ABSTRACT

The present disclosure relates to zinc sulfide nanostructures and a process for synthesis thereof at large scale. The present disclosure particularly relates to a template free synthesis of mono-dispersed, nanostructures of zinc sulfide by using solid state method. The process involves mixing of zinc oxide and thiourea in a molar ratio of 1:2 to 1:10, at a temperature of about 200°C to obtain nanostructures of zinc sulfide.

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We claim,

1. A process for synthesis of nanostructures of zinc sulfide, said process comprising the following steps;
    a) mixing zinc oxide and thiourea under triturationat a molar ratio ranging between 1:2 and 1:10 to obtain a first mixture;
    b) heating the first mixture at a temperature ranging between 100°C and 200°C for a time period ranging between 10hr. and 20hrs. to obtain a second mixture containing nanostructures of zinc sulfide; and
    c) washing the second mixture with a solvent and subsequently drying at a temperature ranging between 50°C and 90°Cfor a time period ranging between 1hrs. and8hrs. to obtain purified nanostructures of zinc sulfide.
2. The process as claimed in claim1, wherein the temperature for heating the first mixture is maintained in the range of 110°C to 150°C for a time period ranging between 15hrs. and 17 hrs.
3. The process as claimed in claim1, wherein the solvent is at least one selected from the group comprising of water, ethanol and methanol.
4. The process as claimed in claim1, wherein the particle size of the nanostructures of zinc sulfide is in the range of 1nm to 30nm; preferably 5nm to 20nm.
5. Nanostructures of zinc sulfide obtained by the process as claimed in claim 1; said nanostructures being characterized by:
    i. A particle size ranging between 1nm and 30nm,preferably 5nm to 20nm.;

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ii. a surface area ranging between 70 m^2/g and 150 m^2/g, preferably 110.9m^2/g;

iii. a trigonal crystal structure;

iv. an optical absorbance of 321nm to 330nm;

v. a band gap in the range of 3.75 eV and 3.86 eV; and

vi. an X-Ray diffraction pattern having 2θ values at 28.29^0, 47.58^0 and 56.41^0.

6. Nanostructures of zinc sulfide as claimed in claim 5, exhibits H_2 generation rate in the range of 143.5 µmol/hr./0.1g to 205µmol/hr./0.1g.

7. A process for generation of H_2, said process comprising the following steps;

I. Preparing nanostructures of zinc sulfide, which comprises;

a) mixing zinc oxide and thiourea under triturationat a molar ratio ranging between 1:2 and 1:10 to obtain a first mixture;

b) heating the first mixture at a temperature ranging between 100°C and 200°C for a time period ranging between 10hrs. and 20hrs. to obtain a second mixture containing nanostructures of zinc sulfide; and

c) washing the second mixture with a solvent and subsequently drying at a temperature ranging between 50°C and 90°C for a time period ranging between 1hr. and 8hrs. to obtain purified nanostructures of zinc sulfide; and

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II. suspending the nanostructures of zinc sulfide in an aqueous solution and subsequently irradiating said aqueous solution by UV radiation to generate H_2.

8. *The process as claimed in claim 7, wherein the amount of zinc sulfide is* maintained in the range of 0.05% to 0.2% with respect to the total mass of the aqueous solution.

9. The process as claimed in claim 7, wherein the aqueous solution comprises water, alcohol and optionally, at least one electrolyte.

10. The process as claimed in claim 7, wherein the process further comprises incorporation of platinum in an amount ranging between 0.2%and 0.8% with respect to the total amount of zinc sulfide.

Dated this 16th day of September, 2013

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FIELD OF THE DISCLOSURE:

The present disclosure relates to nanostructures of zinc sulfide and a process for synthesis thereof.

BACKGROUND:

In recent years, much effort has been devoted to the research of doped metal chalcogenide nanostructured materials. A metal chalcogenide is a compound made from a metallic element and a member of the chalcogenide family, namely the elements under oxygen, sulfur, selenium, and tellurium. Metal chalcogenides include cadmium sulfide (CdS), cadmium selenide (CdSe), cadmium telluride (CdTe), zinc sulfide (ZnS), and lead telluride (PbTe).

The nanomaterials of these metal chalcogenide exhibit improved physical and chemical properties in comparison with their bulk materials, such as size-dependent variation of the band gap energy. Altering the size of the particles changes the degree of confinement of electrons, which affects the electronic structure of the solid especially the band gap edges. As the dimensions of the particle become comparable or less than the Bohr radius of the excitation, its electronic properties change significantly by quantum confinement effect, which can be observed as a blue shift in the band gap or excitation energy.

The nanomaterials of metal chalcogenide have promising applications in multiple technical fields including photochemical catalysis, gas sensors, detectors for laser and infrared, solar cells, nonlinear optical materials, various luminescence devices, optoelectronic devices and the like.

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Among the afore-stated metal chalcogenide, zinc sulfide is one of the first discovered compound semiconductors and probably one of the most important materials in electronic/optoelectronic industries with prominent applications in flat-panel displays, sensors, lasers, and photocatalysis.

However, prior art mainly discloses the use of powdered photo-catalysts for the production of H_2 and O_2. But, these powdered photo-catalyst yields a mixture of H_2 and O_2 since the redox sites to produce H_2 and O_2 are in close proximity.

In this regard, the use of the nanostructures of these photo-catalysts and more particularly, the nanostructures of zinc sulfide in ultra violet light assisted photocatalysis has immense importance because of their narrow band gap. Further, there is also a need to evaluate the photocatalytic water splitting capacity of two and three dimensional structures of the nanostructured zinc sulfide.

Prior art further discloses various methods such as, single-source precursor, solvothermal and microwave (MW) irradiation to fabricate zinc sulfide nanomaterials in various shapes, such as sheet, rod, wire, belt, tube, heptapods and tetrapods, multiangular branched shape and the like. However, these methods require expensive templates and harsh reaction conditions and involve the use of hazardous chemicals.

Therefore, there is felt a need to develop a process for synthesis of nanostructures of zinc sulfide.

OBJECTS:

Some of the objects of the present disclosure, which at least one embodiment herein satisfies, are as follows:

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It is an object of the present disclosure to ameliorate one or more problems of the prior art or to at least provide a useful alternative.

It is another object of the present disclosure to provide a simple and economic process for the synthesis of nanostructures of zinc sulfide.

It is yet another object of the present disclosure to provide nanostructures of zinc sulfide in a cost effective manner.

Other objects and advantages of the present disclosure will be more apparent from the following description when read in conjunction with the accompanying drawing, which are not intended to limit the scope of the present disclosure.

SUMMARY:

In accordance with one aspect of the present disclosure there is provided a process for the synthesis of nanostructures of zinc sulfide, said process comprising the following steps;

a) mixing zinc oxide and thiourea under trituration at a molar ratio ranging between 1:2 and 1:10 to obtain a first mixture;
b) heating the first mixture at a temperature ranging between 100°C and 200°C for a time period ranging between 10hrs. and 20hrs. to obtain a second mixture containing nanostructures of zinc sulfide; and
c) washing the second mixture with a solvent and subsequently drying it at a temperature ranging between 50°C and 90°C for a time period ranging between 1hr. and 8hrs. to obtain purified nanostructures of zinc sulfide.

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Typically, the temperature for heating the first mixture is maintained in the range of 110°C to 150°C for a time period ranging between 15hrs. and 17hrs.

Typically, the solvent is at least one selected from the group comprising of water, ethanol and methanol.

Typically, the particle size of the nanostructures of zinc sulfide is in the range of 1nm to 30nm, preferably 5nm to 20nm.

Typically, the nanostructures of zinc sulfide are characterized by:

i. a particle size ranging between 1nm and 30 nm, preferably 5nm to 20nm;
ii. a surface area ranging between 70 m^2/g and 150 m^2/g, preferably 110.9 m^2/g;
iii. a trigonal crystal structure;
iv. an optical absorbance of 321nm to 330nm;
v. a band gap in the range of 3.75 eV and 3.86 eV; and
vi. an X-Ray diffraction pattern having 2θ values at 28.29^0, 47.58^0 and 56.41^0.

Typically, the nanostructures of zinc sulfide exhibit H_2 generation rate in the range of 143.5 µmol/hr./0.1g to 205 µmol/hr./0.1g.

In accordance with another aspect of the present disclosure there is provided a process for generation of H_2; said process comprising the following steps;

I. preparing nanostructures of zinc sulfide, which comprises;

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a) mixing zinc oxide and thiourea under trituration at a molar ratio ranging between 1:2 and 1:10 to obtain a first mixture,

b) heating the first mixture at a temperature ranging between 100°C and 200°C for a time period ranging between 10hrs. and 20hrs. to obtain a second mixture containing nanostructures of zinc sulfide; and

c) washing the second mixture with a solvent and subsequently drying at a temperature ranging between 50°C and 90°C for a time period ranging between 1hr. and 8hrs. to obtain purified nanostructures of zinc sulfide; and

II. suspending the nanostructures of zinc sulfide in an aqueous solution and subsequently, irradiating said aqueous solution by UV radiation to generate H_2.

Typically, the amount of zinc sulfide is maintained in the range of 0.05% to 0.2% with respect to the total mass of the aqueous solution.

Typically, the aqueous solution comprises water, alcohol and optionally, at least one electrolyte.

Typically, the process further comprises incorporation of platinum in an amount ranging between 0.2% and 0.8% with respect to the total amount of zinc sulfide.

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BRIEF DESCRIPTION OF THE ACCOMPANYING DRAWINGS:

Figure 1: illustrates UV-DRS spectrum of the nanostructures of zinc sulfide in which A and B represent UV-DRS spectrum of the nanostructures of zinc sulfide using zinc oxide and thiourea at a molar ratio of 1:2 and 1:10 respectively; and

Figure 2: illustrates XRD pattern of the nanostructures of zinc sulfide in which A and B represent XRD spectrum of the nanostructures of zinc sulfide using zinc oxide and thiourea at a molar ratio of 1:2 and 1:10 respectively.

Figure 3: illustrates Transmission electron microscopy (TEM) images of nanostructures of zinc sulfide, in which a, b and c, d represents (TEM) images of nanostructures of zinc sulfide using zinc oxide and thiourea at a molar ratio of 1:2 1:10 respectively; and e and f represent electron diffraction (ED) patterns of nanostructures of zinc sulfide using zinc oxide and thiourea at a molar ratio 1:2 and 1:10, respectively.

DETAILED DESCRIPTION:

To overcome the afore-stated problems of the prior art the inventors of the present disclosure have developed a template free synthesis of mono-dispersed and nanostructured zinc sulfide by using a solid state method. These synthesized zinc sulfides are then extensively studied with respect to their structural, morphological and optical properties.

Prior art discloses zinc sulfide as a safe, non-toxic and thermally stable ultra-violet light photocatalyst. Therefore, the inventors have investigated the ability of these

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synthesized zinc sulfides with regard to the evolution of hydrogen by splittingH_2O or organic dyes.

Surprisingly, it has been found that zinc sulfide nanostructures exhibit fivefold enhancement in the hydrogen evolution rate (205 μmole / hr.) as compared with its bulk counterpart (41 μmole / hr.).

In accordance with one aspect of the present disclosure there is provided a process for synthesis of nanostructures of zinc sulfide, said process involves homogenization of zinc oxide and thiourea in various stoichiometric ratios, under solid state condition to obtain nanostructures of zinc sulfide. These nanostructures are then characterized by various techniques to elucidate the physicochemical, morphological and structural properties. The inventors of the present disclosure have surprisingly found that the particle size of the nanostructures increases with an increase in the stoichiometric or molar ratio of zinc oxide and thiourea. Furthermore, the inventors have also found that at a molar ratio of 1:2 and 1:10 (zinc oxide: thiourea) the average particle size of the nanostructures of zinc sulfide can be maintained in the range of 5nm to 6nm and 18nm to 20 nm, respectively.

In one of the exemplary embodiments of the present disclosure zinc oxide and thiourea are mixed and then triturated in various stoichiometric molar ratios (1:2 and 1:10) to obtain a first mixture. The first mixture is then heated at a temperature ranging between100°C and 200°C for a time period ranging between 10hrs. and 20hrs. to obtain a second mixture containing nanostructures of zinc sulfide.

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In accordance with the present disclosure the first mixture may be heated at a temperature ranging between 110°C and 150°C for a time period ranging between 15 hrs. and 17 hrs. to obtain a second mixture containing nanostructures of zinc sulfide.

The second mixture is then washed with a solvent and subsequently dried at a temperature range of 50° C to 90° C for a time period ranging between 1hr and 8 hrs. to obtain purified nanostructures of zinc sulfide.

In one embodiment of the present disclosure the second mixture is washed with distilled water to remove excess thiourea followed by washing with anhydrous ethanol.

Zinc sulfide obtained by the process of the present disclosure is characterized by the particle size in the range of 1 to 30 nm.

In accordance with the present disclosure, the nanostructures of zinc sulfide obtained by using zinc oxide and thiourea in various molar ratios are analyzed in the UV-Vis Diffuse Reflection Spectra. The analysis revealed that there is a red shift in the cut-off edge of zinc sulfidewith an increase in the molar ratio of zinc oxide andthiourea. This also attributes to an increase in the particle size of zinc sulfide. It is further revealed that the optical cut-off edge for zinc sulfide having molar ratio 1:2 is 321 nm and the corresponding band gap is around 3.86 eV.

The nanostructures of zinc sulfide obtained by the process of the present disclosure are characterized by:

i. a particle size ranging between 5nm and 20nm;

ii. a surface area ranging between 70 m^2/g and 150 m^2/g, preferably 110.9m^2/g

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iii. a trigonal morphology;

iv. a band gap in the range of 3.75 eV and 3.86 eV;

v. an X-Ray diffraction pattern having 2θ values at 28.29^0, 47.58^0 and 56.41^0

In accordance with another aspect of the present disclosure there is provided a process for generation of H_2, wherein, 0.05% to 0.2% of the nanostructures of zinc sulfide of the present disclosure are first suspended in an aqueous solution of water and methanol and then subsequently irradiated with UV radiation to generate H_2.The process for generation of H_2further comprises incorporation of 0.2% to 0.8% of platinum with respect to the total amount of zinc sulfide.

In accordance with another embodiment of the present disclosure the aqueous solution may further comprise an electrolyte.

The nanostructures of zinc sulfide synthesized in accordance with the process of the present disclosure exhibit H_2 generation rate in the range of 143.5 μmol/hr./0.1g to 205 μmol/hr./0.1g.

The present disclosure is further described in light of the following examples which are set forth for illustration purpose only and not to be construed for limiting the scope of the disclosure.

EXAMPLE 1

The zinc sulfide (ZnS) nanostructures were prepared by solid state reaction. All analytical grade reagents, bulk zinc oxide (ZnO) and thiourea (NH_2CSNH_2) of purity 99.9% were used without further purification. The zinc oxide and thiourea were mixed

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in molar ratios such as 1:2 & 1:10 and ground by using pestle and mortar. The mixture was placed in an alumina crucible and kept in an electrical oven at 140° C for 16 hours. The product was thoroughly washed with distilled water to remove byproducts and excess thiourea followed by washing with anhydrous ethanol. The final product was dried at 70° C for 4 hours in a laboratory oven.

The nanostructured ZnS obtained was analyzed for its optical properties using UV-Visible spectrophotometer (Fig.1). Fig.1 shows the UV-Vis Diffuse Reflection Spectra of synthesized ZnS of different ratios. The UV spectra reveals that there is a red shift in the cut-off edge of ZnS with an increase in the molar ratio of thiourea and zinc oxide. This also attributed to an increase in the particle size of ZnS. The optical absorbance was measured at 321 nm for ZnS having molar ratio of 1:2 (zinc oxide : thiourea) and the corresponding band gap was around 3.86 eV, which is higher than the band gap of bulk ZnS (3.70 eV).

STRUCTURAL ANALYSIS:

The structural analysis (XRD) of ZnS is as shown in Fig.2. The XRD pattern confirms the formation of a cubic phase of nanostructured ZnS. HRTEM images of ZnS reveal a trigonal morphology with an average particle size of around 5-20 nm. The particle size of ZnS obtained using 1:2 and 1:10 molar ratio was observed to be 5-6 nm (Fig 3 a and b) and 18-20 nm(Fig 3 c and d) respectively. The electron diffraction (ED) pattern of ZnS (1:2 molar ratio) shows low crystallinity as compared to ZnS obtained at 1:10 molar ratios.Interestingly, the particle size increases with increasing molar ratio of zinc oxide and thiourea.

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EXAMPLE 2

The nanostructured ZnS of the present disclosure was tested for its applicability as a photocatalyst. The photocatalytic study was carried out using a photoreactor designed and fabricated in-house. The process that was used to study the photocatalytic activity of nanostructured ZnS is as follows,

Photocatalytic water splitting experiments were conducted in a two neck 250 mL borosilicate round bottom flask. In a typical run, 0.1 g of catalyst (containing 0.5 wt% Pt loading) was suspended in an aqueous solution (100 mL distilled water + 25 mL methanol) and irradiated under 400W high pressure mercury vapor lamp with continuous stirring. The mercury vapor lamp was kept vertically in a quartz tube, provided with water circulation arrangement in order to minimize the heating effect due to IR radiation. The gaseous H_2 evolved was collected in a eudiometer tube having a septum to remove the gas for GC analysis. Prior to each photocatalytic experiment, the reaction mixture was purged with ultra-pure grade argon gas for 15 min to flush out the dissolved gases in the reaction mixture. The eudiometer tube was filled with a saturated solution of NaCl to avoid dissolution of the evolved gas.

The photocatalytic activity of ZnS was tested for splitting H_2O into hydrogen using ultra-violet light as an energy source. The ZnS photocatalyst prepared using the method reported in the present disclosure shows excellent photocatalytic activity for decomposition of H_2O into H_2. Table 1 shows the hydrogen evolution rate from photodecomposition of H_2O using all the synthesized ZnS samples i.e. ZnS 1:2 & 1:10 molar ratio and bulk ZnS. The ZnS of 1:10 molar ratio showed hydrogen

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evolution rate of around 205 μmol h^{-1}, while ZnS of 1:2 molar ratio and bulk ZnS showed hydrogen evaluation rate of 143.5 and 41 μmol h^{-1}respectively. It is noteworthy that among all the ZnS samples, ZnS 1:10 molar ratio shows significant hydrogen evolution rate which is much higher than bulk ZnS.

Table 1.Photocatalytic activity of ZnS samples for hydrogen evolution

Sample	**ZnS 1:2**	**ZnS 1:10**	**Bulk ZnS**
H_2 μmol h^{-1}	143.5	205	41

[a] "Catalyst, 0.1 g; 125 ml (100 ml water + 25 ml of methanol);
400 W Mercury lamp".

Throughout this specification the word "comprise", or variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated element, integer or step, or group of elements, integers or steps, but not the exclusion of any other element, integer or step, or group of elements, integers or steps.

The use of the expression "at least" or "at least one" suggests the use of one or more elements or ingredients or quantities, as the use may be in the embodiment of the invention to achieve one or more of the desired objects or results.

"Whenever a range of values is specified, a value up to 10% below and above the lowest and highest numerical value respectively, of the specified range, is included in the scope of the invention".

While considerable emphasis has been placed herein on the particular features of this invention, it will be appreciated that various modifications can be made, and that many changes can be made in the preferred embodiments without departing from the

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principle of the invention. These and other modifications in the nature of the invention or the preferred embodiments will be apparent to those skilled in the art from the disclosure herein, whereby it is to be distinctly understood that the foregoing descriptive matter is to be interpreted merely as illustrative of the invention and not as a limitation.

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We claim,

1. A process for synthesis of nanostructures of zinc sulfide, said process comprising the following steps;
    a) mixing zinc oxide and thiourea under triturationat a molar ratio ranging between 1:2 and 1:10 to obtain a first mixture;
    b) heating the first mixture at a temperature ranging between 100°C and 200°C for a time period ranging between 10hr. and 20hrs. to obtain a second mixture containing nanostructures of zinc sulfide; and
    c) washing the second mixture with a solvent and subsequently drying at a temperature ranging between 50°C and 90°Cfor a time period ranging between 1hrs. and8hrs. to obtain purified nanostructures of zinc sulfide.
2. The process as claimed in claim1, wherein the temperature for heating the first mixture is maintained in the range of 110°C to 150°C for a time period ranging between 15hrs. and 17 hrs.
3. The process as claimed in claim1, wherein the solvent is at least one selected from the group comprising of water, ethanol and methanol.
4. The process as claimed in claim1, wherein the particle size of the nanostructures of zinc sulfide is in the range of 1nm to 30nm; preferably 5nm to 20nm.
5. Nanostructures of zinc sulfide obtained by the process as claimed in claim 1; said nanostructures being characterized by:
    i. A particle size ranging between 1nm and 30nm,preferably 5nm to 20nm.;

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ii. a surface area ranging between 70 m^2/g and 150 m^2/g, preferably 110.9m^2/g;

iii. a trigonal crystal structure;

iv. an optical absorbance of 321nm to 330nm;

v. a band gap in the range of 3.75 eV and 3.86 eV; and

vi. an X-Ray diffraction pattern having 2θ values at 28.29^0, 47.58^0 and 56.41^0.

6. Nanostructures of zinc sulfide as claimed in claim 5, exhibits H_2 generation rate in the range of 143.5 µmol/hr./0.1g to 205µmol/hr./0.1g.

7. A process for generation of H_2, said process comprising the following steps;

I. Preparing nanostructures of zinc sulfide, which comprises;

a) mixing zinc oxide and thiourea under triturationat a molar ratio ranging between 1:2 and 1:10 to obtain a first mixture;

b) heating the first mixture at a temperature ranging between 100°C and 200°C for a time period ranging between 10hrs. and 20hrs. to obtain a second mixture containing nanostructures of zinc sulfide; and

c) washing the second mixture with a solvent and subsequently drying at a temperature ranging between 50°C and 90°C for a time period ranging between 1hr. and 8hrs. to obtain purified nanostructures of zinc sulfide; and

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II. suspending the nanostructures of zinc sulfide in an aqueous solution and subsequently irradiating said aqueous solution by UV radiation to generate H_2.

8. *The process as claimed in claim 7, wherein the amount of zinc sulfide is* maintained in the range of 0.05% to 0.2% with respect to the total mass of the aqueous solution.

9. The process as claimed in claim 7, wherein the aqueous solution comprises water, alcohol and optionally, at least one electrolyte.

10. The process as claimed in claim 7, wherein the process further comprises incorporation of platinum in an amount ranging between 0.2%and 0.8% with respect to the total amount of zinc sulfide.

Dated this 16th day of September, 2013

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