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. 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.

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 at least ameliorates, one or more of the disadvantages described above.

Summary

According to a first aspect, there is provided a photocatalyst comprising metal oxide semiconductor nanoparticles in crystalline form integrally formed on ~~a~~the surface of a substrate made of the corresponding metal~~.~~, wherein said substrate has been oxidized in an oxidant solution at an oxidation temperature of from 60°C to 80°C to integrally form said nanoparticles, and wherein said oxidized substrate has further been thermally treated from the oxidation temperature to attain a maximum temperature of 450°C at a heating rate of between 5 to 15°C/min.

Advantageously, when in use, the integrally formed metal oxide semiconductor nanoparticles do not give rise 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 the group consisting of ZnO, TiO_2, SnO_2, WO_3, Fe_2O_3, Bi_2O_3, MoO_3, ZrO_2 and Nb_2O_5. 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 at an oxidation temperature of from 60°C to 80°C ~~under conditions~~ to integrally form metal oxide semiconductor nanoparticles in crystalline form thereon ~~.~~; and c. thermally treating the oxidized substrate from the oxidation temperature to attain a maximum temperature of 450°C, wherein said thermal treatment step occurs at a heating rate of between 5 to 15°C/min.

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 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 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 comprises a photocatalyst comprising metal oxide semiconductor nanoparticles in crystalline form integrally formed on ~~a~~the surface of a substrate made of the corresponding metal, wherein said substrate has been oxidized in an oxidant solution at an oxidation temperature of from 60°C to 80°C to integrally form said nanoparticles, and wherein said oxidized substrate has further been thermally treated from the oxidation temperature to attain a maximum temperature of 450°C at a heating rate of between 5 to 15°C/min and wherein each stage further comprises a light source.

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 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 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 a~~the~~ surface of a substrate made of the corresponding metal, wherein said substrate has been oxidized in an oxidant solution at an oxidation temperature of from 60°C to 80°C to integrally form said nanoparticles, and wherein said oxidized substrate has further been thermally treated from the oxidation temperature to attain a maximum temperature of 450°C at a heating rate of between 5 to 15°C/min, 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.

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.

2. The photocatalyst as claimed in claim 1, wherein the metal oxide semiconductor is selected from the group consisting of ZnO, TiO_2, SnO_2, WO_3, Fe_2O_3, Bi_2O_3, MoO_3, ZrO_2 and Nb_2O_5.

3. The photocatalyst as claimed in claim 2, wherein the metal oxide semiconductor is ZnO.

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.

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.

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, 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.

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. A method of producing a photocatalyst comprising the steps of:
    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.

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.

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, HNO_3 and mixtures thereof.

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%.

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%.

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

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

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.

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.

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

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.

Claims

1. A photocatalyst comprising metal oxide semiconductor nanoparticles in crystalline form integrally formed on a surface of a substrate made of the corresponding metal, wherein said substrate has been oxidized in an oxidant solution at an oxidation temperature of from 60°C to 80°C to integrally form said nanoparticles, and wherein said oxidized substrate has further been thermally treated from the oxidation temperature to attain a maximum temperature of 450°C at a heating rate of between 5 to 15°C/min.

2. The photocatalyst as claimed in claim 1, wherein the metal oxide semiconductor is selected from the group consisting of ZnO, TiO_2, SnO_2, WO_3, Fe_2O_3, Bi_2O_3, MoO_3, ZrO_2 and Nb_2O_5.

3. The photocatalyst as claimed in claim 2, wherein the metal oxide semiconductor is ZnO.

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.

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.

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, 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.

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. A method of producing a photocatalyst comprising the steps of:

a. providing a substrate of a transition metal;

b. oxidizing the metal substrate in an oxidant solution at an oxidation temperature of from 60°C to 80°C to integrally form metal oxide semiconductor nanoparticles in crystalline form thereon; and

c. thermally treating the oxidized substrate from the oxidation temperature to attain a maximum temperature of 450°C, wherein said thermal treatment step occurs at a heating rate of between 5 to 15°C/min.

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.

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, HNO_3 and mixtures thereof.

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%.

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%.

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

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

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.

21. The method as claimed in any one of claims 10 to 20, wherein the oxidizing step is conducted for at least 72 hours.

22. The method as claimed in claim 10, wherein the metal oxide semiconductor nanoparticles formed possess an average particle size of from about 30 nm to about 100 nm.

23. 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 a surface of a substrate made of the corresponding metal, wherein said substrate has been oxidized in an oxidant solution at an oxidation temperature of from 60°C to 80°C to integrally form said nanoparticles, and wherein said oxidized substrate has further been thermally treated from the oxidation temperature to attain a maximum temperature of 450°C at a heating rate of between 5 to 15°C/min and wherein each stage further comprises a light source.

24. The photocatalytic water treatment system as claimed in claim 23, wherein said light source is arranged to substantially irradiate at least one planar surface of said photocatalyst.

25. The photocatalytic water treatment system as claimed in claim 23 or claim 24, 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.

26. The photocatalytic water treatment system as claimed in claim 25, wherein said flow path substantially traces the perimeter of said photocatalysts and said light source.

27. 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 a surface of a substrate made of the corresponding metal, wherein said substrate has been oxidized in an oxidant solution at an oxidation temperature of from 60°C to 80°C to integrally form said nanoparticles, and wherein said oxidized substrate has further been thermally treated from the oxidation temperature to attain a maximum temperature of 450°C at a heating rate of between 5 to 15°C/min, 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.