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Performance of nano photocatalysts for the recovery of hydrogen and sulphur from sulphide containing wastewater

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ABSTRACT

Stability of photocatalyst plays an important role in efficient hydrogen recovery from sulphide waste streams. This research focuses on the stability and efficiency of visible light active photocatalysts viz., $\text{RuO}_2/\text{CuGa}_{1.6}\text{Fe}_{0.4}\text{O}_4$, ZnFe_2O_3 , $(\text{CdS} + \text{ZnS})/\text{Fe}_2\text{O}_3$ and Ce/TiO_2 for H_2 production. $\text{RuO}_2/\text{CuGa}_{1.6}\text{Fe}_{0.4}\text{O}_4$ photocatalyst was found to give maximum hydrogen production of $8370 \mu\text{mol/h}$. The reusability of the photocatalysts was tested by multiple cycles of catalyst regeneration along with H_2 production. The result shows that $(\text{CdS} + \text{ZnS})$ coated iron oxide core shell particles were found to be stable than other prepared nano photocatalysts. It is also demonstrated that H_2S can be split into hydrogen and sulphur under visible light irradiation using sulphide and sulphite reaction media at room temperature. This research paper will help in search of stable photocatalysts in recovering hydrogen from sulphide wastewater along with sulphur separation.

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Introduction

Hydrogen is considered to be a promising alternative fuel instead of non-renewable fossil fuels [1–4]. The main advantage of hydrogen fuel is while burning it produces only water vapour and the lack of other pollutant emissions such as CO_2 , NO_x and SO_x . In addition, the amount of energy produced during hydrogen combustion is greater than that of other fuels on a mass basis [3]. Hydrogen sulphide (H_2S) is a poisonous gas emitted in huge quantities from both natural and industrial sources [4–8]. An increasing source of H_2S is produced in large quantities from chemical industries such as natural gas

utilization, hydrodesulphurization of crude oil and coal chemistry [4,6,7]. More importantly, the hydrogen (a highly in-demand raw chemical and energy source) potentially stored in H_2S is not reclaimed in the Claus process [4,9,10]. Growing concerns about the environment and resource utilization have pushed the research for novel technologies to convert H_2S to S and H_2 using solar energy [4,11–13]. Recovery of both hydrogen and sulphur from sulphide wastewater through environmentally friendly photocatalytic technology is an ideal alternative to the Claus process.

The photocatalytic recovery of H_2 from sulphide containing wastewater has been extensively investigated. In this study, sodium sulphide (Na_2S) was used as source for sulphide and

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sodium sulphite (Na_2SO_3) as sacrificial agent. Generally, additional sacrificial agents, like sulphite (SO_3^{2-}) or hypophosphite (H_2PO_2^-) were used along with the sulphide ions to stabilize the catalytic activity. During the photocatalytic reaction the sulphur byproducts like $\text{S}_2\text{O}_3^{2-}$, SO_4^{2-} , $\text{S}_2\text{O}_3^{6-}$ are produced in aqueous solution instead of elemental sulphur (S). The solution with the sulphur products is a major source of pollutants from chemical industry. Separating and purifying these dissolved byproducts is more costly and difficult than treating sulphide wastewater by the conventional Claus process [13]. Hence recovery of H_2 and S from sulphide wastewater using solar energy is the most promising desirable process to solve the environmental problems. Therefore in our study, H_2 and S were separated from sulphide wastewater using photocatalytic process to solve the environmental problems and produce clean energy, H_2 .

Previous studies show that the photocatalytic activity of Pt loaded CdS nanostructures decreased by 20% after four H_2 production runs [14]. Similarly, the H_2 productivity of the EoePt/TiO₂ photocatalytic system also decreased after multiple runs [15]. The potential cause for the decline in photocatalytic activity was attributed to the morphological changes and catalyst surface contamination [16–18]. Similarly, the objective of this research work is also to compare the stability and reusability of various types of photocatalysts for H_2 production under visible light irradiation i.e., $\text{RuO}_2/\text{CuGa}_{1.6}\text{Fe}_{0.4}\text{O}_4$, ZnFe_2O_3 , (CdS + ZnS)/ Fe_2O_3 and Ce/TiO₂. In order to recover hydrogen from sulphide wastewater in large-scale, the photocatalyst should be economical, visibly active and effective in recovering hydrogen. Hence to develop a stable and cheaper photocatalyst for scaling-up, three types of visible active photocatalysts were chosen to analyze the efficiency in recovering hydrogen from sulphide wastewater in lab-scale level. The photocatalysts used in this study were selected in the basis of Spinel type ($\text{RuO}_2/\text{CuGa}_{1.6}\text{Fe}_{0.4}\text{O}_4$, ZnFe_2O_3), magnetically separable photocatalyst - (CdS + ZnS) coated Fe_2O_3 core shell particles and commercially available photocatalyst – Titanium Oxide based (Ce/TiO₂). The Morphology, crystal structure, band gap, particle size, surface area and H_2 production efficiency were tested for all the above photocatalyst. To evaluate its stability and reusability, after completing the photocatalytic activity, the photocatalyst was regenerated by allowing it to settle down in the photolytic solution and separating the photocatalyst at the bottom and repeated rinsing with distilled water. The aim of this research work is to enhance the photocatalytic H_2 production and to develop highly efficient and stable photocatalysts.

Materials and methods

Materials

Metal oxides like CuO, Ga_2O_3 , Fe_2O_3 , RuO_2 , $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, NH_4 , Poly vinyl alcohol (PVA), Sucrose, CdCOOH, ZnCOOH, Na_2S , $\text{Ce}(\text{NO}_3)_3$, Ethanol and Ti(O-Bu)₄

were received from Merck with purity >99%. Distilled water was used throughout the experiment.

Preparation of photocatalysts

The spinel oxide RuO_2 loaded $\text{CuGa}_{1.6}\text{Fe}_{0.4}\text{O}_4$ was prepared by the conventional ceramic route [19]. Oxide precursors of appropriate quantities for the spinel photocatalysts $\text{CuGa}_{2-x}\text{Fe}_x\text{O}_4$ ($x = 0.4$) was thoroughly grounded in agate mortar until they become homogeneous and the mixture was calcined in static air at 800 °C for 15 h and then recalcined at 975 °C for 15 h. After cooling, the samples were collected, ground well and stored. RuO_2 from $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ was loaded to the extent of 1.0 wt% on the naked catalysts by impregnation technique at 500 °C for 2 h duration.

The ZnFe_2O_4 was prepared by co precipitation method [20]. The chemicals used for the preparation of spinel powder were $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Stoichiometric amounts of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ both of purity 99.5% was dissolved in distilled water and the solution is dehydrated in a sand bath until dryness. Then, the amorphous powder was fired in air oven at 800 °C. The reaction was completed usually after two thermal treatments and the end product exhibits a light brown colour.

Fe_2O_3 nano particles were prepared using PVA and Sucrose [21]. An aqueous solution of PVA (10 wt%) was prepared in hot water. Ferric nitrate (0.1 mol) was dissolved in 150 mL of distilled water. These two solutions were mixed and stirred vigorously using a magnetic stirrer. An aqueous solution of sucrose (10 wt% of sucrose with respect to PVA) was added to this mixture and stirred for 1 h at room temperature. It was dried on a hot plate at 125 °C, a dark brown colored fluffy precursor obtained.

(CdS + ZnS)/ Fe_2O_3 was synthesized by co-precipitation method [22,26]. 50 mg of the synthesized Fe_2O_3 were dissolved in 40 mL of distilled water with the assistance of ultrasonication for 30 min. The sonicated Fe_2O_3 particles were added to the 500 mL distilled water and then appropriate quantities of NaOH (0.1 M) solution were added to adjust the pH value to 11.0. Then few drops of Cadmium acetate and then Zinc acetate were added to that distilled water containing Fe_2O_3 nano particles. Then mixed solution was continuously stirred and sodium sulphide solution was added drop by drop. After 24 h, the as-prepared products were washed repeatedly with distilled water and isopropyl alcohol for several times and then dried in an oven at 60 °C for 6 h.

Cerium doped TiO₂ was prepared by sol-gel method [23]. Cerium nitrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, HIMEDIA, U.S.A) was dissolved in distilled water in the ratio of 1:8 and the pH of the mixture solution was adjusted to 1.5 using Nitric acid (HNO_3 , MERCK, U.S.A), then titanium Isopropoxide solution ($\text{C}_{12}\text{H}_{28}\text{Ti}$, SPEC-TROCHEM, India) was added drop by drop to the solution with the constant stirring for 10–12 h. The white precipitate was formed instantaneously. The resulting colloid solution was concentrated at 35–40 °C in a rotary evaporator. The final solution with the precipitate was filtered and dried and given heat treatment at 400 °C for 2 h using muffle furnace.

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