

- 1 -

PHOTOCATALYTIC METAL OXIDE NANOMATERIALS; METHOD OF
MAKING VIA H₂-PLASMA TREATMENT; USE FOR ORGANIC WASTE
DECONTAMINATION IN WATER

RELATED APPLICATION

- 5 This application claims the benefit of U.S. Provisional Application No. 61/568,246, filed on December 8, 2011. The entire teachings of the above application are incorporated herein by reference.

BACKGROUND OF THE INVENTION

- 10 The pollution of groundwater by hazardous organic compounds, such as industrial dyes, gasoline and other petroleum-derived hydrocarbons, is becoming a global problem [1,2]. In the past, conventional biological and physical treatment methods, such as adsorption, ultrafiltration and coagulation, have been widely utilized techniques to remove organic pollutants from various waters and wastewaters. However, the decontamination of many emerging anthropogenic
15 organic pollutants, particularly those with high toxicity at very low concentrations, requires novel techniques to chemically transform the pollutants into non-hazardous compounds [2].

- 20 Recently, efforts have been put forth to examine the decomposition of organic pollutants in water by utilizing photocatalysis fueled by solar energy. In particular, semiconductors have been studied as catalysts. The effectiveness of solar light-driven photocatalytic processes is dictated to a great extent by the semiconductor's capability of absorbing visible and infrared light, as well as its ability to suppress rapid recombination of photo-generated electrons and holes.

- 25 Nanophase titanium dioxide (TiO₂), which has a large surface area with which to facilitate fast rates of surface reactions, is a semiconductor that is widely used as a photocatalyst for solar-driven applications such as water-splitting to produce H₂ and decontamination of water that contains organic pollutants [2-7]. As a photocatalyst, however, TiO₂ absorbs only ultraviolet (UV) light, due to its wide

band gap, which limits the catalytic utility of TiO_2 in visible and IR light. A number of efforts have been put forth to effectively narrow the band gap, which should give the material photocatalytic properties under visible light. Metallic and non-metallic dopants have been used to add donor or acceptor states in the bandgap, however the visible and IR light absorption of such materials has not seen sufficient improvement. More significant improvements in the visible and IR light absorption of these nanoparticles have stemmed from engineering defects into the nanoparticle surface [7,8], however, these methods exhibit the disadvantage of changing the chemical stoichiometry of the nanomaterial.

There is a need to develop methods to improve the visible and IR-light absorbance of semiconductor nanomaterials such as TiO_2 in order to efficiently employ such materials in solar-driven applications such as the decontamination of water.

SUMMARY OF THE INVENTION

The present invention is directed to a metal oxide nanomaterial having photocatalytic properties and having H_2 -plasma-induced surface defects that do not reduce the oxidation state of the metal oxide, wherein the metal oxide is TiO_2 , ZnO , WO_3 , SnO_3 or In_2O_3 . The present invention is further directed to TiO_2 nanomaterials that have H_2 -plasma-induced surface defects that impart a gray to black color to the nanoparticles but do not reduce the oxidation state of TiO_2 . The H_2 -plasma-induced surface defects include structural disorder. The black TiO_2 nanomaterial of the present invention absorbs visible and IR light, and can be a nanoparticle, a nanotube or a nanowire.

The present invention is further directed to a method of making a metal oxide nanomaterial having photocatalytic properties, the method comprises contacting a metal oxide nanomaterial starting material with hydrogen plasma at a temperature, pressure and hydrogen plasma flow rate for a period of time sufficient to produce H_2 -plasma induced surface defects on the metal oxide but not reduce the oxidation state of the metal oxide, wherein the metal oxide nanomaterial has photocatalytic properties and is selected from TiO_2 , ZnO , WO_3 , SnO_3 or In_2O_3 .

The present invention is also directed to a method of making TiO₂ nanomaterials having photocatalytic properties, wherein the metal oxide nanomaterial starting material is white TiO₂ nanomaterial and further wherein the metal oxide nanomaterial having photocatalytic properties is black TiO₂ nanomaterial. The method of making a metal oxide nanomaterial having photocatalytic properties is carried out at a pressure lower than atmospheric pressure. The present invention further describes a method of making a TiO₂ nanomaterial having photocatalytic properties having H₂-plasma-induced surface defects that impart a gray to black color to the nanoparticles but do not reduce the oxidation state of TiO₂. The H₂-plasma-induced surface defects include structural disorder, and the black TiO₂ nanomaterial is a nanoparticle, a nanotube, or a nanowire.

The present invention further describes a method for decomposing an organic compound in water, the method comprises (a) contacting an aqueous solution comprising an organic compound with a metal oxide nanomaterial having photocatalytic properties, wherein the metal oxide is TiO₂, ZnO, WO₃, SnO₃ or In₂O₃, to form a mixture; and (b) exposing the mixture of step (b) to a visible light source, the visible light source optionally including an ultraviolet filter, for an amount of time sufficient to decompose the organic compound.

The present invention further describes a method for decomposing an organic compound in water, wherein the metal oxide nanomaterial having photocatalytic properties is a TiO₂ nanomaterial having H₂-plasma-induced surface defects that impart a gray to black color to the nanoparticles but do not reduce the oxidation state of TiO₂. The H₂-plasma-induced surface defects include structural disorder. The present invention further describes that the TiO₂ nanomaterial having photocatalytic properties absorbs visible and IR light, and that the TiO₂ nanomaterial is a photocatalyst for decomposition of an organic compound, and further that the photocatalyst is reusable in the process of decomposition of an organic compound.

The present invention is further directed to a method for splitting water to form H₂ gas, the method comprises (a) contacting an aqueous solution comprising methanol

and a metal oxide nanomaterial having photocatalytic properties, wherein the metal oxide nanomaterial is TiO_2 , ZnO , WO_3 , SnO_3 or In_2O_3 ; with a platinum species to form a mixture; and (b) irradiating the mixture of step (a) with a visible light source to form H_2 gas.

5 The present invention describes that the metal oxide nanomaterial having photocatalytic properties utilized in a method of splitting water to form H_2 gas is a TiO_2 nanomaterial having H_2 -plasma-induced surface defects that impart a gray to black color to the nanoparticles but do not reduce the oxidation state of TiO_2 . The H_2 -plasma-induced surface defects include structural disorder. Further, the TiO_2
10 nanomaterial having photocatalytic properties absorbs visible and IR light.

 The black TiO_2 nanomaterials described herein exhibit enhanced visible and IR light absorption capabilities. The materials comprise surface defects that generate mid-band gap states, and are particularly advantageous over previously described materials in that the surface defects are structural rather than chemical;
15 that is, the TiO_2 does not contain oxygen defects or reduced titanium species, such as Ti^{3+} . The methods of creating the particles described herein use H_2 -plasma treatment of anatase TiO_2 nanoparticles under low pressure to form black TiO_2 nanoparticles with enhanced visible light photocatalytic properties for efficient decomposition of organic wastes in water. Methods described herein are highly
20 adaptable to an industrial scale, unlike high pressure hydrogenation reactions. The black TiO_2 nanoparticles produced via H_2 -plasma treatment can be used as an efficient photocatalyst for visible light decontamination of organic wastes in water, and further may be used in visible light photocatalytic water splitting to produce H_2 .

BRIEF DESCRIPTION OF THE DRAWINGS

25 The foregoing will be apparent from the following more particular description of example embodiments of the invention, as illustrated in the accompanying drawings.

 FIG. 1 is a schematic showing the visible light photocatalytic decontamination of organic pollutants in water using the interface engineered TiO_2

nanoparticles in the present invention. These TiO₂ nanoparticles have with mid-band gap states that participate in the excitation of electrons.

FIG. 2 is a schematic drawing showing the H₂-plasma treatment of white anatase TiO₂ nanoparticles (NPs) to form the black TiO₂ NPs.

5 FIG. 3 shows the UV-Vis absorption spectrum for white, black, grey and yellow TiO₂ nanoparticles.

FIG. 4 shows X-ray diffraction (XRD) spectra of untreated (white) TiO₂ nanoparticles and H₂-plasma-treated (black) TiO₂ nanoparticles of the present invention.

10 FIG. 5 shows Raman spectra of untreated (white) TiO₂ nanoparticles and H₂-plasma-treated (black) TiO₂ nanoparticles of the present invention.

FIGS. 6A and 6B shows X-ray photoelectron spectroscopy (XPS) spectra of untreated (white) TiO₂ nanoparticles and H₂-plasma-treated (black) TiO₂ nanoparticles of the present invention.

15 FIG. 7 contains digital pictures demonstrating the photocatalytic degeneration of methylene blue (5 mg/L) after simulated sun light irradiation for (a) 0 min, (b) 10 min and (c) 20 min. Vial (1) contains black TiO₂ nanoparticles of the present invention, vial (2) contains white TiO₂ nanoparticles, and vial (3) contains no TiO₂ nanoparticles. At (a) t = 0 min, each vial contains a visually-identical blue solution. At (b) t = 10 min, vial (1) exhibits a mostly gray solution, with a subtle blue tint. Vial (2) is a blue solution, though the blue is less vivid than at t = 0 min. Vial (3) remains the vivid blue color it was at t = 0 min. At (c) t = 20 min, vial (1) is completely gray in color, vial (2) is blue-gray, and vial (3) is a vivid blue color. In FIG. 7, the mass of the black TiO₂ nanoparticles and white TiO₂ nanoparticles used for vials (1) and (2), respectively, is 0.2 mg, the solution volume is 5 mL, and the concentration of methylene blue is 5 mg/L.

20

25

FIG. 8A shows the photocatalytic degradation of methylene blue with black TiO₂ nanoparticles of the present invention under simulated sun light without any filter.

30 FIG. 8B shows absorption spectra of methylene blue solution (5 mg/L) using black TiO₂ under simulated sun light with different exposure durations.

FIG. 9A shows photocatalytic degradation of methylene blue for white (square) and black (upward triangle) TiO_2 nanoparticles of the present invention. The red-colored lines are obtained under irradiation with an optical filter to filter out incident light with wavelengths shorter than 400 nm. The mass of the black TiO_2 nanoparticles is 10 mg, the solution volume is 30 mL, and the concentration of methylene blue is 5 mg/L.

FIG. 9B shows cycling tests of solar-driven photocatalytic degradation of methylene blue for black TiO_2 nanoparticles. The mass of the black TiO_2 nanoparticles is 1 mg, the solution volume is 10 mL, and the concentration of methylene blue is 5 mg/L.

FIG. 10A shows the photocatalytic degradation of Rhodamine B by black TiO_2 nanoparticles under simulated sunlight. FIG. 10B shows photocatalytic degradation of Rhodamine B by black (square) and white (circle) TiO_2 nanoparticles under simulated sunlight. The mass of the black TiO_2 nanoparticles is 0.2 mg, the solution volume is 10 mL, and the concentration of Rhodamine B is 5 mg/L.

FIG. 11A shows the photocatalytic degradation of phenol (15 mg/L) by black TiO_2 under simulated sunlight. FIG. 11B shows photocatalytic degradation of phenol by black (square) and white (circle) TiO_2 under simulated sunlight.

FIG. 12 shows an Ultraviolet Photoelectric Spectroscopy (UPS) spectrum of the valence band of the white TiO_2 nanoparticles and the black TiO_2 nanoparticles.

FIGs. 13A and 13B show Brunauer-Emmett-Teller (BET) data for the white TiO_2 nanoparticles and the black TiO_2 nanoparticles. Specifically, BET measures the specific surface area of a composition to examine physical adsorption of gases onto a solid surface.

FIG. 14 is a graph demonstrating generation of H_2 gas from water splitting catalyzed by black TiO_2 nanoparticles under solar light irradiation.

DETAILED DESCRIPTION OF THE INVENTION

A description of example embodiments of the invention follows.

The present invention is directed to metal oxide nanomaterials that have photocatalytic properties, to methods of making the metal oxide nanomaterials and

to methods of using the metal oxide nanomaterials to decompose organic wastes in water. In one embodiment, the metal oxides are TiO₂ nanomaterials having H₂-plasma-induced surface defects that impart a gray to black color to the nanoparticles but do not reduce the oxidation state of the TiO₂. Although metal oxides in addition
5 to TiO₂ can be made and used in accordance with the methods described herein, for purposes of discussion, the TiO₂ embodiment will be discussed in detail below but such discussion is not intended to be limiting to the TiO₂.

The present invention describes methods of treating anatase TiO₂ nanoparticles with H₂-plasma under low pressure to form black TiO₂ nanoparticles
10 with enhanced visible light photocatalytic properties. The present invention further describes methods of using black TiO₂ nanoparticles with enhanced visible light photocatalytic properties in the decomposition of organic wastes in water, under the frame of environment and water technology. The photocatalytic degradation of organic molecules for black (H₂-plasma treated) TiO₂ nanoparticles of the invention
15 is demonstrated by using methylene blue under simulated sun light irradiation, and is compared to degradation results using white (untreated) TiO₂ nanoparticles. It is found that the efficiency for photocatalytic degradation of organic molecules is about one order of magnitude higher for black TiO₂ nanoparticles of the invention as compared with the white TiO₂ nanoparticles. Even with the use of an optical filter
20 to filter UV-light (wavelength <425nm), the black TiO₂ still displays pronounced efficiency for photocatalytic degradation of methylene blue. The black TiO₂ nanoparticles produced via H₂-plasma treatment can be used as efficient photocatalysts for visible light decontamination of organic wastes in water. The TiO₂ nanoparticles described herein can be also used for visible light photocatalytic
25 water splitting to produce H₂.

Black TiO₂ nanomaterials

The invention described herein is directed to a black TiO₂ nanomaterial comprising a single oxidation state of Ti and further comprising H₂-plasma-induced surface disorder. What is meant by "a single-oxidation state" is that TiO₂ is found
30 only as the Ti(IV) oxidation state as in TiO₂, there are no reduced Ti species such as

Ti³⁺ in the nanomaterial. These novel materials exhibit high efficiency in the degradation of organic compounds in water.

In some embodiments of this invention, the black TiO₂ nanomaterials are nanoparticles. In alternate embodiments of the invention, the black TiO₂ nanomaterials are nanotubes, nanowires, nanoparticles, or mesoporous nanomaterials. In some embodiments of the invention, the nanomaterials comprise black TiO₂ nanoparticles. In alternate embodiments of the invention, the nanomaterials comprise ZnO nanoparticles, ZnO nanotubes, ZnO nanowires, or mesoporous ZnO nanomaterials.

10 The black TiO₂ nanomaterial of the present invention comprises H₂-plasma-induced surface defects. In some embodiments of the invention, the surface defects are created by the H₂-plasma impacting the nanoparticle or nanomaterial surface. In further embodiments of the invention, the surface defects are a layer with structural disorder. The defects created in the TiO₂ nanoparticle or nanomaterial do not
15 comprise oxygen defects, which are the defects manufactured in the method of Sugihara [8].

In some embodiments of the invention, the TiO₂ nanomaterials of the present invention comprising H₂-induced surface disorder are black. In further embodiments, the nanomaterials are a shade of gray. It is noted that for
20 convenience, the nanoparticles of the invention are referred to as black nanoparticles throughout the application. The methods of making or using gray nanoparticles are analogous to the methods of making or using black nanoparticles.

In some embodiments of the invention, the black TiO₂ nanoparticles produced by H₂-plasma treatment absorb visible and IR-light. In further
25 embodiments of the invention, the black TiO₂ nanoparticles absorb visible, IR, and UV light. The absorptivity of IR and visible light by the black TiO₂ nanoparticles of the present invention is much higher than white TiO₂ nanoparticles which have not been treated by H₂-plasma. The black TiO₂ nanoparticles of the present invention show an efficiency for photocatalytic degradation of organic molecules that is one
30 order higher than that of untreated white TiO₂ nanoparticles under visible light and solar light irradiation.

Other Metal Oxide Nanomaterials

The invention described herein is also directed to metal oxide nanomaterials having photocatalytic properties. In some embodiments of the invention, these metal oxide nanomaterials have a black to gray color. In some embodiments of the invention, the metal oxide nanomaterials comprise a single oxidation state of the metal. The metal oxide nanomaterials exhibit visible light absorbance, and further exhibit photocatalytic properties under IR, visible, UV and full spectrum light sources.

The metal oxide nanomaterials of the present invention comprise TiO_2 , as discussed above, and in further embodiments, the metal oxide nanomaterials comprise ZnO , WO_3 , SnO_3 or In_2O_3 . In some embodiments of the invention, the nanomaterials are nanotubes, nanowires, nanoparticles, or mesoporous nanomaterials.

Methods for producing black TiO_2 nanomaterials

The present invention is further directed to methods of making the black TiO_2 nanomaterials comprising a single oxidation state of Ti and further comprising H_2 -plasma-induced surface disorder. The methods of making black TiO_2 nanomaterials described herein impart photocatalytic properties to the material.

Prior methods of manufacturing TiO_2 nanoparticles with surface defects capable of improved visible light absorption have included high-pressure hydrogenation reactions [7] and treatment with H_2 -plasma [8]. Both the Chen [7] and Sugihara [8] methods yield TiO_2 nanoparticles with surface defects, however each method also produces particles with reduced oxidation state, namely containing Ti^{3+} . The presence of reduced titanium species is particularly shown in Fig. 3A of Chen [7], wherein the O1s XPS spectrum of the black TiO_2 nanoparticles exhibits a shift. Conversely, in FIG. 12 of the present invention, the UPS spectra of the valence band of the black and white TiO_2 nanoparticles are closely correlated to one another, and exhibit no new Fermi level of the valence band. There are several disadvantages of having a reduced form of Ti in nanomaterials, disadvantages that are overcome by the black TiO_2 nanomaterials of the present invention. First, reduced Ti species, especially $\text{Ti}(0)$, gives the TiO_2 nanomaterials metallic

properties, causing the band gap to disappear, as shown in valence band XPS spectrum of Chen, Fig.3C [7]. Without a bandgap, electrons that are excited by photons will quickly recombine with the holes because of the metallic properties of the nanomaterial, which decreases the photo-excitation efficiency. Secondly, the presence of reduced Ti species destabilizes the photocatalyst. The reduced Ti species is highly reactive with anions in solution, which corrodes the photocatalyst and disables the photocatalytic reaction process.

This invention presents a new approach to improve the visible light photocatalyzed decontamination of water *via* interface engineering of TiO₂ nanomaterials utilizing exposure to H₂-plasma. This method induces significant surface defects in the form of structural disorder, and therefore generates substantial mid-gap states for enhanced light absorption in visible region, as shown by the schematic in FIG. 1. Importantly, however, the black TiO₂ nanomaterials produced by the method described herein contain no reduced Ti-species, such as Ti³⁺, and no titanium species are found in the metallic form. In the method of manufacturing black TiO₂ nanomaterials from white TiO₂ nanomaterials described herein, the chemical stoichiometry of the TiO₂ material is unchanged. Further advantages over Chen include shorter reaction times, and low pressure H₂ plasma treatment, as compared to the high pressure hydrogenations of Chen, which are difficult to implement on an industrial scale. The present invention also exhibits many advantages over Sugihara. The method for generation of H₂ plasma in Sugihara utilizes a Tesla coil. Conversely, the method of H₂ plasma generation in the present invention utilizes RF frequency discharge between two plate electrodes, generating an H₂ plasma having a higher energy density than that of Sugihara. The methods disclosed herein also enable accelerated hydrogen ions directly bumping on the TiO₂ nanomaterial surfaces with high efficiency. It is of important note that exposure of TiO₂ nanomaterials to H₂ plasma generated by Tesla coil cannot make black TiO₂ nanomaterials.

As depicted in FIG. 2, the black TiO₂ nanomaterials of the invention are fabricated through H₂-plasma treatment of white TiO₂ nanomaterials under low pressure. A TiO₂ nanomaterial of the present invention, having photocatalytic

properties is made by introducing white TiO₂ nanomaterial into a chamber. The white TiO₂ nanomaterial is exposed to H₂-plasma under reduced pressure at an elevated temperature and a H₂-plasma flow rate. In certain embodiments of the invention, the elevated temperature is from about 500 °C to about 750 °C. In
5 preferred embodiments of the invention, the elevated temperature is from about 650 °C to about 750 °C. In certain embodiments of the invention, the H₂-plasma flow rate is from about 30 sccm to about 100 sccm. In preferred embodiments of the invention, the H₂-plasma flow rate is from about 40 sccm to about 80 sccm. In certain embodiments of the invention, the reduced pressure is from about 10⁻³ to
10 about 10⁻⁴ atm. In preferred embodiments of the invention, the reduced pressure is about 8 x 10⁻⁴ atm. The nanomaterial is exposed to the conditions described for a period of time sufficient to generate a TiO₂ nanomaterial of the present invention, having photocatalytic properties. In some embodiments of the invention, the period of time sufficient to generate a TiO₂ nanomaterial is from about 2 hours to about 10
15 hours. In a preferred embodiment of the invention, the period of time sufficient to generate a TiO₂ nanomaterial is from about 7 hours to about 8 hours at 110W. In an example embodiment, commercially available white anatase TiO₂ particles (MTI Corporation, average particle diameter about 8-10 nm) is placed into the chamber of Plasma-enhanced chemical vapor deposition (PECVD). Hydrogen gas with a flow
20 rate of 60sccm are introduced at a temperature of 720 °C, a low pressure (10⁻⁴ to 10⁻³ atm), and an RF plasma of 110W. The black powders are collected after 8 hours. In some embodiments of the invention, the plasma is generated within the PECVD chamber by RF frequency discharge between two plate electrodes.

In some embodiments of the invention, the surface defects are created by the
25 H₂-plasma impacting the nanoparticle or nanomaterial surface. In further embodiments of the invention, the surface defects are a layer with structural disorder. The defects created in the TiO₂ nanoparticle or nanomaterial do not comprise oxygen defects, which are the defects manufactured in the method put forth by Sugihara.

30 In some embodiments of the invention, the longer the duration of white TiO₂ nanomaterial exposure to H₂-plasma, the more the the UV-visible light absorptivity

of the nanomaterial improves (FIG. 3). In some embodiments of the invention, the nanomaterial is exposed to H₂ plasma for about 2 hours to about 10 hours. In preferred embodiments, the nanomaterial is exposed to H₂ plasma for about 7 hours to about 8 hours.

5 *Characterization and structure of the black TiO₂ nanomaterials*

In some embodiments of the invention, the crystal structure of the black TiO₂ nanoparticles is evaluated by X-ray diffractometry (XRD) and Raman spectroscopy. In some embodiments of the invention, the TiO₂ nanoparticles are of the anatase form of TiO₂, the rutile form of TiO₂, the brookite form of TiO₂, or the mixed phase
10 form of TiO₂. In a preferred embodiment, the TiO₂ nanoparticles of the invention are of the anatase form of TiO₂. In further embodiments of the invention, the black TiO₂ nanomaterials may be nanowires or nanowires. X-ray photoelectron spectroscopy (XPS) is carried out on the materials of the invention in order to determine characteristics of the surface of the material, including elemental
15 composition, empirical formula, chemical state and electronic state. The black TiO₂ nanoparticles of the present invention do not exhibit any shift in orbital energy or intensity relative to the white TiO₂ nanoparticle starting material as examined by XPS. This data shows that the black TiO₂ nanomaterials of the present invention do not include any reduced Ti-species, such as Ti³⁺ and further do not include any
20 titanium species in the metallic form (Ti⁰). In some embodiments of the invention, the surface of the TiO₂ nanomaterial comprises surface defects. In further embodiments of the invention, the surface defects include structural disorder and H interstitials.

Photocatalytic decomposition of organic compounds

25 The compositions of the present invention are useful for the photocatalytic degradation of pollutant organic compounds in a water source. In some embodiments of the invention, the water source is groundwater, industrial wastewater, municipal wastewater, hospital wastewater, or laboratory wastewater. In preferred embodiments of the invention, the water source is industrial wastewater
30 or groundwater. When exposed to a light source, the electrons in the valence band

of the compositions of the present invention are excited to a mid-gap state, or similarly, from a mid-gap state to a conduction band. The excited electrons are consumed by O₂ dissolved in water, and this reactive oxygen species oxidizes the organic compounds into CO₂ and water. This reaction necessitates the

5 photoexcitation process of the photocatalyst. H₂-plasma treatment induced mid-gap states enable the photoexcitation of the electrons by visible light enabling the decomposition of organic compounds under visible light irradiation. In some embodiments of the invention, the visible light is solar light. In other embodiments of the invention, the visible light is tungsten light or fluorescent light. The light

10 used for the excitation of the nanomaterial of the invention comprises visible light or infrared (IR) light, and optionally comprises ultraviolet (UV) light.

The water source that is treated with the TiO₂ nanomaterials of the present invention comprises water, organic compounds, and optionally comprises other components including but not limited to pathogens such as viruses and bacteria,

15 non-pathogenic bacteria, organic particulate matter, soluble organic material, inorganic particulate matter, soluble inorganic material, gases, pharmaceuticals, and toxins. Many organic compounds are subject to decomposition upon treatment with a light source and a composition of the present invention. In some embodiments of the present invention, the organic compounds include methylene blue, Rhodamine

20 B, and phenol. Other compounds for use with the invention include aniline, pesticides such as chlorobenzene, and herbicides, such as 4-chlorophenyl isocyanate.

In some embodiments of the invention, the organic compound is treated with a light source and a black TiO₂ nanomaterial for about one minute to about 60 minutes. The length of visible light irradiation required to decompose an organic

25 compound is a function of the concentration of the organic material, the wavelength and intensity of the light source, and the concentration of the photocatalyst in solution. In an example embodiment, a typical length of visible light irradiation is from about 10 minutes to about 20 minutes at a concentration of 5 mg/L of the organic compound.

30 In some embodiments of the invention, the black TiO₂ nanoparticles produced by H₂-plasma treatment show an efficiency for photocatalytic degradation

of organic molecules that is one order higher than that of untreated white TiO₂ nanoparticles under solar light and visible light irradiation.

In further embodiments of the invention, the black TiO₂ nanomaterials described herein are used for photocatalytic water splitting to produce H₂ gas under visible light. A method of water-splitting is described by Chen [7], the teachings of which are incorporated by reference. In an embodiment of the invention, a solar light simulator is used as an excitation source, pointed at a solution of the black TiO₂ nanoparticles of the invention, a catalytic portion of Pt, and a solvent of water and methanol mixture. In some embodiments of the invention, the Pt is Pt(0). In further
10 embodiments of the invention, the Pt is a Pt(II) or Pt(IV) source, such as H₂PtCl₆. In an embodiment of the invention, an amount of Pt from about 0.5 weight % to about 1 weight % is added to a solution of about 20 mg to about 50 mg of the black TiO₂ nanoparticles of the present invention in about 20 ml to about 50 ml of about 4:1 water-methanol solution. The resulting mixture is kept in a sealed beaker with
15 quartz windows, through which light is irradiated. In some embodiments of the invention, the light is generated by a solar simulator. The H₂ gas that is generated is collected into a container connected to the beaker. In some embodiments of the invention, the volume of H₂ is measured in the collection container. In alternate embodiments of the invention, the H₂ is measured by gas chromatography.

20 The black TiO₂ nanomaterials described herein exhibit enhanced visible and IR light absorption capabilities. The materials comprise surface defects that generate mid-band gap states, and are particularly advantageous over previously described materials in that the surface defects are structural rather than chemical; that is, the TiO₂ does not contain oxygen defects or reduced titanium species, such
25 as Ti³⁺. The method of creating the particles described herein uses H₂-plasma treatment of anatase TiO₂ nanoparticles under low pressure to form black TiO₂ nanoparticles with enhanced visible light photocatalytic properties for efficient decomposition of organic wastes in water. This method is highly adaptable to an industrial scale, unlike high pressure hydrogenation reactions. The black TiO₂
30 nanoparticles produced via H₂-plasma treatment can be used as an efficient

photocatalyst for visible light decontamination of organic wastes in water, and further may be used in visible light photocatalytic water splitting to produce H₂.

DEFINITIONS

5 As used herein, “interface engineered” means modified at the surface and interface.

As used herein, a “mid-band gap state” is an accessible electronic state between the conduction band and the valence band of a semiconductor material.

10 The term “nanomaterial” can mean a nanoparticle, nanowire, nanotube, or mesoporous nanomaterial. When used in the context of a photocatalytic reaction of the decomposition of organic compounds or of water-splitting, “nanomaterial” can be used interchangeably with “photocatalyst”.

As used herein, the term “surface defects” means structural defects in the surface of a material.

15 As used herein, “structural disorder” means the atoms are located in disordered positions and not the ordered position. For example, Ti and O atoms are located in disordered positions and not ordered positions as in a TiO₂ crystal. Further, some H interstitials may induce disorder.

20 As used herein “untreated TiO₂” refers to TiO₂ that has not undergone treatment with H₂-plasma. “Untreated TiO₂” may be used interchangeably with “white TiO₂” and “commercially available TiO₂.”

25 The term “metallic form” refers to a form of a compound that exhibits metallic properties. For example, Ti₂O₃ is regarded herein as a metallic form of a titanium species due to its high conductivity. A metallic form of a titanium species may also include Ti(0).

30 An organic compound is a small molecule comprising carbon and hydrogen. Classes of organic compounds for use in the present invention include aromatic compounds, heteroaromatic compounds, aliphatic compounds, alcohols, amines, and other organic compounds that may be oxidized.

EXAMPLES

The following examples are provided to illustrate one or more preferred embodiments of the invention, but are not limited embodiments thereof. Numerous variations can be made to the following examples that lie within the scope of the invention.

5 *Example 1: Production of black TiO₂ nanoparticles*

500 mg of commercially available white anatase TiO₂ particles (MTI Corporation, average particle diameter about 8-10 nm) were placed into the chamber of Plasma-enhanced chemical vapor deposition (PECVD). Hydrogen gases with a flow rate of 60sccm were introduced at a temperature of 720 °C, a low pressure of
10 10⁻⁴ to 10⁻³ atm, and an RF plasma of 110W. The black powders were collected after 8 hours.

Example 2: Characterization and structure of black TiO₂ nanoparticles

The crystal structure of the black TiO₂ nanoparticles was evaluated by XRD as shown in FIG. 4 and Raman spectroscopy as shown in FIG. 5. X-ray
15 diffractometry (XRD) was performed on a Bruker AXS D8 system using Cu K α radiation. Room temperature micro-Raman scattering analyses were carried out with a Renishaw spectrometer using Ar⁺ (514.5nm) laser excitation source. X-ray photoelectron spectroscopy (XPS) was carried out in a homemade ultrahigh vacuum system with Omicron Twin-Anode X-ray gun. As shown in FIG. 4 and FIG. 5, the
20 H₂-plasma treatment does not affect the crystal structure of TiO₂ nanoparticles and they remain in the pristine anatase phase. From XPS measurement (FIGs. 6A and 6B), we did not observe any reduced chemical state for TiO₂, such as Ti³⁺. This suggests that the H₂-plasma treatment mainly induces formation defects related gap states at the surface region of TiO₂ nanoparticles and hence leads to the enhanced
25 visible light absorption. Further, Brunauer-Emmett-Teller (BET) data obtained for the white TiO₂ nanoparticles and the black TiO₂ nanoparticles demonstrates that the surface area and pore volume of TiO₂ nanoparticles changes only slightly after treatment with H₂ plasma (FIG. 13).

Example 3: Photocatalytic decomposition of methylene blue

The photocatalytic degradation of methylene blue under visible light irradiation by filtering out incident light with wavelengths shorter than 425 nm was carried out with Abet technologies sun 2000 solar simulator ($100\text{mW}/\text{cm}^2$). In a typical experiment, 10 mg of the white or black TiO_2 was added into an aqueous solution (30 mL) containing 5mg/L methylene blue. The mixed solution was placed in a 50ml beaker and stirred with a magnetic stirrer. The circulated water jacket was used to keep the temperature of the beaker at around 25 °C during irradiation. After a given irradiation time, the UV-visible absorption spectrum (Shimadzu UV3600) was measured to estimate the concentration of the remaining methylene blue in the solution by the integration of the absorption peak.

FIG. 7 shows the digital pictures of photocatalytic degradation of methylene blue (5mg/L) after simulated sun light irradiation using 0.2 mg black and white TiO_2 in comparison with the condition of without any TiO_2 nanoparticles. Clearly, black TiO_2 nanoparticles displays much better efficiency in terms of photocatalytic decomposition of methylene blue. FIG. 8 shows the corresponding summarized results for photocatalytic decomposition of methylene blue with different concentration, and representative UV-Vis spectra during the photocatalytic decomposition of methylene blue and with different durations. FIG. 9 shows the comparison of the photocatalytic decomposition of methylene blue using black and white TiO_2 , and with or without optical filter. It is found that the efficiency for photocatalytic degradation of organic molecules is about one order higher for black TiO_2 as compared with the white TiO_2 nanoparticles. In particular, by using optical filter to filter out UV-light (wavelength $< 425\text{ nm}$), the black TiO_2 still displays pronounced efficiency for photocatalytic degradation of methylene blue. Further, the photocatalytic degradation of methylene blue using the black TiO_2 of the present invention proceeds to completion with less irradiation time (FIG. 9A) than with the black TiO_2 of Chen [7] under analogous conditions (Chen, Fig. 2A).

Example 4: Photocatalytic decomposition of Rhodamine B and phenol

The photocatalytic degradation of Rhodamine B and phenol under simulated sun light were also carried out with Abet technologies sun 2000 solar simulator. A mass of 0.2mg of the white or black TiO_2 was added into an aqueous solution

(10mL) containing 5mg/L Rhodamine B or 15mg/L phenol. After a given irradiation time, the UV-visible absorption was recorded to estimate the concentration of the remaining Rhodamine B or phenol in the solution (FIG. 10A and FIG. 11A). FIGs. 10B and 11B show the comparison of the photocatalytic decomposition of Rhodamine B and phenol, respectively, using black and white TiO₂. Results show higher performance of black TiO₂ than white TiO₂ in Rhodamine B and phenol degradation by solar light irradiation.

Example 5: Hydrogen production from photocatalytic water splitting

50 mg black TiO₂ nanoparticles of the invention were dispersed in 5 ml DI water by ultrasonication and 100 µl Chloroplatinic Acid (H₂PtCl₆) solution (10.5mg/ml) was added. The mixed solution was kept in UV irradiation (Philips 8W, 253.7nm) for 2 hours and dried in an oven at 90 °C for 10 hours. The dried black TiO₂ with 1 wt% Pt was then added into methanol solution ($V_{\text{methanol}}: V_{\text{water}} = 1:4$). The pH value of the solution was measured by a pH meter (Fisher Scientific, accumant AB15) and adjusted to pH = 7 by additions of NaOH solution. The final solution was then transferred and sealed in a beaker with a quartz window. Light irradiation generated by the solar generator (Abet technologies sun 2000 solar simulator) was then applied onto the samples through the window. H₂ gas generated from the beaker was then collected by a bottom-up water container connected to the reaction beaker by a pipe. The whole reaction was kept at room temperature and atmospheric pressure (1 atm). The H₂ gas volume was recorded according to the irradiation time to get the H₂ production rate. As seen in FIG. 14, the H₂ production rate in the water-splitting reaction catalyzed by H₂-plasma treated black TiO₂ nanoparticles of the present invention is 23 mmol·h⁻¹·g⁻¹, which is two times greater than the H₂ production rate in the analogous experiment performed using the black TiO₂ nanoparticles of Chen [7] (Chen, page 748, H₂ generation rate reported as 10 mmol·h⁻¹·g⁻¹).

REFERENCES

1. Shannon, M. A., *et al. Nature* 452, (2008), 301-310.

2. Pozzo, R. L., *et al. Catalysis Today* 39, (1997), 219-231.
3. Grätzel, M. *Nature* 414, (2001), 338.
4. Chen, X. *et al. Chem. Rev.* 110, (2010), 6503.
5. Chen, X. *et al. Chem. Rev.* 107, (2007), 2891.
- 5 6. Fujishima, A. *et al. Surf. Sci. Rep.* 63 (2008), 515.
7. Chen, X., *et al.* Increasing Solar Absorption for Photocatalysis with Black Hydrogenated Titanium Dioxide Nanocrystals. *Science* 331 (2011), 746-750.
8. Sugihara, S. Visible Radiation Type Photocatalyst and Production Method Thereof. US patent 6,908,881 B1. 21 June 2005.

10

The teachings of all patents, published applications and references cited herein are incorporated by reference in their entirety.

While this invention has been particularly shown and described with references to example embodiments thereof, it will be understood by those skilled in
15 the art that various changes in form and details may be made therein without departing from the scope of the invention encompassed by the appended claims.

CLAIMS

What is claimed is:

1. A metal oxide nanomaterial having photocatalytic properties and having H₂-plasma-induced surface defects that do not reduce the oxidation state of the metal oxide, wherein the metal oxide is TiO₂, ZnO, WO₃, SnO₃ or In₂O₃.
5
2. The nanomaterial of Claim 1 wherein the metal oxide is TiO₂ and wherein the nanomaterial has H₂-plasma-induced surface defects that impart a gray to black color to the nanoparticles but do not reduce the oxidation state of TiO₂.
3. The nanomaterial of Claim 2, wherein the H₂-plasma-induced surface defects include structural disorder.
10
4. The nanomaterial of Claim 3, wherein the black TiO₂ nanomaterial absorbs visible and IR light.
5. The chemical composition of Claim 4, wherein the TiO₂ nanomaterial is a nanoparticle, a nanotube or a nanowire.
- 15 6. A method of making a metal oxide nanomaterial having photocatalytic properties, the method comprising:
contacting a metal oxide nanomaterial starting material with
hydrogen plasma at a temperature, pressure and hydrogen plasma
flow rate for a period of time sufficient to produce H₂-plasma induced
20 surface defects on the metal oxide but not reduce the oxidation state
of the metal oxide, wherein the metal oxide nanomaterial has
photocatalytic properties and is selected from TiO₂, ZnO, WO₃, SnO₃
or In₂O₃.
7. The method of Claim 6, wherein the metal oxide nanomaterial starting
25 material is white TiO₂ nanomaterial.

8. The method of Claim 6, wherein the metal oxide nanomaterial having photocatalytic properties is black TiO₂ nanomaterial.
9. The method of Claim 6, wherein the pressure is a pressure lower than atmospheric pressure.
- 5 10. The method of Claim 9, wherein the TiO₂ nanomaterial having photocatalytic properties is black TiO₂ nanomaterial having H₂-plasma-induced surface defects that impart a black color to the nanoparticles but do not reduce the oxidation state of TiO₂.
- 10 11. The method of Claim 10, wherein the H₂-plasma-induced surface defects include structural disorder.
12. The method of Claim 11, wherein the TiO₂ nanomaterial is a nanoparticle, a nanotube, or a nanowire.
13. A method for decomposing an organic compound in water, the method comprising:
 - 15 (a) contacting an aqueous solution comprising an organic compound with a metal oxide nanomaterial having photocatalytic properties, wherein the metal oxide is TiO₂, ZnO, WO₃, SnO₃ or In₂O₃, to form a mixture; and
 - 20 (b) exposing the mixture of step (b) to a visible light source, the visible light source optionally including an ultraviolet filter, for an amount of time sufficient to decompose the organic compound.
14. The method of Claim 13, wherein the metal oxide nanomaterial having photocatalytic properties is a TiO₂ nanomaterial having H₂-plasma-induced surface defects that impart a gray to black color to the nanoparticles but do
25 not reduce the oxidation state of TiO₂.
15. The method of Claim 14, wherein the H₂-plasma-induced surface defects include structural disorder.

16. The method of Claim 14, wherein the TiO_2 nanomaterial having photocatalytic properties absorbs visible and IR light.
17. The method of Claim 16, wherein the TiO_2 nanomaterial having photocatalytic properties is a photocatalyst for decomposition of an organic compound.
18. The method of Claim 17, wherein the photocatalyst is reusable in the process of decomposition of an organic compound.
19. A method for splitting water to form H_2 gas, the method comprising:
- (a) contacting an aqueous solution comprising methanol and a metal oxide nanomaterial having photocatalytic properties, wherein the metal oxide nanomaterial is TiO_2 , ZnO , WO_3 , SnO_3 or In_2O_3 ; with a platinum species to form a mixture; and
 - (b) irradiating the mixture of step (a) with a visible light source to form H_2 gas.
20. The method of Claim 19, wherein the metal oxide nanomaterial having photocatalytic properties is a TiO_2 nanomaterial having H_2 -plasma-induced surface defects that impart a gray to black color to the nanoparticles but do not reduce the oxidation state of TiO_2 .
21. The method of Claim 20, wherein the H_2 -plasma-induced surface defects include structural disorder.
22. The method of Claim 21, wherein the TiO_2 nanomaterial having photocatalytic properties absorbs visible and IR light.