in

FIG. 2 serve to confirm that the photocurrents were contributed largely by the dye rather than the metal-oxide, as observed from the progressive improvement in the photocurrent in the increasing presence of dye. There was also an optimum dye concentration which could be easily calibrated by the dye addition process.

[00103] Based on the I-V curve, the photo-conversion efficiency (PCE) was computed and plotted in **FIG. 3**. It was observed that the PCE achieved by the invention was comparable to reported results using semiconductor photoelectrodes.

[00104] **Example 5: Operational Lifetime (without CNT)**

[00105] To demonstrate the improvement in the operational lifetime provided by the invention, ZnO-based photoelectrode (Sample 2) were prepared according to the steps stipulated by the invention with the dye quantity of 0.125 ml. Another ZnO-based photoelectrode sample (Sample 1) was prepared using the conventional technique for comparison against Sample 2. In preparing Sample 1, ZnO seed layer was first grown on cleaned FTO glass substrate. This is done by dripping ZnO nanoparticles solution on the FTO surface and subsequently air-drying the substrate. The seeded substrates were then immersed in zinc acetate solution added with ammonia over 16 hrs at a constant temperature of 70 °C. The precipitate formed on the seeded layer comprised of ZnO nanorods of a few micrometers in length. The substrate was then annealed in a furnace at 450 °C for 30 minute. After annealing, the substrate was immersed into ruthenium dye solvent (N719) and placed into the oven at 50 °C for 20 min. The resulting photoelectrode was then characterized in the same three-arm electrolytic system comprising of 0.1 M/L Na₂SO₄ electrolytic solution.

[00106] The photocurrent at zero voltage potential versus Ag/AgCl electrode of the two samples were acquired, normalized with their initial values and plotted against the operational time as shown in **FIG. 4**. It was observed that the Sample 2 of the invention possessed a vastly improved lifetime as compared to Sample 1 using the conventional technique. In Sample 1, the photocurrent reduced rapidly to 50 % after operating for 7 min. In Sample 2, on the other hand, the photocurrent reduced at a much slower rate such that the half-life hits 107 min. The improvement in the lifetime was likely due to the better anchorage of dye provided by the invention wherein the dye was directly mixed into the ZnO paste. As a result, the dye molecules were loaded more extensively and deeply into the mesoporous ZnO film. This gave rise to lesser desorption and dissolution of dye when the photoelectrode was operated in the electrolyte medium.

[00107] **Example 6: Effects of CNT**

[00108] To investigate the enhancement role of the carbon nanotubes (CNT), the nanoparticle was incorporated into the dye-ZnO composite paste of the invention. The ZnO paste was first prepared by mixing and stirring 30 mg of grinded ZnO nanoparticle powder in 0.25 ml of deionized water. 0.125 ml of N719 dye was then dripped onto the ZnO paste and the mixture was again stirred. CNT solution was also prepared by mixing 13 mg of CNT into 16 ml of 2 methoxyethanol and 8 ml of ethylene glycol, and the mixture sonicated for 2 hours. 15 ml of the CNT solution was dispensed onto the sensitized ZnO paste and stirred continuously. The CNT-added paste was then dispensed onto the FTO glass substrate by Doctor's blade technique. After which, the coated substrate was then air-dried in the dark. The photoelectrodes formed were then characterized in the same three-arm electrolytic system comprising of the photoelectrode, Ag/AgCl reference electrode and Pt counter electrode in 0.1 M/L Na₂SO₄ electrolytic solution. The photoelectrode was exposed to white light of 100 mW/cm², while the I-V, photoconversion efficiency and lifetime curves were being extracted as shown in **FIG. 5**, **FIG. 6**, and **FIG. 7** respectively. Another photoelectrode sample fabricated using the conventional method similar to Sample 1 was also characterized in the same system for comparison.

[00109] It was observed from **FIG. 5** that the photoelectrode prepared according to the invention with CNT produced a significantly higher photocurrent than the non-CNT counterpart. Both photoelectrodes, with and without CNT, disclosed herein were also significantly higher than the conventional photoelectrode. In the conventional photoelectrode, the measured photocurrent was the lowest due to rapid dissolution of dye into the electrolyte. At the point of measurement, a significant quantity of dye had already been desorbed into the electrolyte. In the photoelectrode without CNT disclosed herein, the photocurrent was higher than that of the conventional photoelectrode as the dye molecules had been effectively retained in the mesoporous layer at the time of measurement. With CNT, photoelectrode disclosed herein produced an improved photocurrent which was approximately 50% higher than the non-CNT counterpart. This was due to the presence of CNT providing for a highly conductive network for facilitating electron transport within the mesoporous bulk layer. The improvement in the photocurrent is translated into a higher photoconversion efficiency, as shown in **FIG. 6**.

[00110] As observed from **FIG. 7**, the CNT-enhanced photoelectrode disclosed herein produced a significantly longer lifetime as compared to the non-CNT counterpart. The improved lifetime of the CNT enhanced photoelectrode stretched to the 370 min, more than 3 times of the non-CNT counterpart. This was attributed to the additional support structure provided by the CNT, which reinforced the anchorage of dye on the ZnO as well as the adhesion of the ZnO on the substrate.

[00111] A method for producing photoelectrodes with improved lifetime and efficiency is provided. The resulting photoelectrode is highly suitable for use in an electrolytic system where electrode corrosion is a critical concern. Method disclosed herein also allows the photoelectrode to be mass produced in a faster and cheaper process than the conventional techniques.

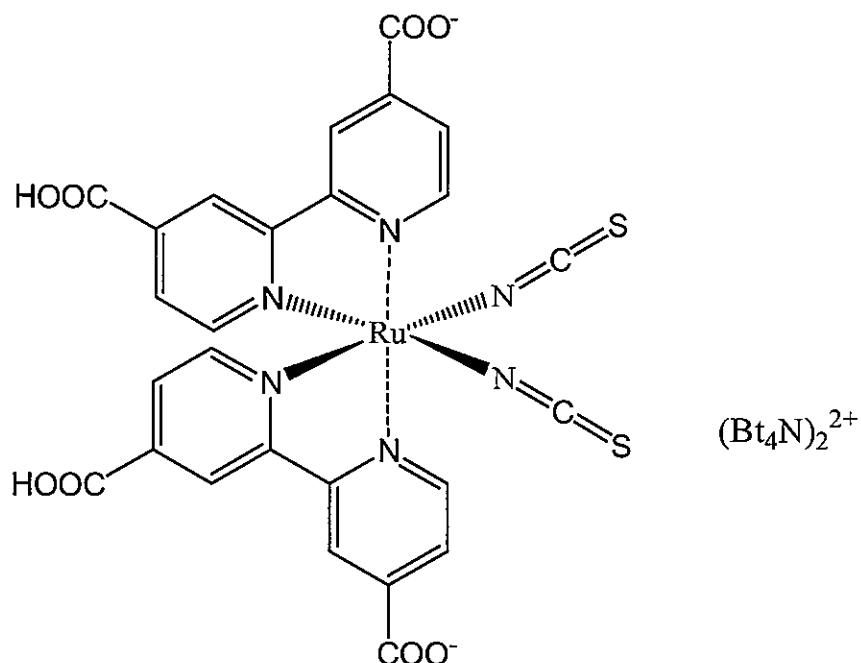
[00112] This is realized with the techniques disclosed herein for dye-sensitizing the mesoporous metal-oxide, fabricating the mesoporous metal oxide layer on the substrate and adding CNT for photocurrent and lifetime enhancement. These new techniques can replace the cumbersome steps in the conventional process involving crystal growth, annealing and absorption of dye so as to render photoelectrochemical cell commercially viable.

[00113] While the present invention has been particularly shown and described with reference to exemplary embodiments thereof, it will be understood by those of ordinary skill in the art that various changes in form and details may be made therein without departing from the spirit and scope of the present invention as defined by the following claims.

CLAIMS

1. Sensitized aqueous composite paste comprising metal oxide particles, photosensitizer, and optionally carbon nanotubes.
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2. Sensitized aqueous composite paste according to claim 1, wherein the metal oxide particles comprise oxide of a metal selected from Group 4 to Group 14 of the Periodic Table of Elements.
- 10 3. Sensitized aqueous composite paste according to claim 1 or 2, wherein the metal oxide particles comprise oxide of a metal selected from the group consisting of titanium, zinc, tin, iron, tungsten, and combinations thereof.
- 15 4. Sensitized aqueous composite paste according to any one of claims 1 to 3, wherein the metal oxide particles are selected from the group consisting of ZnO, TiO₂, Fe₂O₃, WO₃, and combinations thereof.
- 20 5. Sensitized aqueous composite paste according to any one of claims 1 to 4, wherein the metal oxide particles comprise or consist of ZnO.
- 25 6. Sensitized aqueous composite paste according to any one of claims 1 to 5, wherein the metal oxide particles are metal oxide nanoparticles.
7. Sensitized aqueous composite paste according to any one of claims 1 to 6, wherein the photosensitizer is selected from the group consisting of an organic dye, a metal-complex dye, polymers capable of producing free electrons under light irradiance, chromophores, and combinations thereof.
- 30 8. Sensitized aqueous composite paste according to claim 7, wherein the metal-complex dye is a ruthenium-based dye.

9. Sensitized aqueous composite paste according to claim 8, wherein the ruthenium-based dye has formula



- 5 10. Method for manufacturing a sensitized aqueous composite paste according to any one of claims 1 to 9, the method comprising
- a) providing metal oxide particles, optionally grinding the metal oxide particles;
 - b) mixing the metal oxide particles with an aqueous solution, preferably deionized water, to form a paste-like mixture;
 - 10 c) adding a photosensitizer to the paste-like mixture in the dark;
 - d) optionally adding carbon nanotubes to the paste-like mixture; and
 - e) mixing evenly to form the sensitized aqueous composite paste.
11. Method according to claim 10, wherein the photosensitizer is added in a drop-wise
15 manner to the paste-like mixture.
12. Method according to claim 10 or 11, wherein the carbon nanotubes is added to the paste-like mixture after the photosensitizer has been added.
- 20 13. Method for manufacturing a photoelectrode, the method comprising

- a) providing a sensitized aqueous composite paste according to any one of claims 1 to 9 or a sensitized aqueous composite paste manufactured by a method according to any one of claims 10 to 12;
 - b) depositing the sensitized aqueous composite paste on an electrically
5 conducting substrate to form a sensitized aqueous composite paste layer; and
 - c) drying the sensitized aqueous composite paste layer to form a photoelectrode.
14. Method according to claim 13, wherein the photoelectrode is mesoporous.
 - 10 15. Method according to claim 13 or 14, wherein drying the sensitized aqueous composite paste layer is carried out at ambient conditions.
 16. Method according to any one of claims 13 to 15, further comprising annealing the composite paste layer at a temperature that is less than about 200 °C after drying.
 - 15 17. Photoelectrode manufactured by a method according to any one of claims 13 to 16.
 18. Photochemical cell comprising a photoelectrode manufactured by a method according to any one of claims 13 to 16.
 - 20 19. Method for manufacturing a photochemical cell, the method comprising
 - a) providing a photoelectrode manufactured by a method according to any one of claims 13 to 16, and
 - b) encapsulating the photoelectrode with an electrolyte and a counter electrode to
25 form the photochemical cell.