International Journal of Science and Research (IJSR)
ISSN (Online): 2319-7064
Index Copernicus Value (2015): 78.96 | Impact Factor (2015): 6.391

Development of Bismuth Sulphide Quantum Dot's in Silicate Glass Matrix

Amit B. Kathare

Student, Department of Chemical Engineering, Sinhgad College of Engineering, Vadgaon (BK), Pune-411041 (India)

Abstract: ***The successful growth of Bi_2S_3 nanocrystals in glass matrix using SiO_2 (Silicon Dioxide), K_2O (Potassium Oxide), Na_2O (Sodium Oxide), B_2O_3 (Boron Trioxide), ZnO (Zinc Oxide) and TiO_2 (Titanium Dioxide) as key components is done using the fusion method. Different sizes of nanocrystals in glass matrix were grown by annealing the glass (dispersed with Bi_2S_3 nucleons) under two different conditions. The glass was annealed between 6 and 48 hrs at constant temperature of 550 ^oC. The glass was also annealed at the temperature between 550, 575 and 600 ^oC at constant annealing time 6 hrs. The photocatalytic H_2 generation under solar light has been performed and utmost H_2 generation i.e. 5545 µmole $h^{-1}g^{-1}$ has been achieved, which is higher than Bi_2S_3 powder The Bi_2S_3 nanocomposite obtained was characterized by Optical Transmission (OT) spectroscopy and Transmission Electron Microscopy (TEM). Optical Transmission (OT) spectroscopy revealed strong red shift in transmission cut off which indicates increase in particle size of nanocrystals under both the conditions. TEM analysis demonstrated the nanocrystal size in the range of 3 to 12 nm.***

Keywords: Bismuth Sulphide (Bi_2S_3), Quantum Dots (QD), Photocatalytic Hydrogen Evolution

1. Introduction

Semiconductor nanoparticles have exceptional size dependant optical properties, which are having most extreme criticalness in optoelectronics. Semiconductor nanoparticles with size of a couple of nanometers in a glass network demonstrates an alluring properties and totally unique in relation to mass materials on account of quantum restriction impact [1], in which electron and gap wave capacities are bound by profound potential provided by glass lattice [2]. Recent reports demonstrates that semiconductor nanoparticles of size under 10 nm in glass have huge optical nonlinearity and quick reaction time which has pulled in consideration because of their wide applications such as in optical switches, nonlinear material, optical sensors and so on [3-5].

Bismuth sulfide (Bi_2S_3) is a normal lamellar organized semiconductor with a mass direct band crevice of 1.3 eV. Nanostructures of this material have pulled in much consideration because of their potential applications, for example, in electrochemical hydrogen stockpiling, hydrogen sensors, X-beam figured tomography imaging, biomolecule recognition, and as photoresponsive materials. Lately, Bi_2S_3 nanostructures with different morphologies including nanotubes, nanorods or nanowires, nanoribbons, and nanocomposites have been prepared through various techniques. Single precious stone orthorhombic Bi_2S_3 nanostructures with different morphologies, including wires, poles, and blossoms have been controllably synthesized [6].Bismuth sulfide (Bi_2S_3) is a piece of a group of mixes (Pn_2X_3 where Pn = Sb, Bi and X = S, Se, Te), which are thought to be most encouraging for thermoelectric applications, as exhibited by the exponential development of productions in regards to this material beginning from 1990 [7]. X-ray processed tomography applications of Bi_2S_3 nanoparticles are described by Rabin et al. Bi_2S_3 nanoparticles are better than the iodinated particles, which are utilized these days have high X-ray absorption and course times i.e. long circulation times (>2 hrs) [8].

The decade ago, the majority of the examination was centered on silicate or borosilicate glass frameworks. There are numerous approaches to alter the optical properties of the composite materials and one of them could be the change of the glass grid arrangement. Limited literature is available for the synthesis of glass nanocomposite using variety of glass compositions. These glasses are pertinent as optical channels and nonlinear material as optical switching gadgets [9]. Absorption and PL of PbS QD's in the 1-2 µm wavelength region were realized by controlling the sizes of QD's through thermal treatment [10]. Energy relaxation time of QD's is measured by T. Okuno et al. They confirmed that smaller dots have shorter decay times [11]. The controlled synthesis of QD's with narrow size distribution was achieved through phase decomposition of nanocomposite of PbSe solid solution in phosphate glass [12]. Second-order non-linear optical effect of CdS QD's doped with lead silicate glass is investigated by H. Liu et al [13]. Second Harmonic Generation (SHG) and two photon luminescence upconversion in glasses doped with ZnSe QD's is investigated by N. Thantu [14]. Bi_2S_3 doped glasses were combined by just sol gel technique [2]. Glasses combined by Sol gel are tedious and it is hard to make expansive size specimens. So far there are no reports on blend of Bi_2S_3 doped glasses by customary high temperature liquefying and throwing technique. The metal sulfide QD's (Quantum Dots) semiconductor have produced great deal of interest for an extensive variety of field of science and technology [15, 16]. The requirement for pursuit clean energy generation innovation has prompt the surge in sustainable energy research. These days, hydrogen (H_2) generation has essentialness as a clean fuel [17-19]. Usage of sunlight based energy for the creation of H_2 utilizing visible light dynamic semiconductor photocatalyst is attracting much consideration in view of worldwide issue identified with energy and environment [20-22].

Presently, hydrogen created from water utilizing regular steam changing of methane is very costly. Hydrogen sulfide (H_2S) is a waste discharged by oil and natural gas refineries (15-20%). Likewise, alkali industries and numerous

agrochemical enterprises create H_2S as a byproduct. Consequently, the H_2S which is environmental pollutant is copiously accessible and necessities to use for H_2 generation as perfect energy fuel [23]. Henceforth, the production of H_2 by means of photocatalytic splitting of H_2S has awesome significance. There are reports on oxide based catalysts like TiO_2, ZnO are being used for photocatalytic H_2 production [24, 25]. It is well known that photocatalytic action is relies on the particle size. Bringing down particle size creates more surface area and henceforth more active sites are accessible for photocatalytic activity [26]. However, because of the stability issue, look for new exceedingly proficient stable noticeable light active photocatalyst is imperative. To conquer this stability issue, synthesis of Bi_2S_3 QD's in glass matrix has been completed by melt and quench method to upgrade the strength of the QD's [22]. In the present investigation, they built up the Bi_2S_3 QD's (0.5-0.7 %) glass nanosystem and tuned the span of Bi_2S_3 QD's with striking temperature. The glass nanosystem has been characterized completely for the investigation of structural and optical properties. The impact of Bi_2S_3 QD's size on the hydrogen production has been exhibited for the principal time. It is essential that the H_2 production accomplished is substantially higher than the reported bulk Bi_2S_3 powder photocatalyst [27].

1.1 Objectives of the Work

- To synthesize Bi_2S_3 powder by simple hydrothermal method and develop Bi_2S_3 Quantum Dot's in Silica glass matrix.
- To study Bi_2S_3 nanocomposite characterizations on X-Ray Diffractometry (XRD), Transmission Electron Microscopy (TEM), Ultraviolet-visible Spectroscopy (UV), Photoluminescence (PL) and and its effect on photocatalytic hydrogen generation.

In this paper, the union of Bi_2S_3 doped silicate glasses utilizing fusion method has been given. The combined glass nanocomposite materials are portrayed by different physical methods, for example, X-Ray Diffractometry, Transmittance Electron Microscopy and Optical Transmittance Spectroscopy.

2. Experimental Section

2.1 Material preparation

SiO_2 (Silicon Dioxide) and different chemicals, K_2O (Potassium Oxide), Na_2O (Sodium Oxide), B_2O_3 (Boron Trioxide), BaO (Barium Oxide), ZnO (Zinc Oxide) and TiO_2 (Titanium Dioxide) were of LR grade acquired from S. D. Fine-Chem Limited, Mumbai, Maharashtra (India). The multi segment glass composition i.e. 55% SiO_2, 10% Na_2O, 5% MgO, 5% B_2O_3, 11% K_2O, 10% ZnO, and 4% TiO_2 has been designed. The bulk Bi_2S_3 designed by Hydrothermal method is utilized as source of Bi_2S_3 QD's for nanocomposite which is presented in the glass directly. The composition is mixed utilizing a pestle and mortar to acquire a homogeneous mixture. The same homogeneous mixture was melted in a recrystallized alumina crucible utilizing an electrically heated muffle furnace (Thermolyne-U3200) at 1100-1150 °C. The glass melt was mechanically homogenized at the same temperature for 2 hr. Subsequent to refining, the glass melt was air quenched on a preheated metal (brass) plate and handled instantly for annealing. The glass was annealed in a programmable furnace at its transition temperature (Tg) i.e. 450-500 °C and chilled off gradually to room temperature to expel the stresses. The doped glass (0.5%) is cut into three pieces. To study about the impact of temperature furthermore, time of annealing on crystallization of Bi2S3 in the glass matrix, the cut pieces of as prepared glass nanosystems are heat treated at 550, 575 and 600 °C for 8 hr.

2.2 Material characterization

The crystalline stages and the crystallite size of the photocatalyst were investigated utilizing X-ray powder diffraction (XRD) method (XRD, Advance D8, Bruker-AXS). Room temperature smaller scale Raman scattering (RS) was performed utilizing a HR 800 Raman Spectroscopy, Horiba Jobin Yvon, France, with an excitation at 632.82 nm by a He–Ne particle laser and a fluid nitrogen cooled CCD (Charge-coupled device) identifier. The optical properties of the powder tests were considered utilizing an UV-Visible-Near Infrared spectrometer (UV-Vis-NIR, Perkin ElmerLambda-950) and Photoluminescence spectrofurometer (Horiba Jobin Yvon Fluorolog). The morphologies of the Bi_2S_3 QD's glass nanocomposites were explored by High resolution transmission electron microscopy (HRTEM, JEOL, 2010F). For HRTEM, the examples were set up by scattering the glass powder in ethanol, trailed by sonication in an ultrasonic bath for 6 min and after that drop-throwing the specimen on a carbon covered copper matrix and by consequent drying in a vacuum. The Collected Hydrogen (H_2) gas test was examined utilizing a GC (Gas Chromatograph) framework (Shimadzu GC-2025) combined with TCD (Thermal Conductivity Detector) identifier and pressed segment (Shin Carbon ST).

2.3 Photocatalytic study for H_2S splitting

The photocatalytic activity was carried out in tube barrel shaped quartz reactor stacked with 700 ml 0.5 M KOH. At room temperature, the excitedly blended suspension was rinsed with argon for 1 hr and after that hydrogen sulfide (H_2S) was ascended through the solution for around 1 hr. Every trial was finished in indistinct condition with H_2S stream 2.6 ml min^{-1}. The catalyst were brought as a suspension into a reactor and enlightened with Xe light source (LOT ORIEL GRUPPE, EUROPA, LSH 302, for Xe light range) of energy 300 W. The created H_2 was collected in the graduated eudiometric tube. The faultlessness of the gathered gas was analyzed by gas chromatograph (Model Schimadzu GC-14B, MS-5 Å area, TCD, Ar bearer).

3. Result and Discussion

The Bi_2S_3 QD's glass nano framework has been created utilizing diverse wt% of guest material i.e. Bi_2S_3 (0.5-0.7%). All the glass structures were tried for their Bi_2S_3 dissolution capacity inside the matrix amid the melting procedure, which is the key stride in manufacturing Bi_2S_3 QD's glass substances. The Bi_2S_3 QD's glass nanocomposite like GP-12

and GP-14 [28] were incorporated by melt and quench strategy and analyzed by XRD. XRD of GP-11 synthesized by melt and quench method is a shown (Fig 2a). The XRD example is having expansive hump in the 2θ scope of 20-40° with some week/noisy peaks of Bi_2S_3/Bi signifying the amorphous glass containing Bi_2S_3/Bi nanoparticles. The XRD of sample GP-11 (0.5% Bi_2S_3) demonstrates increment in peak force of 2θ= 28.40° (230) and 27.36° (021) characteristic of the presence of orthorhombic Bi_2S_3 in glass matrix which coordinates well with the JCPDS Card No. 06-0333. It is observed that with increment in doping of Bi_2S_3 powder in glass matrix, the intensity of peak at 2θ= 28.40° decreases, while, the peak at 2θ= 27.36° somewhat moved to 27.12° which is near (012) plane of rhombohedral bismuth (JCPDS Card No. 85-1332). It uncovers that with increment in Bi_2S_3 doping rate in glass, there is a development of little Bismuth alongside Bi_2S_3. In any case, the XRD of Bi_2S_3 bulk powder shows the presence of Bi_2S_3 (Fig 1a). The higher concentration of Bi_2S_3 may leads into the slight decay of Bi_2S_3 to Bismuth (Bi) during melting. At lower concentration of Bi_2S_3 the disintegration of Bi_2S_3 in glass matrix is sufficient. Notwithstanding, at higher grouping of Bi_2S_3 doping, the disintegration takes longer time at melting condition which prompts decomposition of Bi_2S_3 present at the surface to Bismuth. Subsequently, bring down doping indicates just Bi_2S_3 and higher doping demonstrates slight formation of Bismuth which is very self-evident.

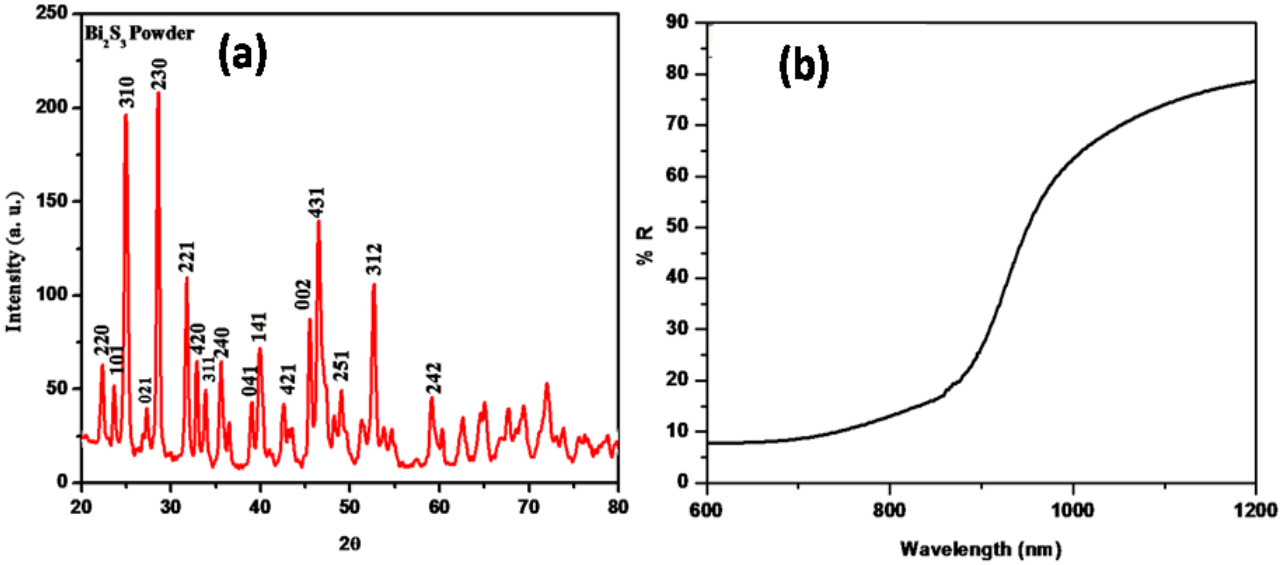

Figure 1: a) X-ray Diffractogram of Bi_2S_3 Bulk powder b) UV-DRS of Bi_2S_3 bulk powder

The structural and phase formation of the synthesized bulk Bi_2S_3 material investigated by X-Ray diffraction technique and results are shown in Fig.1 (a). The XRD reveals the formation of orthorhombic Bi_2S_3 [JCPDS (Joint Committee on Powder Diffraction Standards, JCPDS 1969) card no. 06-0333] and matches well with the previously reported Bi_2S_3 powder XRD [13]. The optical properties of the as synthesized Bi_2S_3 by facile hydrothermal method was investigated by UV-Visible Diffuse Reflectance spectroscopy (UV-DRS) and depicted in the Fig.1 (b). Reflectance cut off of Bi_2S_3 powder is observed ~ 930 nm (1.4 eV) which is in near IR range.

The Bi_2S_3 glass nanocomposite synthesized by melt and quench method such as GP-11 annealed at 600 ^{0}C for 8 hours is analyzed by XRD and shown in Fig 2.

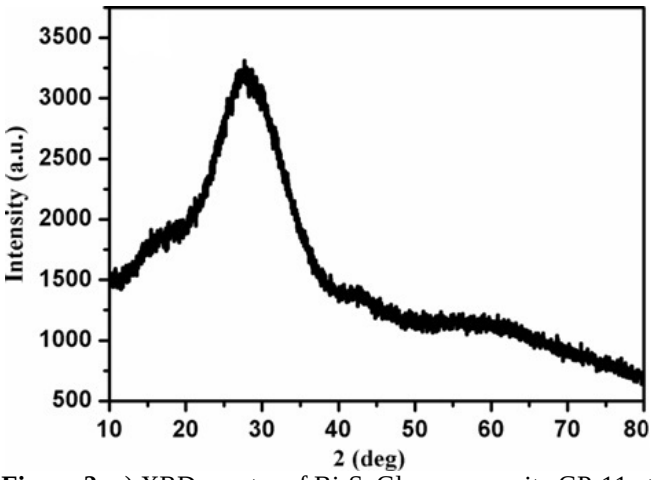

Figure 2: a) XRD spectra of Bi_2S_3 Glass composite GP-11 at 600 ^{o}C (0.5 %)

The XRD spectrum is having broad peak in the 2θ range of 20-40° with some weak/ noisy peaks of Bi_2S_3 signifying the amorphous glass containing Bi_2S_3 nanoparticles. The XRD pattern of sample GP-11 (0.5% Bi_2S_3) shows increase in peak intensity at 2θ= 28.40 (230) and 27.36 (021) indicative of the presence of orthorhombic Bi_2S_3 in glass matrix (JCPDS card no. 06-0333) [13]. The low intensity peak values are 2θ =25, 26, 28, 32, 33, 40 and 53 demonstrates the nearness of orthorhombic Bi_2S_3 crystals or QD embeded

in silicate glass. The foundation of upper curve is because of glass dispersing [13]. The broadening of peaks is induced by the small size of nanocrystals caped in glass matrix.

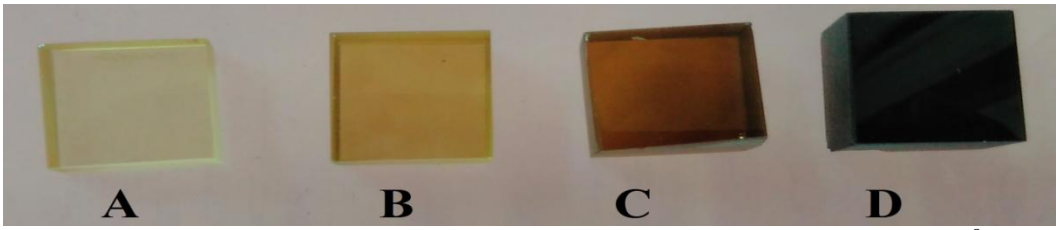

Figure 3: Actual photograph of GP-11 (0.5 wt %).A. As prepared glass B. Heat treated glass at 550 ^{o}C for 8 hrs C. Heat treated glass at 575 ^{o}C for 8 hrs and D. heat treated glass at 600 ^{o}C for 8 hrs

As prepared glass is of pale yellow in colour and after heat treatment it changes to dark yellow/brown depending on heat treatment temperature (see Fig 3 for actual photograph of glass nanocomposite). The color obtained to the glass ascribed to the growth of Bi_2S_3 or Bi QD's into the silicate glass matrix.

Average crystallite size was determined from XRD data using well-known Scherrer's formula

$$d = (0.9 \times \lambda) / \beta \cos \theta$$

And it is observed to be 3-4 nm.

The noisy nature of peaks is due to incorporation of nanocrystal into amorphous glass matrix [13, 14]. The Bismuth sulfide nanocrystals framed are small and hence the glass shows great transmittance. The homogeneous shade of the glass additionally indicates uniform circulation of nanocrystals in the glass matrix. However, the color of the Bi_2S_3 doped glass nano system changed from colorless to dark brown upon heat treatment of glass at 550–600^{o}C temperature (Fig 3). Amid the glass melting, Bi_2S_3 separates into Bi and S particles what's more, scattered into the glass matrix. The heat treatment of glass at its softening temperature brings about the development of Bi_2S_3 QD's through nucleation and precious crystal development system. The further development of these QD's is quickened by drawn out thermal treatment at high temperature because of Ostwald ripening [1, 26, 27].

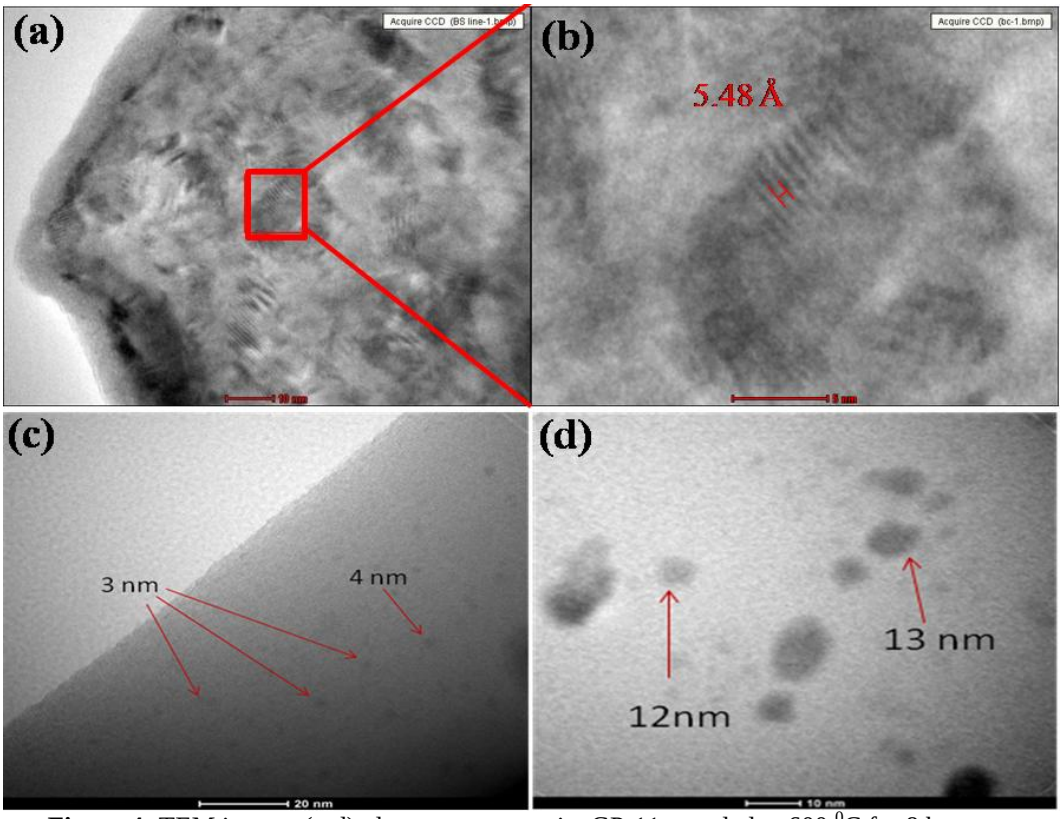

Figure 4: TEM images (a-d) glass nanocomposite GP-11annealed at 600 ^{0}C for 8 hrs

The further structural investigation of the synthesized sample was done by TEM analysis and depicted in the Fig. 4. The Bi_2S_3 glass sample, obtained by heat treating the glass at 600°C for 8 hrs was ground to fine powder and used for TEM study and is shown in Fig.4. From the TEM images, it is quite clear that spherical Bi_2S_3 QD's are homogeneously distributed in the glass matrix [12]. The size of the Bi_2S_3 QDs was determined to be 3-12 nm (Fig 4 a-d).

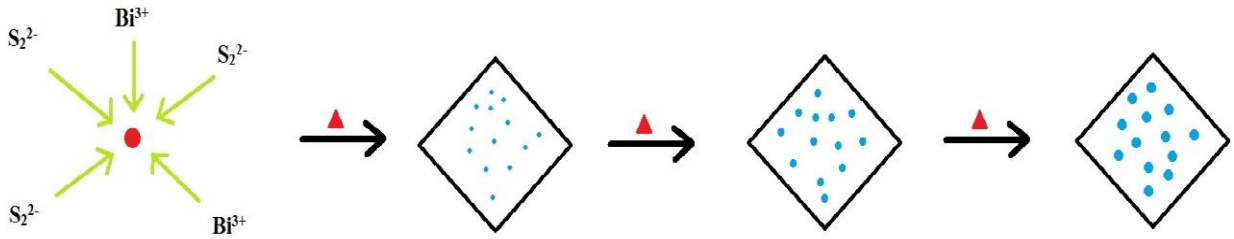

Figure 5: Schematic illustration of formation and growth mechanism of Bi_2S_3 QD's in glass matrix

Possible development system is schematically appeared in Fig. 5. Schematic representation of growth mechanism of Bi_2S_3 QD's is as shown in Fig 5.

The Raman spectroscopy is an intense and non-ruinous system broadly used to portray different materials. It gives exceptionally exact and correct data about the adjustment in bond separate and mechanical properties, for example, strain, stress, transition of phase and so forth.

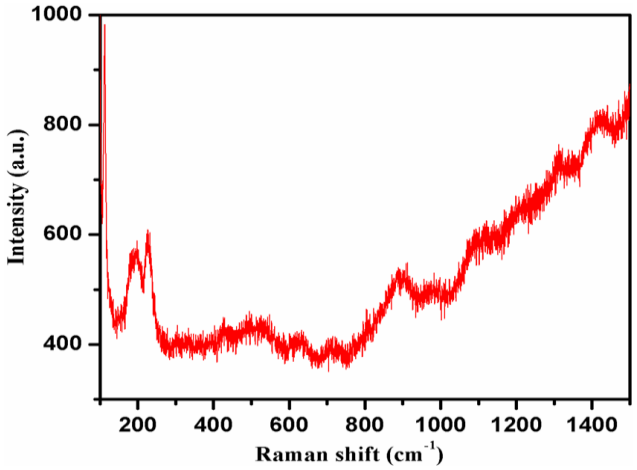

Figure 6: Raman spectra of Bi_2S_3 QDs in glass GP-11 annealed at 600 ^oC

Raman spectroscopy is an effective method for structural characterization of the materials. Hence, room-temperature Raman spectra of Bi_2S_3 QD's glass nanocomposite were recorded in the range 50-1500 cm^{-1} and are shown in Fig. 6. The Raman spectra of Bi_2S_3 glass composite with percent doping variation shows characteristics peak at 95.8, 114, 198 cm^{-1} etc. which is close to Bi_2S_3 powder and matches very well with the reported value of Bi_2S_3 glass composite [27].

4. Photocatalytic Hydrogen Evolution

The Bi_2S_3 silica glass nanocomposite has narrow band gap 2.5–3.5 eV, considering the band gap of synthesized glass composite material the photocatalytic activity were carried out in presence of visible light. The results of hydrogen generation by photocatalytic H_2S splitting are depicted in the Table 1 and Fig.7

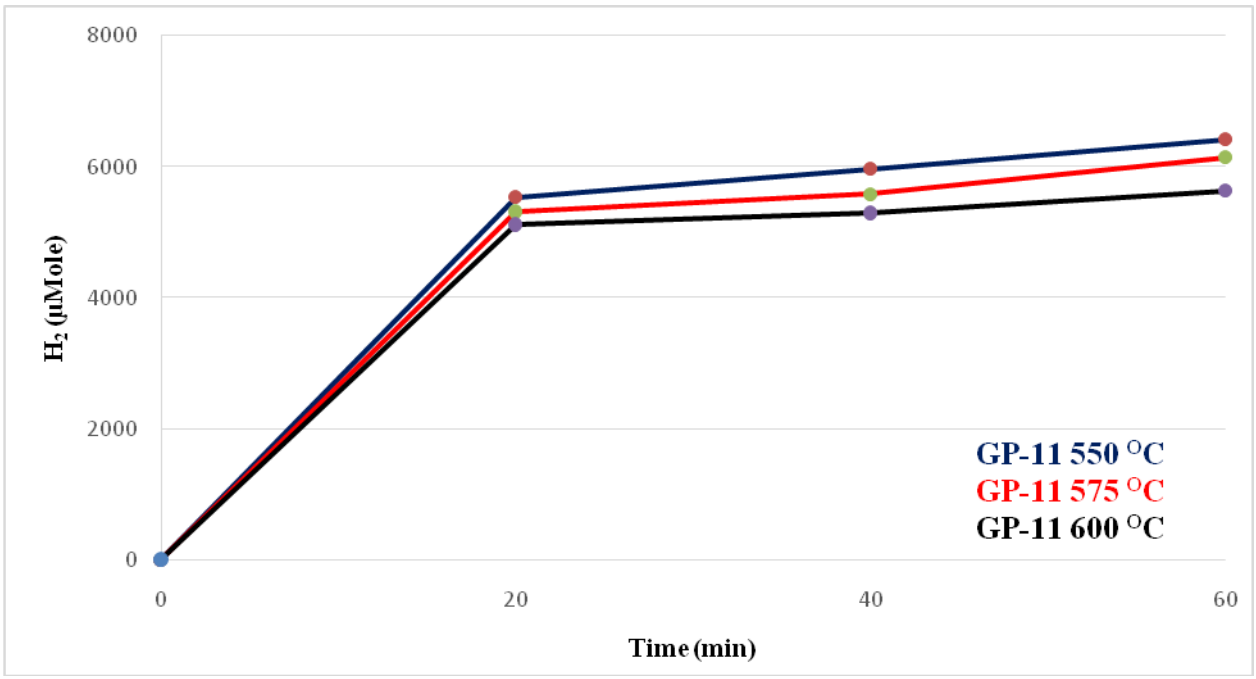

Figure 7: Photocatalytic H_2 generated for GP-11 striked glasses at 550, 575 and 600 ^oC

Table 1: Identification Table

Sample Code	% Doping	550 °C	575 °C	600 °C
GP-11	0.5	5545 µmole $h^{-1}g^{-1}$	5312.5 µmole $h^{-1}g^{-1}$	5122.9 µmole $h^{-1}g^{-1}$

The maximum H_2 production achieved was 5545 µmole $h^{-1}g^{-1}$ for the GP-11 striked glass at 550 °C (Table 1). It is observed that with increase in particle size of Bi_2S_3 QDs photocatalytic activity goes on decreasing which is obvious [26]. The obtained results are much higher than the previously reported [3] bulk Bi_2S_3 semiconductor catalyst. The higher hydrogen production in the present case can be ascribed to the lower particle size of Bi_2S_3 QDs (3-5 nm) in glass. With increase in striking temperature increase in particle size is observed. Due to the slightly higher striking temperature the crystal growth was slightly more, resulting in the larger QDs in the silica glass matrix. The overall particle density on the glass surface decreases with increase in particle size. Hence, decrease in H_2 generation with increase in striking temperature is observed.

The H_2S splitting under visible light takes place as follows:

$$H_2S + HO^- \longrightarrow HS^- + H_2O \quad \text{----------i}$$

$$Bi_2S_3 \text{ QDs Semiconductor} \xrightarrow{h\nu} h^+_{VB} + e^-_{CB} \quad \text{---------- ii}$$

$$\text{Oxidation reaction: } 2HS^- + 2h^+_{VB} \longrightarrow S_2^{2-} + 2H^+ \quad \text{---------- iii}$$

$$\text{Reduction reaction: } 2H^+ + 2e^-_{CB} \longrightarrow H_2 \quad \text{----------iv}$$

In 0.5 M KOH arrangement having pH 12.5 (pKa= 7.0) and the weak di-protic acid H_2S (pKa= 11.97) separates keeping up a harmony with HS^- particles. The Bi_2S_3/Bi QDs assimilate the visible light and create the electron (e^-) and hole (h^+). Because of the little size and more surface range, produced e-and h+ effectively goes to the surface of the impetus and promptly accessible for the photocatalytic activity. The photo-generated h^+ from catalyst in valence band oxidizes the SH^- particle to proton H^+ and disulfide S_2^{2-} particle. The photo-generated e^- in conduction band from the catalyst produces the molecular H_2 by diminishing the proton. The free electrons are in charge of hydrogen generation. The efficiency of our photocatalyst was confirmed by performing experiment in absence of catalyst. We did not observed H_2 generation activity in absence of bulk Bi_2S_3 semiconductor powder catalyst. This indicates that the hydrogen generation is due to photoreaction using glass nanocomposites as a catalyst. It is observed that QDs of Bi_2S_3 in glass matrix are more stable than the powdered Bi_2S_3 catalyst [28, 29].

5. Conclusion

The Bi_2S_3 QD's glass nanocomposites have been successfully developed using melt and quench method. The Bi_2S_3 QD's size can be observed 3-12 nm with controlled heat treatment at 550 and 600 °C, respectively. The photocatalytic H_2 generation under solar light has been performed and utmost H_2 generation i.e. 5545 µmole $h^{-1}g^{-1}$ has been achieved, which is higher than Bi_2S_3 powder. It is noteworthy that the glass nano composite contain only 5 mg of Bi_2S_3 QD's. The higher H_2 evolution rate was obtained for glass nanocomposite having lower Bi_2S_3 QD's the recycle study shows the stability of photocatalyst.

6. Acknowledgement

The author would like to acknowledge the Department of Science Technology (DST, Govt. of India) and Department of Information and Electronics Technology (DEITY), Ministry of Communication & IT, Govt. of India for financial support. I am also thankful to Director, Dr. B. B. Kale, Dr. Yogesh Sethi and Dr. Rajendra Panmand, C-MET, Pune and also Dr. Sunil Kadam, Centre for Advanced Studies in Materials Science, Department of Physics, Savitribai Phule Pune University, Ganeshkhind, Pune for facilities and support.

I would like to express my deepest and sincerest gratitude to Dr. S. R. Shirsath my internal guide, for his dynamic and valuable guidance and keen interest in my paper work. I am grateful to him for his constant encouragement in the fulfillment of the paper work. This paper cannot be considered complete without mention of our Head of Department Dr. S. M. Chavan and our Principal Dr. S. D. Lokhande. They have always been supportive and helpful throughout the course of our Master of Engineering.

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