

A Photocatalyst

Technical Field

The present invention generally relates to a
5 photocatalyst. The present invention also relates to a
method of producing the photocatalyst, a photocatalytic
water treatment system and a method of treating water.

Background

10 Several known technologies have been used to remove
organic contaminants present in wastewater.

Non-destructive processes, such as activated carbon
adsorption processes and air stripping, can be used to
remove contaminants in wastewater. However, activated
15 carbon adsorption processes generate hazardous solid
wastes which must be disposed off safely. Furthermore, air
stripping converts a liquid contaminant in wastewater into
a gaseous pollutant.

On the other hand, chlorination uses a strong oxidant
20 such as chlorine gas to remove contaminants in wastewater
and is thus termed as a "destructive process". However,
due to the formation of toxic, carcinogenic
trihalomethanes (THMs) and other by-products, chlorination
may be hazardous to the health of humans and also to the
25 environment.

Other destructive processes include advanced
oxidation processes (AOPs) which typically involve the
treatment of wastewater with ultraviolet (UV) light and/or
chemical oxidation. AOPs may fully oxidize the target
30 organic contaminants in wastewater to relatively innocuous
end products such as carbon dioxide, water and inorganic
salts. As AOPs do not leave any residual contaminants that
require an additional treatment, these processes are well
suited for the destruction of organic contaminants. AOPs

use compounds such as O_3 , H_2O_2 , TiO_2 and ZnO to generate hydroxyl radicals ($HO\cdot$) during the oxidation process. The rapid, non-selective reactivity of $HO\cdot$ radicals allows them to act as initiators of the oxidative degradation of organic contaminants. However, the efficiency of AOPs depends on factors including the structure of the contaminants, which in turn determines the mechanism of destruction and formation of intermediates, the pH of the wastewater, the design of the photoreactor and the presence of $HO\cdot$ scavengers such as HCO_3^- . Furthermore, AOPs require long residence times to destroy some organic contaminants.

For AOPs that use O_3 and/or H_2O_2 , the UV photolysis of O_3 and/or H_2O_2 generates the $HO\cdot$ radicals. However, such AOPs cannot utilize solar energy as the source of UV light as the required UV energy for the photocatalysis of O_3 and/or H_2O_2 is not available in the solar spectrum. Furthermore, while the photocatalysis of H_2O_2 exhibits relatively high efficiency of mineralizing organic contaminants, it exhibits slow reaction kinetics. On the other hand, while the photocatalysis of O_3 exhibits lower efficiency of mineralizing organic contaminants, it exhibits relatively faster reaction kinetics. Furthermore, in order to oxidize the organic contaminants efficiently, O_3 has to be bubbled through the wastewater at a feed rate sufficient enough to result in effective generation and mass transfer. Such a system thus requires a large amount of energy.

For AOPs that use TiO_2 or ZnO as a photocatalyst, the photocatalytic oxidation of the TiO_2 or ZnO semiconductor absorbs UV light and generates $HO\cdot$ radicals mainly from the adsorbed water or OH^- ions. However, the overall oxidation is mainly limited by O_2 reduction at cathodic sites on the semiconductor surface. Other factors

affecting the degradation efficiency are the semiconductor surface area, catalytic properties of the semiconductor and the electron/hole recombination.

There is a known method of entrapping or immobilizing
5 TiO_2 nanoparticles in a concentric mesh and wrapping the
mesh coaxially to an emitting light source in a
photocatalytic reactor. However, TiO_2 in the desired
crystalline anatase form may not be achieved as there are
several layers of the mesh that cover the emitting source
10 and thus, a very limited fraction of the mesh may be
irradiated. Furthermore, there is a lack of intimate,
controlled and uniform contact of the wastewater with the
mesh as the wastewater stream may by-pass the mesh. Thus,
a low generation of electron/hole pairs can be expected
15 with such technology.

A number of methods have been proposed for the use of
 ZnO as a photocatalyst, including suspending ZnO
nanoparticles in wastewater. However, with the suspension
of ZnO nanoparticles in a slurry photocatalytic reactor,
20 even with low to medium concentrations of ZnO
nanoparticles, it is difficult to control uniform
irradiation of UV light on the suspension of ZnO
nanoparticles. Furthermore, it may be difficult to recover
 ZnO nanoparticles from the treated water and hence, ZnO
25 slurry suspensions may pose a secondary contamination of
water.

There also have been many methods developed to
synthesize ZnO nanoparticles including wet chemical
processes such as vapor-liquid-solid processes, sol-gel
30 processes, homogeneous precipitation, microemulsion,
hydrothermal methods and solvent evaporation; and dry
chemical processes such as vapor phase growth, soft
chemical methods and electrophoretic deposition. Whilst
dry chemical processes require lower synthesis

temperatures, shorter preparation times and are simple and solvent-free processes for easy control, the produced particles may aggregate easily, thereby requiring secondary processes to treat the aggregated particles.

5 Furthermore, dry chemical processes require precise stoichiometry. On the other hand, whilst wet chemical processes can precisely control the composition of particles, such processes may be tedious and may require high temperatures and pressures.

10 Accordingly, there is a need to provide a photocatalyst that overcomes, or at least ameliorates, one or more of the disadvantages described above.

Furthermore, there is a need to provide a photocatalytic water treatment system that overcomes, or
15 at least ameliorates, one or more of the disadvantages described above.

Summary

According to a first aspect, there is provided a
20 photocatalyst comprising metal oxide semiconductor nanoparticles in crystalline form integrally formed on the surface of a substrate made of the corresponding metal.

Advantageously, when in use, the integrally formed metal oxide semiconductor nanoparticles do not give rise
25 to secondary contamination of the treated water. Without being bound by theory, it is believed that by being integrally formed, the metal oxide nanoparticles are resistant to being sloughed off due to abrasive forces.

The metal oxide semiconductor may be selected from
30 the group consisting of ZnO, TiO₂, SnO₂, WO₃, Fe₂O₃, Bi₂O₃, MoO₃, ZrO₂ and Nb₂O₅. In one embodiment, the metal oxide semiconductor is ZnO.

Advantageously, ZnO is insoluble and non-toxic. Further, ZnO has a powerful oxidizing ability and its

ground state electrons are capable of being excited by absorbing photons from UV radiation. A photocatalytic water treatment system utilizing ZnO activated by UV radiation thus achieves high degradation efficiency of the contaminants that are present in the wastewater. Further advantageously, ZnO is able to degrade or mineralize a wide spectrum of contaminants present in wastewater and also air-borne contaminants. Such contaminants may be for example phenols, cathecol, naphthol, chlorophenols, polychlorinated biphenyls (PCBs), benzene, benzoic acid and salicylic acid. Moreover, ZnO may effectively photocatalytically degrade surfactants frequently used in industries.

According to a second aspect, there is provided a method of producing a photocatalyst comprising the steps of: a. providing a substrate of a transition metal; b. oxidizing the metal substrate under conditions to integrally form metal oxide semiconductor nanoparticles in crystalline form thereon.

Advantageously, the disclosed method is relatively simple and is easily scalable. Advantageously, the photocatalyst produced by the disclosed method has a relatively lower energy transmittance than photocatalysts produced by prior art processes. Accordingly, lesser energy from the light source is transmitted away from the photocatalyst, resulting in more energy being utilized for the photocatalytic activity of the photocatalyst. Thus, the photocatalyst produced by the disclosed method has a higher efficiency in utilizing the energy from the light source.

Further advantageously, the photocatalyst produced by the disclosed method has a relatively higher specific surface area, thereby increasing the area for contact with wastewater and increasing the efficacy of subsequent

mineralization/degradation of the organic contaminants present in wastewater.

In one embodiment, the method further comprises a step of thermally treating the oxidized substrate to
5 activate the metal oxide semiconductor nanoparticles formed thereon. Advantageously, the thermal treatment step increases the crystallinity of the metal oxide semiconductor nanoparticles formed on the surface of the substrate. Advantageously, the increased crystallinity has
10 been found to increase the photocatalytic activity of the photocatalysts.

According to a third aspect, there is provided a photocatalytic water treatment system having a treatment zone comprising: a plurality of stages, wherein each stage
15 comprises a photocatalyst comprising metal oxide semiconductor nanoparticles in crystalline form integrally formed on the surface of a substrate made of the corresponding metal and wherein each stage further comprises a light source.

20 Advantageously, the plurality of stages provides increased surface area for contact between the photocatalysts and wastewater present in the treatment zone. Advantageously, the plurality of stages further promotes the mineralization/degradation of persistent
25 organic contaminants present in the wastewater by increasing the residence time of wastewater in the photocatalytic water treatment system and the contact between the photocatalyst and the wastewater.

In one embodiment, each stage is characterized by at
30 least one light source disposed substantially between the photocatalyst of that stage and a photocatalyst of an adjacent stage. The light source and the at least two photocatalysts define a flow path for the contaminated feed water to flow therethrough. In one embodiment, the

flow path of the feed wastewater traces the perimeter of the at least one light source and the at least two photocatalysts. In another embodiment, the flow path of the feed water in each stage is of a substantially U-shape, such that the flow is in a countercurrent direction within a single stage.

The light source may be arranged to substantially irradiate at least one exposed planar surface of the photocatalytic substrate. In one embodiment, the light source is arranged in between two photocatalytic planar substrate surfaces to thereby irradiate the top surface of one photocatalytic planar substrate and the bottom surface of the other photocatalytic planar substrate. Advantageously, such an arrangement allows the light source to irradiate substantially the entire exposed surface of the planar substrate, thereby achieving uniform irradiation across the substrate surface. Advantageously, the uniform irradiation provides an increased degradation or mineralization of the contaminants present in the wastewater.

According to a fourth aspect, there is provided a method of treating water containing organic contaminants, the method comprising: irradiating a photocatalyst comprising metal oxide semiconductor nanoparticles in crystalline form integrally formed on the surface of a substrate made of the corresponding metal with a light source to activate the metal oxide semiconductor nanoparticles; and contacting said water with the activated metal oxide semiconductor nanoparticles to thereby produce water containing relatively less organic contaminants.

Definitions

The following words and terms used herein shall have the meaning indicated:

5 The term "integrally formed" is to be interpreted broadly to refer to a first element/feature extending or transiting in a continuous manner from a second element/feature as a unitary whole and not as two separate and distinguishable elements.

10 The term "semiconductor" is to be interpreted in its broadest sense to refer to materials that are not conductors in its natural state but may easily be excited into a state of conduction.

15 The term "transition metal" as used in the context of the specification refers to elements with electrons in a "d" or "f" orbital and in particular, elements of groups III-XII of the Periodic Table as well as lanthanides and actinides.

20 The prefix "nano" and the term "nanoparticle" as used in the context of the specification is to be interpreted broadly to, unless specified, refer to an average particle size of between about 1 nm to about 1000 nm, specifically between about 1 nm to about 100 nm. The prefix "macro" as used in the context of the specification is to be interpreted broadly to, unless specified, refer to an
25 average particle size of between about 1 μm to about 1000 μm , and preferably between about 10 μm to 100 μm . The particle size may refer to the diameter of the particles where they are substantially spherical. The particles may be non-spherical and the particle size range may refer to
30 the equivalent diameter of the particles relative to spherical particles or may refer to a dimension (length, breadth, height or thickness) of the non-spherical particle.

The word "substantially" does not exclude "completely" e.g. a composition which is "substantially free" from Y may be completely free from Y. Where necessary, the word "substantially" may be omitted from
5 the definition of the invention.

Unless specified otherwise, the terms "comprising" and "comprise", and grammatical variants thereof, are intended to represent "open" or "inclusive" language such that they include recited elements but also permit
10 inclusion of additional, unrecited elements.

As used herein, the term "about", in the context of concentrations of components of the formulations, typically means $\pm 5\%$ of the stated value, more typically $\pm 4\%$ of the stated value, more typically $\pm 3\%$ of the
15 stated value, more typically, $\pm 2\%$ of the stated value, even more typically $\pm 1\%$ of the stated value, and even more typically $\pm 0.5\%$ of the stated value.

Throughout this disclosure, certain embodiments may be disclosed in a range format. It should be understood
20 that the description in range format is merely for convenience and brevity and should not be construed as an inflexible limitation on the scope of the disclosed ranges. Accordingly, the description of a range should be considered to have specifically disclosed all the possible
25 sub-ranges as well as individual numerical values within that range. For example, description of a range such as from 1 to 6 should be considered to have specifically disclosed sub-ranges such as from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4, from 2 to 6, from 3 to 6 etc.,
30 as well as individual numbers within that range, for example, 1, 2, 3, 4, 5, and 6. This applies regardless of the breadth of the range.

Detailed Disclosure of Embodiments

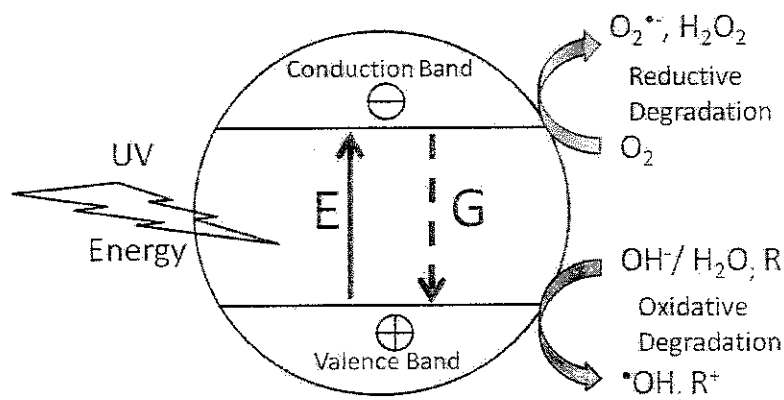
Exemplary, non-limiting embodiments of a photocatalyst according to the first aspect will now be disclosed.

5 In one embodiment, there is provided a photocatalyst comprising metal oxide semiconductor nanoparticles in crystalline form integrally formed on the surface of a substrate made of the corresponding metal.

The metal of the substrate may be a transition metal.

10 In one embodiment, the metal of the substrate is selected from the group consisting of Zn, Ti, Sn, W, Fe, Bi, Mo, Zr and Nb. The corresponding metal oxide semiconductor nanoparticles may be integrally formed from and on the substrate metal. Hence, the corresponding metal oxide semiconductor nanoparticles may be selected from the group
15 consisting of ZnO, TiO₂, SnO₂, WO₃, Fe₂O₃, Bi₂O₃, MoO₃, ZrO₂ and Nb₂O₅ respectively.

The absorption of radiation energy by the metal oxide semiconductor nanoparticles may be exemplified by the
20 diagram as follows.



The photocatalytic degradation of organic compounds or contaminants is based on semiconductor photochemistry. The semiconductor photocatalyst is irradiated by a light
25 source, such as UV radiation or solar radiation, with a wavelength sufficient to displace the electrons of the photocatalyst from the valence band to the conduction band.

In the embodiment where the metal oxide semiconductor is ZnO, the wavelength of light required is above 387.5 nm. As electrons are displaced from the valence band, a localized positively charged "hole" is produced and an
5 electron/hole pair is formed on the semiconductor surface.

The organic pollutant may then be adsorbed on the surface of the semiconductor photocatalyst, where the electrons of the pollutant fill the positively charged
holes, thereby oxidizing the organic pollutant.

10 The organic pollutant may also be oxidized by the HO• radicals, which are powerful oxidizing agents. HO• radicals are generated from the H₂O molecules of the wastewater when the displaced electrons of the metal oxide semiconductor returns to the positively charged hole in
15 the valence band, thereby releasing the binding energy of the electron/hole pair. The binding energy released is capable of splitting the H₂O molecules into HO• radicals and oxidation of the organic pollutant takes place.

Both types of oxidation reaction mechanisms may
20 proceed simultaneously and which mechanism dominates depends on the chemical and adsorption properties of the pollutant. Oxidation of the organic pollutant decomposes the pollutant to harmless end products, such as CO₂ and H₂O. Accordingly, a wide spectrum of organic contaminants can
25 be advantageously degraded by the disclosed photocatalyst. In one embodiment, the metal of the substrate is Zn and the corresponding metal oxide semiconductor nanoparticles are ZnO. Advantageously, ZnO is a direct band gap semiconductor with room temperature energy gap of 3.37 eV,
30 a large exciton binding energy of 60 meV and low power threshold. In particular, irradiation with a light beam having a wavelength of less than 390 nm is required to excite ZnO. In one embodiment, a light beam having a

wavelength of 365 nm may achieve the degradation of chloro-organic molecules completely.

The average nanoparticle size may be from about 30 nm to about 100 nm, or about 50 nm to about 100 nm, or about 5 70 nm to about 100 nm, or about 30 nm to about 70 nm, or about 30 nm to about 50 nm. In one embodiment, the crystalline metal oxide semiconductor nanoparticles possess an average particle size of from about 30 nm to about 100 nm.

10 Advantageously, the crystalline metal oxide semiconductor nanoparticles integrally formed on the metal substrate possess high specific surface area which increases the photocatalytic activity of the photocatalyst. The increased photocatalytic activity may
15 be due to the quantum size effect of the nanoparticles. The quantum size effect refers to the unusual properties exhibited by extremely small crystals that arise from the confinement of electrons to small regions of space. Due to the quantum size effect of the nanoparticles, the band gap
20 between the highest valence band and the lowest conduction band increases with a decrease in size of the nanoparticles. Thus, more energy is needed to excite the electrons of the nanoparticles and more energy is also released when the nanoparticles return to their ground
25 state. Accordingly, the increase in the band gap increases the redox capabilities of the electron/hole pair of the excited nanoparticles, thereby increasing the photocatalytic activity of the nanoparticles.

The substrate may be in the form of a sheet or wire
30 or in powder form. In the embodiment where the substrate is in the form of a sheet, metal oxide semiconductor nanoparticles may be integrally formed on both sides of the sheet. In another embodiment, metal oxide semiconductor nanoparticles may be integrally formed on

one side of the sheet. In the embodiment where the substrate is in the form of a wire, metal oxide semiconductor nanoparticles may be integrally formed co-axially on the circumference of the wire. In the
5 embodiment where the substrate is in powder form, the metal oxide semiconductor nanoparticles may be integrally formed on the surface of the powder.

In one embodiment, the Zn substrate is composed of substantially pure metallic zinc. The substantially pure
10 metallic zinc substrate may possess a purity of about 95% purity of Zn or higher, or about 98% purity of Zn or higher, or about 99% purity of Zn or higher. In another embodiment, the substrate is an alloy of zinc and other metals. In yet another embodiment, the substrate is a
15 metal composite material comprising Zn and other inorganic materials, such as, quartz, or ceramic material.

In one embodiment, the average thickness of the substrate having metal oxide semiconductor nanoparticles integrally formed thereon is from about 0.1 μm to about 1
20 mm.

The metal oxide semiconductor nanoparticles may be formed by oxidizing the metal substrate with an oxidizing agent. In one embodiment, the oxidizing agent is a liquid oxidant.

25 Exemplary, non-limiting embodiments of a method according to the second aspect will now be disclosed.

In one embodiment, there is provided a method of producing a photocatalyst comprising the steps of: a. providing a substrate of a transition metal; b. oxidizing
30 the metal substrate under conditions to integrally form metal oxide semiconductor nanoparticles in crystalline form thereon.

The liquid oxidant used in the oxidizing step may be any chemical capable of oxidizing the metal substrate. The

oxidizing agent may be selected from the group consisting of chlorine, organic chlorines, chlorine dioxide, peroxide, persalt, peracids, persulfates and peroxyphthalates. In one embodiment, H_2O_2 is used as the
5 oxidant in the oxidizing step.

In another embodiment, the oxidant solution may further comprise a mixture of NaF , NaCl and Na_2SO_4 .

The oxidizing step may be conducted for at least 72 hours. The oxidizing step may be conducted at a
10 temperature from about 60°C to about 80°C . Advantageously, H_2O_2 decomposes at a temperature from about 60°C to about 80°C to produce strongly oxidizing radicals, which leads to the formation of ZnO nanoparticles on the surface of the Zn substrate.

15 In one embodiment, the method further comprises the step of pickling the substrate in a pickling solution to remove contaminants, such as undesirable metal oxides, from the surface of the substrate. The pickling step may be performed before the oxidizing step.

20 The pickling solution may comprise of an acid. In one embodiment, the acid is selected from the group consisting of HF , HNO_3 and mixtures thereof.

The pickling solution may further comprise of water. In one embodiment, the water is deionized water.

25 In one embodiment, the pickling solution comprises HF , HNO_3 and water. The HF may have a concentration of about 38 wt% to about 55 wt%, or about 38 wt% to about 50 wt%, or about 38 wt% to about 45 wt%, or about 45 wt% to about 55 wt%, or about 40 wt% to about 50 wt%.

30 In one embodiment, the pickling solution comprises of a mixture of HF , HNO_3 and water. The mixture of HF , HNO_3 and water may comprise of HF in the range of about 1 vol% to about 25 vol%, HNO_3 in the range of about 10 vol% to about 50 vol% and water in the range of about 45 vol% to

about 75 vol%, wherein the volume of HF, HNO₃ and water makes up 100 vol%. In one embodiment, the volume ratio of HF:HNO₃:water is 1:3:6.

5 The pickling step may be conducted at a temperature suitable to remove undesirable particles from the surface of the substrate. The temperature of the pickling step may be in the range of about 15°C to about 30°C, or about 20°C to about 30°C, or about 25°C to about 30°C, or about 15°C to about 25°C, or about 15°C to about 20°C. In one embodiment,
10 the pickling step is conducted at ambient temperature (about 15°C to 30°C).

The method may further comprise the step of thermally treating the oxidized substrate to activate the metal oxide semiconductor nanoparticles formed thereon. The
15 thermal treatment step may be performed after the oxidation step.

In the embodiment where the method additionally comprises both the pickling step and the thermal treatment step, the steps are performed sequentially such that the
20 pickling step is performed before the oxidation step and the thermal treatment step is performed after the oxidation step.

In one embodiment, the heating rate of the thermal treatment step is from about 5°C/min to about 15°C/min. In
25 another embodiment, the heating rate of the thermal treatment step is about 10°C/min. The maximum temperature attained during the thermal treatment step may be from about 300°C to about 600°C, or from about 400°C to about 600°C, or from about 300°C to about 500°C. In one
30 embodiment, the maximum temperature attained during the thermal treatment step is 450°C.

The morphology of the metal oxide semiconductor nanoparticles may be altered by altering the temperature attained during the thermal treatment step. Specifically,

the crystallinity and the particle size of the nanoparticles may be altered by altering the temperature attained during the thermal treatment step.

5 In one embodiment, the thermal treatment step advantageously increases the crystallinity of the metal oxide semiconductor nanoparticles formed on the surface of the substrate, thereby increasing the photocatalytic activity of the photocatalysts. The crystallinity of nanoparticles may be determined by X-ray diffraction,
10 wherein an increase in crystallinity is characterized by sharp diffraction peaks due to the reflection of photons off the regularly-spaced crystal structures. On the other hand, crystal structures with low crystallinity exhibit weak, diffuse diffraction peaks.

15 The thermal treatment step may also increase the particle size of the metal oxide semiconductor nanoparticles formed on the surface of the substrate. However, with an increase in particle size, the specific surface area of the crystals of the metal oxide semiconductor nanoparticles decreases, which may lead to a
20 reduction in photocatalytic activity of the photocatalyst.

Advantageously, it has been surprisingly found that a maximum temperature of 450°C attained during the thermal treatment step can increase the crystallinity of the metal
25 oxide semiconductor nanoparticles with a minimal decrease of the specific surface area of the crystals, thereby optimizing the photocatalytic activity of the photocatalyst.

The metal oxide semiconductor nanoparticles formed by
30 the method defined above possess an average particle size of from about 30 nm to about 100 nm. Advantageously, as discussed, such nanoparticles possess high specific surface area which increases the photocatalytic activity of the photocatalyst.

Furthermore, the crystalline metal oxide semiconductor nanoparticles formed by the method defined above possess relatively lower absorbance than photocatalysts produced by prior art processes.

5 Exemplary, non-limiting embodiments of a photocatalytic water treatment system according to the third aspect will now be disclosed.

In one embodiment, there is provided a photocatalytic water treatment system having a treatment zone comprising:
10 a plurality of stages, wherein each stage comprises a photocatalyst comprising metal oxide semiconductor nanoparticles in crystalline form integrally formed on the surface of a substrate made of the corresponding metal and wherein each stage further comprises a light source.

15 The disclosed system may comprise of two or more stages. In one embodiment, the system comprises four stages.

The metal oxide semiconductor nanoparticles of the plurality of stages may be composed of the same metal
20 oxide or may compose of different metal oxides.

The photocatalyst may be supported on a removable frame within the treatment zone. The removable frame may be made of any UV resistant material, such as stainless steel. The frame may be removed from the system for
25 maintenance or cleaning when required. The removable frame may be configured to secure the substrate in place such that at least two planar surfaces of the substrate are exposed for contact with wastewater.

The light source may emit a wavelength of light
30 sufficient to excite the metal oxide semiconductor nanoparticles. In one embodiment, the light source is a UV light source. In one embodiment, the UV light source is solar radiation. In another embodiment, the UV light

source is a UV lamp. The UV lamp may be any suitable lamp known in the art, such as a xenon lamp or a mercury lamp.

For disinfection-type treatment, the UV lamp used may be a high pressure xenon lamp or a low pressure mercury lamp. For purification-type treatment, the UV lamp used may be a high pressure mercury lamp.

The light source may be configured such that the longitudinal axis through the light source is substantially parallel to the longitudinal axis passing through the substrate of the photocatalyst. In one embodiment, the light source is arranged to substantially irradiate at least one planar surface of said photocatalyst. In another embodiment, the light source is arranged to substantially irradiate at least two planar surfaces. In yet another embodiment, the flow path substantially traces the perimeter of the photocatalysts and the light source. Advantageously, with such a configuration, the flow path of the wastewater is made to flow substantially along the perimeter of the photocatalyst and the light source, thereby maximizing the contact of the wastewater with the photocatalyst whilst concurrently illuminating the entire length of the flow path as the wastewater contacts the photocatalyst.

In another embodiment, the light source and the photocatalyst of each stage may be configured such that the flow of wastewater in the treatment zone is in a countercurrent direction.

The flow of the contaminated feed water may be in a substantially parallel direction to the longitudinal axes of the substrate and the light source. Advantageously, the contact of the feed water with the photocatalyst and the light source may be maximized.

In one embodiment, the photocatalysts and the light sources are arranged alternately to thereby define a

substantially U-shaped flow path in each stage for the contaminated feed water to flow therethrough. In this embodiment, the contaminated water may flow between the photocatalyst and the light source in a U-shaped flow path
5 in each stage of the photocatalytic reactor. In one embodiment, the flow of the feed water within the treatment zone is in a countercurrent direction. Advantageously, the contact of the feed water with the photocatalyst and the light source may be maximized.

10 The light source may be enclosed by a cover within the treatment zone. The cover may be made of any suitable material able to withstand the conditions within the treatment zone. In particular, the cover may be made of any UV resistant material that also allows light to pass
15 through. In one embodiment, the cover is made of quartz.

The cover may be equipped with a switch to operate the light source. The switch may include a safety feature that automatically switches the light source off when the cover is open.

20 The treatment zone of the photocatalytic water treatment system may be enclosed by a container. The container may be made of any UV resistant material, such as stainless steel.

The container enclosing the treatment zone may be
25 sized according to the requirements of the water treatment process. The container enclosing the treatment zone may also be sized according to the number of stages in the system. In one embodiment, the container has a capacity of 50 liters.

30 The system may comprise of sensors placed within the treatment zone so that the process may be monitored in real time. The sensors may monitor the temperature and/or the pressure in the treatment zone.

The system may further comprise a flow rate limiter to adjust the flow rate of contaminated water entering the treatment zone. The flow rate limiter may be a flow meter. The flow rate limiter may be used as a safety measure to
5 limit the flow rate to a predetermined maximum allowable value. The flow rate limiter may also advantageously control the residence time of the contaminated feed water.

The system may comprise of a tank to store contaminated feed water. The tank may be of any suitable
10 size. The tank may also be made of any suitable material capable of containing contaminated feed water.

A filtration membrane may be provided in the tank. The filtration membrane may be any suitable porous membrane capable of removing contaminants in the
15 contaminated feed water. The filtration membrane may be used to remove suspended particles in the contaminated feed water before being treated in the treatment zone. The filtration membrane may also be used to remove particles resulting from the degradation of organic contaminants in
20 the treatment zone. In one embodiment, the pores of the filtration membrane are micro-sized.

Sensors may be provided in the tank for real time monitoring. An example of a sensor that may be provided in the tank is a sensor that monitors the chemical oxygen
25 demand (COD) of the water in the tank.

The system may also comprise a pump to pump the feed water into the treatment zone. The pump may be capable of providing variable feed flow rates suitable for operation of the water treatment system. In one embodiment, the pump
30 delivers a flow rate of about 100 mL/min to about 1000 mL/min. The pump may also permit the system to be capable of recirculating the feed water.

Exemplary, non-limiting embodiments of a method of treating water containing organic contaminants according to the fourth aspect will now be disclosed.

5 In one embodiment, there is provided a method of treating water containing organic contaminants, the method comprising: irradiating a photocatalyst comprising metal oxide semiconductor nanoparticles in crystalline form integrally formed on the surface of a substrate made of the corresponding metal with a light source to activate
10 the metal oxide semiconductor nanoparticles; and contacting said water with the activated metal oxide semiconductor nanoparticles to thereby produce water containing relatively less organic contaminants.

The feed water containing organic contaminants may
15 have more than about 50% of the contaminants degraded to produce treated water. In one embodiment, the water containing organic contaminants has more than 75% of the contaminants degraded. In another embodiment, the water containing organic contaminants has more than 85% of the
20 contaminants degraded. In yet another embodiment, the water containing organic contaminants has more than 95% of the contaminants degraded.

The pH of the feed water may be adjusted before treatment. In one embodiment, the pH of the feed water is
25 adjusted between about 6 to about 9. In another embodiment, the pH of the feed water is adjusted to 7.5.

The method may further comprise a step of removing suspended particles from the feed water before contacting the feed water with the activated metal oxide
30 semiconductor nanoparticles. In one embodiment, the removing step comprises membrane filtration. The membrane may be any suitable micro-sized, porous membrane for removing the mineralized contaminants.

Brief Description Of Drawings

The accompanying drawings illustrate a disclosed embodiment and serves to explain the principles of the disclosed embodiment. It is to be understood, however, 5 that the drawings are designed for purposes of illustration only, and not as a definition of the limits of the invention.

Figs. 1a and 1b shows field emission scanning electron microscope (FE-SEM) micrographs of the ZnO 10 nanoparticles formed on the surface of the Zn sheets obtained from Example 1 at 33,000x and 80,000x magnification respectively.

Fig. 2 shows the energy dispersive spectrum (EDS) of the integrally formed ZnO nanoparticles obtained from 15 Example 1.

Fig. 3 shows the FE-SEM micrograph of the commercial ZnO nanoparticles used in Comparative Example 1 at 40,000x magnification.

Fig. 4 shows the FE-SEM micrograph of the Zn sheets 20 printed with ZnO nanoparticles obtained from Comparative Example 1 at 40,000x magnification.

Fig. 5 shows a schematic diagram of a four-stage photocatalytic water treatment system used in Example 13.

Fig. 6 shows a schematic diagram of a four-stage 25 photocatalytic water treatment system powered using solar energy.

Figs. 7a, 7b and 7c show graphs of the degradation efficiency of the photocatalytic water treatment system of Example 13 to degrade phenol with initial concentrations 30 of 5 $\mu\text{g/mL}$, 10 $\mu\text{g/mL}$ and 20 $\mu\text{g/mL}$ respectively versus irradiation time.

Fig. 8 shows a graph of the natural logarithm of normalized initial concentrations of 5 µg/mL, 10 µg/mL and 20 µg/mL of phenol in Example 13 versus irradiation time.

Fig. 9 shows a graph of the degradation efficiency of the photocatalytic water treatment system of Example 14 to degrade phenol with an initial concentration of 10 µg/mL in the different pH solutions versus irradiation time.

Fig. 10 shows the effect of pH value on the apparent rate constant (k_{app}) of Example 14.

Fig. 11 shows a graph of the discoloration efficiency of the photocatalytic water treatment system of Example 16 to degrade Rhodamine B (RB) having an initial concentration of 15 µg/mL.

Fig. 12 shows a UV-Vis absorption spectrum of the discoloration efficiency of the photocatalytic water treatment system of Example 15 to degrade RB with and without the ZnO photocatalyst.

Examples

Non-limiting examples of the invention will be further described in greater detail by reference to specific Examples, which should not be construed as in any way limiting the scope of the invention.

Preparation Of A Photocatalyst

Testing methods

In the following Examples, the following testing methods were used to characterize the ZnO nanoparticles produced.

(1) Average particle diameter

The average particle diameter was determined by repeatedly determining the average volume of 20 particles taken at from a random field of view in a field emission
5 scanning electronic microscope (FE-SEM, JEOL Ltd., Japan).

(2) Mean film thickness

The mean film thickness was determined by stylus surface profilometer (DEKTAK 6M, Veeco Company, New York,
10 United States of America).

(3) Ultraviolet absorptivity

The absorbance of the samples thereof was determined at 275 nm to 400 nm by UV-Vis spectrometer (UV-1800,
15 Shimadzu Corporation, Japan) to evaluate the light transmittances in the ultraviolet and visible ray region.

Example 1

Zn sheets purchased from Titan Engineering Pte Ltd, Singapore (99.5% in purity) with a size of 2.5 cm × 2.0 cm × 0.1 cm were pickled in a pickling solution consisting of concentrated HF, concentrated HNO₃ and deionized water with a volume ratio of 1:3:6 at ambient temperature.

The Zn sheets were then cleaned ultrasonically
25 cleaning in deionized water. Thereafter, each piece of Zn sheet was oxidized in 50 ml of an oxidant solution of 30 wt% H₂O₂ and subjected to a first step of thermal treatment by heating at 80°C in an oven for 72 hours to produce ZnO nanoparticles formed on each Zn sheet. The Zn sheets were
30 then removed from the oven, rinsed with deionized water and dried in air.

The Zn sheets were then subjected to a second step of thermal treatment, which was conducted in a furnace at a

heating rate of 10°C/min to attain the designated temperature of 450°C. The temperature was maintained for 1 hour, followed by furnace cooling to ambient temperature.

5 The FE-SEM micrographs of the ZnO nanoparticles integrally formed on the surface of the Zn sheets is shown in Figs. 1a and 1b. It can be seen that the nanoparticles formed have smaller average particle sizes and thus have a larger specific surface area.

10 The energy dispersive spectrum of the integrally formed ZnO nanoparticles can be seen from Fig. 2. The oxygen atom has 898.39 wt% and 60.88 atomic%, while the Zinc atom has 2358.97 wt% and 39.12 atomic%.

The properties of the ZnO nanoparticles obtained from Example 1 is shown in Table 1 below.

15

Examples 2 to 9

The procedure described in Example 1 was repeated except that different substances were added to the oxidant solution. The different substances added are described in
20 Table 1 below.

Table 1

Example	Zn	Additional substance in oxidant solution	Average particle sizes (nm)	Apparent specific area (m ² /g)	UV absorbance @ λ=365 nm T%
1	Sheet	None	~ 30-100 nm	85	26
2	Sheet	5 mM NaF	~ 30-60 nm	68	28
3	Sheet	5 mM NaCl	~ 30-100 nm	85	26
4	Sheet	5 mM Na ₂ SO ₄	~ 50-90 nm	80	30

5	Sheet	5 mM Na ₂ CO ₃	amorphous	-	-
6	Sheet	5 mM Na ₂ C ₂ O ₄	amorphous	-	-
7	Sheet	3 mM TaCl	-	-	-
8	Sheet	15 mM NaCl	-	-	-
9	Sheet	15 mM HCl	-	-	-

As can be seen from Table 1 above, the addition of NaF, NaCl or Na₂SO₄ in the H₂O₂ oxidant solution results in distinct crystalline ZnO nanoparticles. Furthermore, the specific surface area of the crystalline ZnO nanoparticles is relatively high, while the absorbance of UV characterized by the percentage of transmittance (T%) at $\lambda=365$ nm is relatively low.

10 Comparative Example 1

Commercial ZnO nanoparticles (obtained from Alfa Aesar, Massachusetts, United States Of America) with an average particle size of 40-100 nm and specific surface area of 10-25 m²/g were deposited on zinc sheets using a screen-printing technique. The screen-printing procedure used is described as follows.

The following chemicals used are obtained from Sigma Aldrich, Missouri, United States Of America. Ethyl cellulose solutions with viscosities of 10 mPas and 50 mPas were mixed in equal proportions, and dissolved in 10 wt% of ethanol. 10 wt% of α -terpineol was added into the ethanolic mixture. An aliquot of the final mixture of solvents was drawn and added into a quartz mortar containing 6g of the commercial ZnO nanoparticles and ground slowly to completely disperse the nanoparticles.

The homogeneous paste was then milled by a three roll mill to produce a paste composed of 82 wt% ZnO, 9 wt% α -terpineol and 9 wt% ethyl cellulose.

5 The paste was printed by a 136 μ m sieved screen on zinc sheets with a size of 2.5cm $\times$ 2.0cm $\times$ 0.1cm, to obtain deposited layers of 50 g/m². The printed sheets were then calcined at 300°C to remove the organic solvents used in the paste preparation.

10 The properties of the zinc sheets printed with ZnO nanoparticles were determined in the same way as in Examples 1 to 9. The FE-SEM micrograph of the commercial ZnO nanoparticles is shown in Fig. 3 and the FE-SEM micrograph of the zinc sheets printed with ZnO nanoparticles obtained from Comparative Example 1 is shown
15 in Fig. 4. It can be seen that the crystals of the commercial ZnO nanoparticles and that of the ZnO nanoparticles obtained from Comparative Example 1 is larger in average size and is less uniform than those obtained from Examples 1 to 9. Specifically, the average
20 particle size of the screen-printed ZnO nanoparticles is about 70 to 120nm. Accordingly, since the commercial ZnO nanoparticles and the ZnO nanoparticles screen-printed on zinc sheets possess larger average particle sizes, these nanoparticles possess a smaller specific surface area. The
25 specific surface area of the screen-printed ZnO nanoparticles is about 46 m²/g.

The zinc sheets printed with ZnO nanoparticles obtained from Comparative Example 1 had a more intensive absorbance of UV characterized by the percentage of
30 transmittance (T%) at λ =365 nm of 35%.

Example 10

The procedure described in Example 1 was repeated except that a larger zinc sheet is used in this example. The zinc sheet used in this example is 15cm × 12.5cm × 0.1
5 cm.

The properties of the ZnO nanoparticles obtained from Example 10 are similar to that of Example 1. Hence, the properties of the ZnO nanoparticles are not dependent on the size of the metallic substrate.

10

Comparative Example 2

The procedure described in Comparative Example 1 to obtain ZnO nanoparticles screen-printed on a zinc sheet was repeated except that a larger zinc sheet is used in
15 this example. The zinc sheet used in this example is 15cm × 12.5cm × 0.1 cm. The properties of the ZnO nanoparticles obtained from Example 10 are similar to that of Example 1. Hence, the properties of the ZnO nanoparticles are not dependent on the size of the metallic substrate.

20

Examples 11 and 12

The procedure described in Example 1 was repeated except that the designated temperature of the thermal treatment step attained is 450°C and 700°C respectively.

25 The crystal structure of the ZnO nanoparticles integrally formed on the surface of the Zn sheets obtained from Examples 11 and 12 are similar to that of Example 1.

The properties of the ZnO nanoparticles obtained from Examples 11 and 12 as compared to that of Example 1 is
30 shown in Table 2 below.

Table 2

Ex	Thermal treatment temp, °C	Grain size, nm	Specific surface area, m ² /g	Total pore volume, cm ³ /g	Average pore diameter, nm	Photocatalytic activity, 10 ⁻² min ⁻¹
1	-	31.4	85.20	0.30	10.4	2.53
11	450	34.6	68.41	0.43	17.3	1.53
12	700	42.7	20.28	0.17	34.3	0.47

The photocatalytic activity was calculated by the photocatalytic degradation of rhodamine B (RB).

5 It can be seen from Table 2 above that the ZnO nanoparticles obtained from Example 1 has the highest specific surface area and the smallest particle size. As the temperature of the thermal treatment step increased to 450°C, the particle size slightly increased, leading to a
10 decrease in specific surface area. However, when the temperature of the thermal treatment step increased to 700°C, the particle size increased and the specific surface area decreased dramatically.

Hence, it can be seen that ZnO nanoparticles
15 integrally formed on the surface of zinc sheets obtained from Example 11 retained their small grain size and high specific surface area when the temperature of the thermal treatment step increased up to a temperature of 450°C.

20 Treatment Of Wastewater

In the following examples, the ZnO nanoparticles integrally formed on the surface of the Zn sheets obtained from Example 1 were used in a four-stage photocatalytic water treatment system 100 shown in Fig. 5 in accordance
25 with an embodiment of the invention.

As seen in Fig. 5, the four-stage photocatalytic water treatment system 100 is fitted with four pieces of Zn sheets 106 having ZnO nanoparticles integrally formed thereon as the photocatalyst. The Zn sheets 106 are

supported by a removable frame 108. Eight ultraviolet-C (UVC) lamps 102 with 9 w are used as the irradiation source and the lamps 102 are each protected with a quartz cover 104 within container 114. Lamps 102 are also covered
5 at one end with covers 115 which are equipped with a safety switch (not shown). The safety switch will automatically switch off the UV lamps 102 when covers 115 are open. Covers 115 may also provide connection to a power supply (not shown) and a data processing system (not
10 shown).

A single sheet 106 and two lamps 102 form a stage 116. The sheets 106 and lamps 102 are arranged parallel to each other so that contact of a solution containing contaminants with the sheets 106 and lamps 102 is
15 maximized. The system 100 is enclosed by container 114 that is able to hold 50 L of phenol solution. The flow rate of pump 110 may be adjusted and is adjusted to 16.8 L/hr in the following examples unless otherwise stated.

Referring still to Fig. 5, when system 100 is in use,
20 the phenol solution from tank 112 flows through pump 110 into flow rate limiter 120 and into system 100. Tank 112 may be divided into two compartments by a micro-sized porous membrane 118. Membrane 118 is used to remove suspended particles present in the solution in tank 112.
25 The flow of the phenol solution in system 100 follows arrow A in a U-shaped direction, so that the flow of the solution passing through each stage 116 is in a countercurrent direction. The flow may then be recirculated back to tank 112 to be pumped back to system
30 100 for further treatment.

In accordance with another embodiment of the invention, a four-stage photocatalytic water treatment

system 200 powered by solar energy is shown in Fig. 6. Like numbers denote like parts.

Contaminated water from tank 212 having a porous membrane 218 is pumped by pump 210 through flow rate
5 limiter 220 into system 200. In system 200, each stage 216 comprises a photocatalyst and UV lamps (not shown). UV lamp covers 215 are linked via wires 222 to a data processing system 224 with a power supply 226. Power supply 226 comprises a solar panel 228, an accumulator 230
10 and a controller 232. Power supply 226 obtains solar energy from the sun via solar panel 228 to power system 200. Thus, minimum energy cost is required to run system 200.

15 **Example 13**

In this example, the four-stage photocatalytic water treatment system 100 shown in Fig. 5 was used to treat a phenol solution which is used as an exemplary water contaminant.

20 The pH of the phenol solution was adjusted to pH 7 by adding HCl. Different initial concentrations of phenol solution was passed through the system 100. The degradation efficiency of the system 100 to degrade phenol having initial phenol concentrations of 5 $\mu\text{g/mL}$, 10 $\mu\text{g/mL}$
25 and 20 $\mu\text{g/mL}$ is shown in the graphs in Figs. 6a to 6c respectively when the UV lamp 102 was switched off (without UV) and when the UV lamp 102 was switched on (with UV).

In correlation with the graphs of degradation
30 efficiency as a function of irradiation time in Figs. 7a to 7c, plots of the natural logarithm of normalized concentrations of solutes versus irradiation time shown in Fig. 8 showed good linearity. Accordingly, the

mineralization of phenol in this example approximate first-order kinetics. Furthermore, as seen in Figs. 7a to 7c, the phenol was degraded to a high degree (>95% of degradation of phenol).

5 This behavior can be rationalized in terms of the modified forms of the L-H kinetic treatment, which has been used successfully as a qualitative model to describe solid-liquid reactions. Moreover, the kinetics equations and relative parameters were summarized in Table 3 below.

10

Table 3

Initial conc of phenol (µg/mL)	Kinetic reaction equation	r	K _{app} (min ⁻¹)	T _{1/2} (min)
5	$\ln(C_0/C_t) = -0.08346 + 0.00766t$	0.9900	7.66×10^{-3}	101.39
10	$\ln(C_0/C_t) = -0.11411 + 0.00623t$	0.9874	6.23×10^{-3}	129.58
20	$\ln(C_0/C_t) = -0.00509 + 0.00214t$	0.9913	2.14×10^{-3}	326.28

Example 14

15 The procedure described in Example 13 was repeated except that phenol solutions with a pH value of pH 2, pH 3, pH 6, pH 7.5 and pH 9 were used. Further, the initial concentration of phenol was fixed at 10 µg/mL. The results obtained are shown in Fig. 8.

20 Referring to Fig. 9, the plots of different pH versus irradiation time show that the degradation reactions agree with the first-order kinetic model.

On the other hand, as seen in Fig. 10, the apparent rate constants, K_{app} (min⁻¹ × 10⁻²), increases with an increase of pH when pK_a is less than 9.95, and reaches a maximum at pH 7.5. Hence, the rate of phenol degradation is at the maximum at a pH of 7.5.

Table 4 summarizes the kinetics equations and relative parameters for the different pH of solutions.

Table 4

pH	Kinetic reaction equation	r	K_{app} (min^{-1})	$T_{1/2}$ (min)
2	$\ln(C_0/C_t) = 0.02449 + 0.00499t$	0.9996	4.99×10^{-3}	134.0 0
3	$\ln(C_0/C_t) = 0.02748 + 0.00586t$	0.9978	5.86×10^{-3}	113.6 0
6	$\ln(C_0/C_t) = 0.02177 + 0.00688t$	0.9985	6.88×10^{-3}	97.58
7.5	$\ln(C_0/C_t) = -0.00771 + 0.01154t$	0.9976	11.54×10^{-3}	60.73
9	$\ln(C_0/C_t) = -0.06069 + 0.00509t$	0.9974	5.09×10^{-3}	148.1 0

5

Example 15

Among dyestuffs, Rhodamine B (RB) is one of the most important xanthene dyes and is famous for its good stability. Thus, the treatment of effluents containing such dye compounds is important. Degradation of RB was carried out in a four-stage photocatalytic water treatment system 100 shown in Fig. 5 in order to study the degradation efficiency of a moderate initial concentration of RB. The degradation of RB is characterized by its discoloration.

The procedure described in Example 13 was repeated except that the initial concentration of RB was fixed at 15 $\mu\text{g/mL}$.

The results obtained are shown in Fig. 11. It can be seen that almost 100% discoloration efficiency was obtained in just 30 minutes using the four-stage water treatment system fitted with Zn sheets having ZnO nanoparticles integrally formed thereon as the photocatalyst.

The discoloration efficiency of the system to degrade RB with and without the photocatalyst as determined by a UV-Vis spectrometer is shown in Fig. 12.

5 **Example 16**

The procedure described in Example 13 was repeated except that a bisphenol A (BPA) solution having an initial concentration of 5 µg/mL was used. Further, the flow rate of the pump was adjusted to 120 mL/min. In this example,
10 the degradation efficiency of BPA is more than 90%.

Applications

The disclosed photocatalyst comprising metal oxide
15 semiconductor nanoparticles in crystalline form integrally formed on the surface of a substrate made of the corresponding metal, when used in a water treatment system, does not give rise to secondary contamination of the treated water.

20 The metal oxide semiconductor nanoparticles disclosed herein may be able to degrade or mineralize a wide spectrum of contaminants present in wastewater and also air-borne contaminants, such as phenols, cathecol, naphthol, chlorophenols, polychlorinated biphenyls (PCBs),
25 benzene, benzoic acid, salicylic acid and surfactants.

The photocatalyst produced by the disclosed method may possess a relatively high specific surface area, thereby increasing the degradation or mineralization of organic contaminants present in wastewater.

30 The disclosed method may comprise a thermal treatment step which advantageously increases the crystallinity of the metal oxide semiconductor nanoparticles formed on the

surface of the substrate, thereby increasing the photocatalytic activity of the photocatalysts.

The disclosed photocatalytic water treatment system may comprise a plurality of stages that increases the
5 extent of the mineralization of persistent organic contaminants present in the wastewater. The flow of wastewater in the treatment zone may be in a countercurrent direction so that contact between the wastewater and the photocatalyst may be maximized. The
10 light source may be configured to uniformly irradiate the photocatalyst to provide an increased degradation or mineralization of the contaminants present in the wastewater.

Using the disclosed system, more than about 50% of
15 the organic contaminants present in the feed water may be degraded. In one embodiment, more than about 95% of the organic contaminants present in the feed water may be degraded.

It will be apparent that various other modifications
20 and adaptations of the invention will be apparent to the person skilled in the art after reading the foregoing disclosure without departing from the spirit and scope of the invention and it is intended that all such modifications and adaptations come within the scope of the
25 appended claims.

Claims

1. A photocatalyst comprising metal oxide semiconductor nanoparticles in crystalline form integrally formed on the surface of a substrate made of the corresponding metal.
5
2. The photocatalyst as claimed in claim 1, wherein the metal oxide semiconductor is selected from the group consisting of ZnO, TiO₂, SnO₂, WO₃, Fe₂O₃,
10 Bi₂O₃, MoO₃, ZrO₂ and Nb₂O₅.
3. The photocatalyst as claimed in claim 2, wherein the metal oxide semiconductor is ZnO.
15
4. The photocatalyst as claimed in any one of the preceding claims, wherein the nanoparticles possess an average particle size of from about 30 nm to about 100 nm.
20
5. The photocatalyst as claimed in claim 1, wherein the metal of the substrate is selected from the group consisting of Zn, Ti, Sn, W, Fe, Bi, Mo, Zr and Nb.
25
6. The photocatalyst as claimed in claim 5, wherein the metal of the substrate is Zn.
7. The photocatalyst as claimed in any one of the preceding claims, wherein the substrate is a sheet,
30 wire or powder.
8. The photocatalyst as claimed in any one of the preceding claims, wherein the metal oxide

semiconductor nanoparticles are formed by oxidizing the substrate of the corresponding metal.

- 5 9. The photocatalyst as claimed in claim 8, wherein the metal oxide semiconductor nanoparticles are formed by oxidizing the substrate of the corresponding metal with a liquid oxidant.
- 10 10. A method of producing a photocatalyst comprising the steps of:
- 15 a. providing a substrate of a transition metal;
- b. oxidizing the metal substrate in an oxidant solution under conditions to integrally form metal oxide semiconductor nanoparticles in crystalline form thereon.
- 20 11. The method as claimed in claim 10, further comprising, before said oxidizing step b., a step of pickling said substrate in a pickling solution to remove contaminants from the surface of said substrate.
- 25 12. The method as claimed in claim 11, wherein the pickling solution comprises an acid.
13. The method as claimed in claim 12, wherein the acid is selected from the group consisting of HF, HNO₃ and mixtures thereof.
- 30 14. The method as claimed in claims 12 or 13, wherein the pickling solution further comprises water.
15. The method as claimed in claim 14, wherein the water is deionized water.

16. The method as claimed in claim 13, wherein the HF has a concentration of about 38 wt% to about 55 wt%.

5

17. The method as claimed in claim 14, wherein the pickling solution comprises HF in the range of about 1 vol% to about 25 vol%, HNO_3 in the range of about 10 vol% to about 50 vol% and deionized water in the range of about 45 vol% to about 75 vol%, wherein the total volume of HF, HNO_3 and deionized water makes up 100 vol%.

10

18. The method as claimed in claim 17, wherein the volume ratio of HF: HNO_3 :water is 1:3:6.

15

19. The method as claimed in any one of claims 10 to 18, wherein the oxidant solution comprises H_2O_2 .

20

20. The method as claimed in any one of claims 11 to 19, wherein the pickling step occurs at a temperature in the range of about 15°C to about 30°C .

25

21. The method as claimed in any one of claims 10 to 20, wherein the temperature of the oxidizing step is in the range of from about 60°C to about 80°C .

30

22. The method as claimed in any one of claims 10 to 21, wherein the oxidizing step is conducted for at least 72 hours.

35

23. The method as claimed in any one of claims 10 to 22, further comprising the step of thermally treating the oxidized substrate to activate the

metal oxide semiconductor nanoparticles formed thereon.

24. The method as claimed in claim 23, wherein during the thermal treatment step, the heating rate is between about 5 to about 15°C/min.

25. The method as claimed in claim 23 or claim 24, wherein said thermal treatment step is undertaken to attain a maximum temperature of from about 300°C to about 600°C.

26. The method as claimed in claim 25, wherein the maximum temperature is 450°C.

27. The method as claimed in claim 26, wherein the metal oxide semiconductor nanoparticles formed possess an average particle size of from about 30 nm to about 100 nm.

28. A photocatalytic water treatment system having a treatment zone comprising:
a plurality of stages, wherein each stage comprises a photocatalyst comprising metal oxide semiconductor nanoparticles in crystalline form integrally formed on the surface of a substrate made of the corresponding metal and wherein each stage further comprises a light source.

29. The photocatalytic water treatment system as claimed in claim 28, wherein said light source is arranged to substantially irradiate at least one planar surface of said photocatalyst.

30. The photocatalytic water treatment system as claimed in claim 28 or claim 29, wherein said light source and said photocatalysts are arranged alternately to thereby define a flow path for a stream of feed wastewater to flow therethrough.

31. The photocatalytic water treatment system as claimed in claim 30, wherein said flow path substantially traces the perimeter of said photocatalysts and said light source.

32. A method of treating water containing organic contaminants, the method comprising:
irradiating a photocatalyst comprising metal oxide semiconductor nanoparticles in crystalline form integrally formed on the surface of a substrate made of the corresponding metal with a light source to activate the metal oxide semiconductor nanoparticles; and
contacting said water with the activated metal oxide semiconductor nanoparticles to thereby produce water containing relatively less organic contaminants.