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Environmental benign enhanced hydrogen production via lethal H$_2$S under natural sunlight using hierarchical nanostructured Bismuth Sulfide

Orthorhombic bismuth sulfide nanomaterial of unique morphologies including nanorods, dandelion flower like hierarchical nanostructures were successfully synthesized by solvothermal method. Considering the tunable band gap of these nanostructures within visible region and near IR, photocatalytic hydrogen production under sunlight has been demonstrated. We observed excellent hydrogen production ($8.899\text{mmole}\text{h}^{-1}\text{g}^{-1}$) under sunlight (on a sunny day between 11.30am to 2.30pm).
Environmental benign enhanced hydrogen production via lethal \( \text{H}_2\text{S} \) under natural sunlight using hierarchical nanostructured Bismuth Sulfide


The nanorods and hierarchical nanostructures (dandelion flower) of bismuth sulfide were synthesized by solvothermal method. The effect of solvent such as water and ethylene glycol on the morphologies and size of Bismuth sulfide were studied. The structural study shows the orthorhombic phase of bismuth sulfide. We have observed nanorods of size 30-50nm and dandelion flowers assembled with these nanorods. The formation mechanism of hierarchical nanostructures of bismuth sulfide has also been proposed. Considering the tuneable band gap of these nanostructures within visible region and near IR, photocatalytic hydrogen production from \( \text{H}_2\text{S} \) under normal sunlight has been demonstrated for the first. The abundantly available toxic \( \text{H}_2\text{S} \) has been utilised to produce hydrogen under normal sunlight. We observed an excellent hydrogen production i.e. 8.88 mmole g\(^{-1}\)h\(^{-1}\) under sunlight (on a sunny day between 11.30am to 2.30pm) for the \( \text{Bi}_2\text{S}_3 \) flowers and 7.08 mmole g\(^{-1}\)h\(^{-1}\) for nanorods. Hierarchical nanostructures supress the charge carrier recombination due to defects which ultimately responsible for higher activity. The hydrogen evolution obtained is quite stable when the catalyst has been used repeatedly. The hydrogen evolution via water splitting was observed to be lower than \( \text{H}_2\text{S} \) splitting. The bismuth sulphide was observed to be good eco-friendly visible light active photocatalyst under natural sunlight. Photosresponse study shows that \( \text{Bi}_2\text{S}_3 \) microstructures are a good candidate for applications in high-sensitivity photo detectors and photo electronic switches.

1. Introduction

Considering the paramount significance of hydrogen (\( \text{H}_2 \)) as a clean energy source, efforts have been made worldwide to investigate new methods for cheaper hydrogen production. Fujishima and Honda investigated the solar assisted water splitting using \( \text{TiO}_2 \) which opens new doors of solar energy conversion.\(^1\) This photocatalytic process has attracted much attention and appears to be promising strategy for clean, low cost and environmentally hydrogen production by utilizing solar energy.\(^2\) The photo cleavage of \( \text{H}_2\text{S} \) to \( \text{H}_2 \) and \( \text{S} \) has immense importance because of its waste disposal and environment problem. Acidic \( \text{H}_2\text{S} \) is a product of oil refineries, which is toxic and corrosive in nature and creates the environmental problems. The currently used Claus process has limitations and is utilizing only negligible amount of \( \text{H}_2\text{S} \) for preparation of liquid sulphur for agriculture and pharmaceutical industries. The photo-splitting of hydrogen sulphide for production of hydrogen and sulphur has significance as this reaction require less energy (79.9 kJ/mole) compared to photosplitting of \( \text{H}_2\text{O} \) (285.83 kJ/mole). Bismuth Sulfide is known to be effective for water splitting. There are very limited reports on the water splitting using \( \text{Bi}_2\text{S}_3 \) as a photocatalyst.\(^4\) Recently, we have demonstrated photocatalytic production of \( \text{H}_2 \) from \( \text{H}_2\text{S} \) using a variety of nanostructured photocatalysts.\(^5\) However, in commercial point of view, there is a need of search of a highly efficient stable catalyst. In this context, we have studied nanostructured \( \text{Bi}_2\text{S}_3 \) photocatalyst for \( \text{H}_2\text{S} \) splitting for hydrogen production.

\( \text{Bi}_2\text{S}_3 \) is a semiconductor material with direct band gap 1.3eV\(^11\)\(^-\)\(^13\) has numerous potential applications in photovoltaic, IR spectroscopy and thermo-electric devices. It is also used for the synthesis of Zeolite, inorganic materials as an imaging agent in x-ray computed tomography and as a liquid junction solar cell. Particularly in photocatalysis, Bismuth sulfide has been used as photocatalyst for organic dye degradation in the composite form\(^14\)\(^15\) The composites like \( \text{Bi}_2\text{S}_3/\text{TiO}_2 \), \( \text{Bi}_2\text{O}_3-\text{Bi}_2\text{S}_3 \) are also reported for photo electrochemical hydrogen evolution as well as photochemical hydrogen production from water.\(^16\)\(^-\)\(^19\)
The photo electrochemical and photo response study was also reported. Recently, due to encouraging properties of hierarchical nanostructures, research has been focused on the fabrication of controlled size, shape & hierarchically assembled nanostructures. Many researchers have studied different morphologies such as nanotubes, nanoparticles, nanowires, nanorods bundles and dandelion like nanostructure, urchin like nanospheres using various synthesis methods. However, the use of nanostructured bismuth sulfide as a visible light active photocatalyst has not been studied in detail for the hydrogen generation from H$_2$O splitting. More significantly, effect of nanostructures of Bi$_2$S$_3$ on the photocatalytic activity under sunlight has not been studied thoroughly. In view of this, we have demonstrated synthesis of bismuth sulfide nanostructures i.e. nanoparticle/hierarchical nanostructures and their photocatalytic activity.

In the present investigation, we report the photocleavage of waste H$_2$S to H$_2$ under normal sunlight by a Bi$_2$S$_3$ semiconductor photocatalyst which is hitherto unattempted. We also report the effect Bi$_2$S$_3$ nanostructures such as nanorods and hierarchical nanostructures on the production of hydrogen and its mechanism. The hydrogen evolution via water splitting has also been performed using these nanostructures. The structural and optical study of these nanostructures has been presented in detail.

2. Experimental

2.1. Material synthesis

All the reactants and solvents used in our experiments were analytical grade purchased from reputable firm. Bi$_2$S$_3$ nanostructures were prepared by dissolving 2 mmole of Bi(NO)$_3$.5H$_2$O and 8 mmole of thiourea(TU) into 80ml solvent [in water and mixture of (1:3) water : ethylene glycol (EG)]. After stirring for one hour, the solution was transferred into a 100ml Teflon lined stainless steel autoclave. Then the system was sealed and kept in the oven at 150°C. After reaction, the system during photo reduction. Bi$_2$S$_3$ was introduced into reactor and irradiated with normal solar light with constant stirring. The excess hydrogen sulfide was trapped in NaOH solution. The amount of hydrogen evolved was measured using a graduated gas burette. The experimental Setup for measurements of hydrogen production from H$_2$S splitting. More significantly, effect of nanostructures of Bi$_2$S$_3$ on the photocatalytic activity under sunlight has not been studied thoroughly. In view of this, we have demonstrated synthesis of bismuth sulfide nanostructures i.e. nanoparticle/hierarchical nanostructures and their photocatalytic activity.

The cylindrical quartz photochemical thermostatic reactor was filled with 700 ml 0.5 M water KOH and purged with argon for 1 h. Hydrogen sulfide (H$_2$S) was bubbled through the solution at the rate 2.5 ml min$^{-1}$ at a 298 K. H$_2$S is continuously fed into the system during photo reduction. Bi$_2$S$_3$ was introduced into reactor and irradiated with normal solar light with constant stirring. The excess hydrogen sulfide was trapped in NaOH solution. The amount of hydrogen evolved was measured using a graduated gas burette. The experimental Setup for measurements of hydrogen production from H$_2$S splitting.

2.4. Photocatalytic study for H$_2$S splitting

The cylindrical quartz photochemical thermostatic reactor was filled with 700 ml 0.5 M water KOH and purged with argon for 1 h. Hydrogen sulfide (H$_2$S) was bubbled through the solution at the rate 2.5 ml min$^{-1}$ at a 298 K. H$_2$S is continuously fed into the system during photo reduction. Bi$_2$S$_3$ was introduced into reactor and irradiated with normal solar light with constant stirring. The excess hydrogen sulfide was trapped in NaOH solution. The amount of hydrogen evolved was measured using a graduated gas burette. The experimental Setup for measurements of hydrogen production from H$_2$S splitting.

3. Results and Discussion

Fig 1 shows the XRD pattern of bismuth sulfide sample synthesized in (a) water medium- 24 hr (S1), (b) water: ethylene glycol (1:3)-24hr (S2) and (c) water: ethylene glycol (1:3)-30hr (S3), respectively. All the diffraction peaks are matching with the standard JCPDS data (No-060333). All the
planes were indexed which shows the pure orthorhombic phase of Bi$_2$S$_3$ and they are equally crystalline.

![XRD of Bi$_2$S$_3$ synthesized by hydrothermal at 150°C with different solvent: (a) water- 24 hr (S1), (b) water: ethylene glycol (1:3)24hr (S2) and (c) water: ethylene glycol (1:3) 30hr (S3).]

The optical properties were investigated by UV-visible diffused reflectance spectroscopy. Fig 2 shows the UV-DRS spectrum of bismuth sulfide synthesized by solvothermal method using different solvents. The direct band gap of the Bi$_2$S$_3$ sample S1, S2 and S3 was observed to be 1.42, 1.48 and 1.45 eV respectively which is higher than bulk (1.3 eV). The blue shift in band gap energy has been observed due to the nanocrystalline nature of the samples.

![UV-visible spectra of Bi$_2$S$_3$ synthesized by hydrothermal at 150°C: (a) S1, (b) S2, (c) S3.]

Fig 3 (a, b) shows the FE-SEM image of Bi$_2$S$_3$ prepared at 150°C for 24hr (S1) in water medium. These images show the nanorods of 30-50 nm diameter and 2-4 µm in length. The nanorods are random in size and not aligned. In water medium, the growth of Bi$_2$S$_3$ is very fast and hence randomly distributed and uneven sized nanorods are observed.

When the reaction is carried out for 24 hrs in water: ethylene glycol (1:3) medium, hierarchical nanostructured dandelion flowers (c, d) of 1-2 µm in size were observed. The nanorods of size 20-50nm are self-aligned and orient to form flower like morphology. All nanorods grow radially out of the centre part. When the reaction was prolonged to 30 hrs, hierarchical nanostructured flowers (e, f) of size 2-4µm were formed by self alignment of nanorods of diameter 100-150nm. The flowers obtained are well defined, formed by self alignment of well separated nanorods (puffy) as compared to the Bi$_2$S$_3$ obtained within 24 hrs. It is quite obvious to have bigger flowers with higher diameter of nanorods because the crystal growth is favoured due to prolonged reaction time via Ostwald ripening phenomenon.

TEM studies (Fig. 4) reveals the morphological variation in hierarchical Bi$_2$S$_3$ with solvent as discussed in earlier. Fig 4 (a) shows the Bi$_2$S$_3$ rods of size in the range of 30 to 50nm which also confirmed by the FESEM analysis. The corresponding ED pattern shows good crystallinity and d values calculated are matching with the XRD results. TEM of sample S2 (fig 4(c)) and S3 (fig 4(e)) shows flower like morphology as discussed in FESEM. From TEM images, diameter of rods was observed to be consistent with FESEM investigations. The corresponding electron diffraction (ED) pattern also shows orthorhombic structure as per the calculated d values. The bright spots of ED pattern also show the single crystalline nature of the material.

![FE-SEM images of the Bi$_2$S$_3$ synthesized by hydrothermal at 150°C: (a, b) S1, (c, d) S2, (e, f) S3.]

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Photoluminescence (PL) measurement of Bi$_2$S$_3$ was performed at room temperature with excitation wavelength of 450 nm (fig 5). The spectrum consists of one strong emission peak at 510 nm that can be ascribed to high level transition in Bi$_2$S$_3$ semiconductor nanocrystallites. It is observed that all of the products have a peak around 510 nm. However, peak intensity in the case of urchin like flower morphology is less than nanorods. This is due to the surface defects or surface states created by morphology and lower particle size.

4. Mechanism

The hydrothermal method provides uniform heating environment under pressure and simultaneous nucleation than the conventional methods due to its uniform heating effect. The solvents have an influence on the product morphologies and favour the synthesis of Bi$_2$S$_3$ with different pathways. The formation reaction may be described as follows.

\[
\begin{align*}
\text{Bi(NO}_3\text{)}_3 + \text{H}_2\text{O} &\leftrightarrow \text{BiO(NO}_3\text{)}_2 + 2\text{HNO}_3 \\
\text{NH}_2\text{CSNH}_2 + 2\text{HNO}_3 + 2\text{H}_2\text{O} &\rightarrow \text{H}_2\text{S} + 2\text{NH}_4\text{NO}_3 + \text{CO}_2 \\
2\text{Bi(NO}_3\text{)}_3 + 3\text{H}_2\text{S} &\rightarrow \text{Bi}_2\text{S}_3 + 6\text{HNO}_3 \\
2\text{Bi(NO}_3\text{)}_3 + 3\text{NH}_2\text{CSNH}_2 + \text{H}_2\text{O} &\rightarrow \text{Bi}_2\text{S}_3 + 6\text{NH}_4\text{NO}_3 + 3\text{CO}_2
\end{align*}
\]

Whereas, in our reaction, when Ethylene Glycol (EG): water used as reaction medium then EG acts as a co-ordination agent. Bismuth nitrate and Thiourea was dissolved in mixed solvent (EG and water) under magnetic stirring respectively. When two solutions were mixed together no precipitation was observed and solution was yellowish and transparent under stirring unlike water system. This might be attributed to the co-ordination of EG. The employ of EG, complex of bismuth produced with hydroxide via the coordination. In the solvothermal process because of temperature and pressure, the complex gradually decomposed to release the bismuth ions. The Bi$_2$S$_3$ nuclei are formed by reaction of Bi$^{3+}$ ions present in the solution and H$_2$S at solvothermal condition.
It is indicated that both TU and EG plays an important role in the formation of hierarchical nanostructures i.e. flower. The TU complexes are favourable for the oriented growth of the nanorods and also acted as a ligand in the formation of flower.26 As well as powder synthesized in water and mixed solvent (water: ethylene glycol) were benefit of forming nanorods and hierarchical flowers, respectively. The high viscosity substance is able to modify the mobility of the particles in suspension as well as collision rates. Ethylene glycol in the solution implies high adosption on the inorganic substances, which is able to induce the steric hindrance.34 probably this chemical event leads to a minimizing in the growth process, causing reduction in particle size. The interface energy with high surface tension between Bi$_2$S$_3$ and mixed solvent (water: ethylene glycol) is higher as compared to water. This interface energy and high surface tension35,36 are also promoting the formation of well, self aligned and organized flower like morphology. Hence, the nanorods formation by water mediated reaction and hierarchical nanostructures i.e. flowers by water: ethylene glycol (1:3) mediated reaction is quite understood.

5. Photoresponse

The Photoresponse of the obtained Bi$_2$S$_3$ nanorods (S1) as well as Bi$_2$S$_3$ micro flowers (S2 and S3) was measured as a function of time using the white light source (Figure 6). The current increased by 1.06X for S1 (nanorods) and 1.44X and 1.65X for S2 and S3 (micro flowers) upon exposure to white light (Figure a, b and c). After switching off the lamp, the current was instantaneously fallen down to original value. The on/off cycles could be repeated many times without any detectable degradation in current, indicating that all three Bi$_2$S$_3$ samples could be reversibly switched between low and high conductivity. The I-V curves measured at a large bias range for the micro flowers under light and dark conditions are shown in Figure 6 (e –f), which shows that the slope of the I-V curve became higher when the light was on, indicating an enhanced conductivity. However, microflower (sample S3) shows increase in slope compared with sample S2. In case of the nanorods, there was also a slight increase in the slope of the I-V curve after switching on the light; however, the increase in the slope of the I-V curve was not significant as compared to the both microflowers samples (Figure 6d). In these cases, the energy from the light, excited the electrons in the semiconductor Bi$_2$S$_3$ from the valence band into the conduction band, increasing the charge carrier concentration via direct electron-hole pair creation and thus enhancing the conductivity of the materials.37 It is obvious that the conductivity of the Bi$_2$S$_3$ microflowers is more sensitive to the white light exposure than the nanorods. It is believed that the multiple internal reflections of light within the interior voids of the microflowers are responsible for the enhanced photoresponsive sensitivity of the microflower structure than nanorods.38 Particularly, for microflowers (sample S3) has slight enhancement in photoresponse than sample S2 and it may be due to change in nature of flower. These results suggest that the prepared hierarchical Bi$_2$S$_3$ microstructures are a good candidate for applications in high-sensitivity photo detectors and photo electronic switches.

6. Photocatalytic activity and measurement

Bismuth sulfide is a semiconductor with band gap 1.3-1.7eV and because of its good spectral response to solar light; the photocatalytic activities of bismuth sulfide have been investigated. Here, we have reported extremely high hydrogen evolution from H$_2$S splitting under solar light irradiation especially for hierarchical nanostructured bismuth sulfide flowers as compared to rods (Table 1). The photocatalytic activities of the as synthesized Bi$_2$S$_3$ were evaluated without further treatment under direct sunlight. In 0.5M KOH solution, the weaker, diprotic acid H$_2$S dissociates and maintains equilibrium with hydrogen disulfide HS$^-$ ions. The sulfide semiconductor absorbs light and generates electron hole pairs. The photo generated valance band hole (h$_{vb}^+$) after band gap excitation of powder of Bi$_2$S$_3$ oxidizes the HS$^-$ ion to disulfide ion (S$_2^{2-}$), liberating a proton from HS$^-$ ion. The conduction band electron (c$_{cb}$) from Bi$_2$S$_3$ photocatalyst reduces protons to produce molecular hydrogen.10

$$\text{Bi}_2\text{S}_3 + \text{OH}^- \leftrightarrow \text{HS}^- + \text{H}_2\text{O}$$

**Semiconductor: Bi$_2$S$_3 \rightarrow h^++e^-_{cb}$$

**Oxidation reaction: ZHS$^- + 2h^+_{vb} \rightarrow S_2^{2-} + ZH^+$

**Reduction reaction: ZH$^+ + 2e^-_{cb} \rightarrow H_2$
The photocatalytic hydrogen evolution reaction was performed using as synthesized nanostructures Bi$_2$S$_3$ under ambient condition. Different series of experiments were performed to compare the hydrogen evolution rate by bismuth sulfide synthesized by different solvent and the results along with BET surface are summarized in Table 1. The maximum hydrogen evolution i.e. 8.88 mmole g$^{-1}$ h$^{-1}$ was obtained using hierarchical nanostructured bismuth sulphide (sample S3) is higher (20%) than that of bismuth sulfide (S1) nanorods [7.08 mmole g$^{-1}$ h$^{-1}$]. However, the sample S2 shows slightly less (2%) hydrogen evolution compared to sample S3. Both are hierarchical flower like structure and had good hydrogen evolution but due to puffy nature, sample S3 gives slightly higher evolution rate. PL study clearly shows the lower intensity broad peaks due to surface defects and states created by the hierarchical structure which ultimately suppress the charge carriers recombination resulting into higher photocatalytic activity. Also, the hydrogen evaluation rate via H$_2$S splitting using sample S3 is better than other reported one. The comparative study of H$_2$ generation using Bi$_2$S$_3$ nanostructures and other reported metal sulphide nano catalyst also performed and is shown in Table. (See supporting information ESI III). Though the ZnIn$_2$S$_4$ has good photocatalyst but is very expensive and the hydrogen evolution reported using xenon lamp and in the present study, we used natural sunlight. All other catalysts are cadmium based (toxic) and also showed hydrogen evolution under xenon lamp. However, still they show lower activity as compared to present Bismuth sulphide nanostructures. If we see the FESEM and TEM images of sample S1 carefully, the rods of different size with agglomeration have been observed which ultimately reduces the effective surface sites available for photoreaction. This is responsible for getting slightly lower hydrogen evolution in case of sample S1.

Figure 8 shows a typical time course of hydrogen evolution from water splitting using sample S1, S2 and S3 under visible light. Hydrogen evolution was not observed without light irradiation (kept for 2 hrs) Further, upon irradiation of light, only hydrogen was evolved steadily with time. The maximum hydrogen evolution i.e.0.019mmoleg$^{-1}$h$^{-1}$, was obtained using hierarchical nanostructured bismuth sulphide(S3) which is higher than sample S1 and S2 [0.012 and 0.017 mmole g$^{-1}$ h$^{-1}$]. Since, the reaction was carried out in the presence of sacrificial agent Na$_2$S and Na$_2$SO$_3$, an electron donor and the O$_2$ was not evolved. The GC analysis showed absence of O$_2$ as well as N$_2$ from air.
The stability of the photocatalyst S1, S2 and S3 has also been examined by reusing the photocatalyst samples (after H$_2$S splitting). XRD of reused catalyst (RS1, RS2 and RS3) did not show a change in the phase purity of bismuth sulfide (See supporting information ESI V). The hydrogen evolution rate of reused catalyst (RS1, RS2 and RS3) is also shown in supporting information (ES VI). The hydrogen evolution rate by H$_2$O splitting is quite low as compared to that of H$_2$S splitting. It is noteworthy that the bismuth sulfide is a good photocatalyst for the production of hydrogen from H$_2$S.

Conclusions

In summary, we have demonstrated the fabrication of single crystalline nanorods and hierarchical nanostructures by simple “one pot” solvothermal method. The water mediated reaction gives nanorods and mixed solvent (water: ethylene glycol) mediated reaction confer hierarchical nanostructures (flower) of bismuth sulfide. The high interface energy and surface tension create are responsible for such flower like morphology. The as prepared Bi$_2$S$_3$ photocatalyst exhibited higher photocatalytic activity for H$_2$ evolution by H$_2$S splitting under normal sunlight. Excellent photocatalytic activity for hydrogen production via H$_2$S splitting under normal sunlight has been obtained. It is noteworthy that hierarchical nanostructured Bi$_2$S$_3$ i.e. dandelion flowers show significant H$_2$ evolution rate without any promoters. The hydrogen evolution from water splitting was also observed for all samples where flower like Bi$_2$S$_3$ shows higher hydrogen as compared to other structures.

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