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Photocatalytic Transformation of H_2S Plentiful-Perilous Pollutant to Hydrogen Clean Fuel and Sulfur Element Using MnS Nanostructured Energy-Material

Majid Ghanimati and Mohsen Lashgari*

Department of Chemistry, Institute for Advanced Studies in Basic Sciences (IASBS), Zanjan, Iran

lashgari@iasbs.ac.ir

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INTRODUCTION

H_2S is a highly dangerous/poisonous and corrosive pollutant that is harmful to living creatures and damaging for metallic structures. Moreover, this hazardous chemical is produced in huge amount in sour oil and gas industries [1-4], routinely or accidentally, during the extraction, storage, transportation, or processing stages. Only negligible quantity of this gas is conventionally treated through the two-step burning Claus process (Equations 1 and 2), whereas most of H_2S is not properly dealt with and eventually released into the atmosphere [4,5].

$$H_2S + \tfrac{3}{2}O_2 \rightarrow SO_2 + H_2O \qquad (1)$$

$$2H_2S + SO_2 \rightarrow \frac{3}{2}S_2 + 2H_2O \qquad (2)$$

The current Claus approach not only needs a complicated infrastructure, but during the process, the hydrogen energy stored in H_2S is also set aside. Furthermore, the emission of SOx and NOx is another drawback of this process [3,5].

Photocatalytic conversion of H_2S to hydrogen clean fuel and valuable sulfur element is a new alternative green/economic strategy to replace the Claus industrial process [1-5]. To this end, the design and synthesis of low-price, eco-friendly, effective photocatalyst/solar-energy materials are highly in demand. In this regard, metal sulfides are suitable choices, owing to their high chemical stability in H_2S media, visible-light absorption and the ability of chemical bond formation with proton species [2,3]. Manganese sulfide (MnS) is an affordable, environmentally friendly, p-type sulfide semiconductor which is stable in sulfide media. Moreover, Mn compounds have a good potential to be employed as an effective catalyst for oxidative processes. In addition, Mn^{2+} cation has a good potency to adsorb hydrogen sulfide, and Mn-containing compounds are commonly employed as an H_2S sorbent in the oil and gas industries [6-8]. Based on the facts mentioned above, in the present work, a mesoporous/ nanostructure MnS was synthesized and employed for the photocatalytic degradation of H_2S alkaline medium to generate hydrogen fuel and elemental sulfur under ambient conditions.

EXPERIMENTAL PROCEDURE

PHOTOCATALYST PREPARATION

MnS was synthesized through a hydrothermal route. Briefly, a 50 ml aqueous solution containing 0.36 M Mn^{2+} [$Mn(CH3COO)_2$; 98%; Fluka] and 0.4 M thioacetamide was first prepared. Moreover, the solution was transferred into a homemade autoclave reactor, and then heated up to 160 °C for 8 h. After cooling the reactor, the resulting precipitate was washed several times with distilled water and dried at 70 °C for 12 h [2].

PHOTOCATALYTIC ACTIVITY TEST

Similar to our previous report, the photodecomposition process of the H_2S saturated solution was carried out in a home-made, T-controlling, double-walled, cylindrical glass reactor contained 0.2 gr photocatalyst and illuminated by a xenon light source with irradiative intensity set at 1 sun. Since the amount of hydrogen gas being photo-evolved is pH-dependent, the photo-splitting process was done at pH=11 [2]. To extract sulfur element, disulfide solution was acidified with a 1M HCl solution to pH~5. In addition, the precipitated sulfur was then filtered and dried [9].

RESULTS AND DISCUSSION

XRD pattern of the energy material synthesized here is depicted in Fig.1. The pattern recorded here for MnS corresponds to JCPDS card number 65-3413 and confirms the synthesis of this compound.

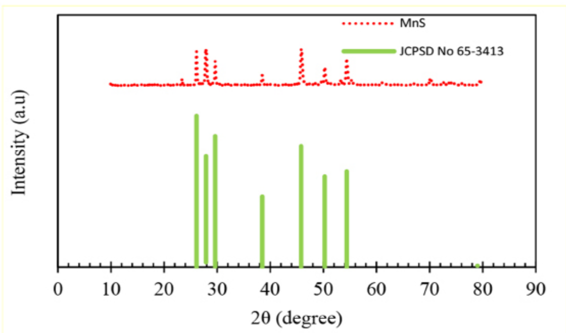

Figure 1: XRD pattern of synthesized photocatalyst.

The synthesis of photocatalyst was also approved by EDS/EDX evidence and Raman spectra (see Table 1 and Fig. 2).

Table1: Energy dispersive X-ray spectroscopy (EDS/ EDX) data (Wt. %).

Semiconductor	Mn	S
MnS	61.06	38.94

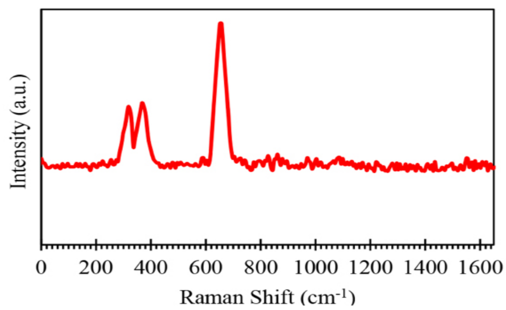

Figure 2: Raman spectrum of synthesized sample.

FESEM and TEM images of MnS are presented in Fig. 3. This figure demonstrated that the energy material synthesized here had a nano-particulated structure.

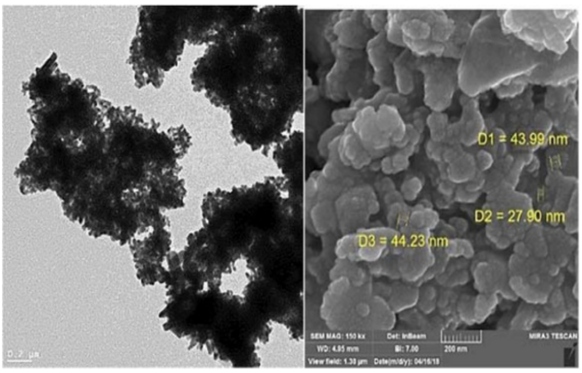

Figure 3: FESEM (right) and TEM (left) images of the solar-energy material under consideration.

BET analysis (Fig. 4) revealed that the photocatalyst energy-material under consideration was mesoporous (the pore size between 2 to 50 nm) [5].

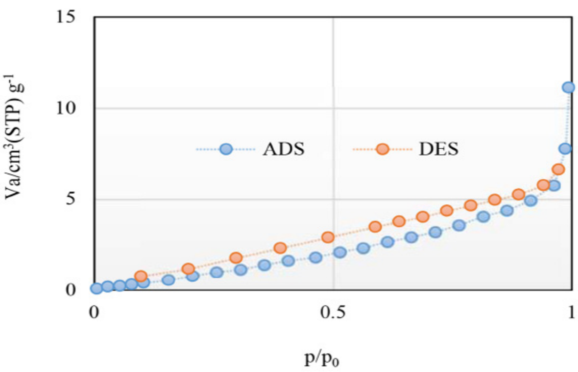

Figure 4: Nitrogen adsorption-desorption isotherm of the photocatalyst synthesized in this work.

Diffuse reflectance spectra of the photocatalyst synthesized here is plotted in Fig. 5. This figure showed that MnS has a good absorption in the visible region. Photocatalytic activity tests revealed that the energy material under consideration has a good ability to generate hydrogen fuel (see Fig. 6) and produce sulfur element (The extent of sulfur product was obtained 42 mg).

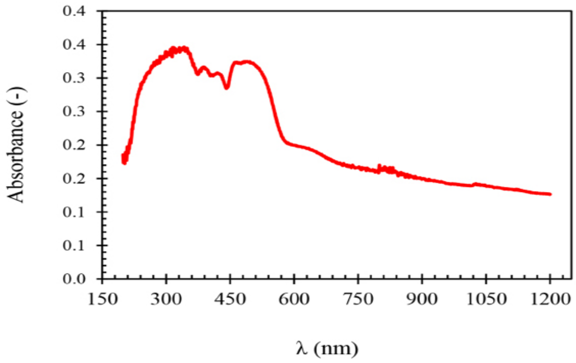

Figure 5: Diffuse reflectance UV– visible spectra of the energy material synthesized in this laboratory.

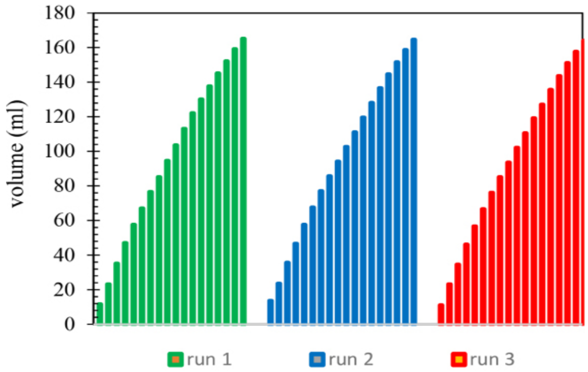

Figure 6: The volume of hydrogen gas evolved over 1 g of the photocatalyst, measured for 3 successive runs; each run lasted 3 h and the volume of gas recorded after each 10 min (the pH was 11).

CONCLUSIONS

In this article, using a facile hydrothermal method, a new nanostructured/low-price/eco-friendly photocatalyst was synthesized and employed for the photocatalytic conversion of H2S hazardous material to H2 green fuel and elemental sulfur. In addition, the photocatalyst material synthesized here was characterized using DRS, TEM, BET, FESEM, XRD and Raman techniques. The adsorption–desorption isotherms revealed a hysteresis loop which indicated the synthesis of a mesoporous material. Moreover, the nanostructured morphology of the photocatalyst was approved by field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM) and XRD (Scherrer formula) analyses. Finally, the results demonstrated that the photocatalyst material synthesized in this work had a good ability to produce hydrogen fuel and generate sulfur element.

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