Photocatalytic Degradation of Methyl Orange using MoS_2 nanoparticles as catalyst

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Abstract: ***MoS_2 is a semiconductor transition metal dichalcogenide material (TMD) which has exciting optoelectronic properties. Due to its band gap (BG) energy lying in the visible range it shows good photocatalytic behavior. In this report, we have synthesized MoS_2 nanoparticles (NPs) and its morphology is characterized using XRD and SEM. EDX is performed to analyze the composition of the as-synthesized material. Multiple BG energy in the visible light range is observed from the analysis of UV-Visible spectroscopy. We have investigated the photocatalytic property by the degradation of Methyl Orange (MO) using MoS_2 nanoparticles as catalyst. It is observed that the as-synthesized MoS_2 NPs degrade MO very efficiently with 98% degradation using 1mg in 1ml 10µM dye solution in 2hr.***

Keywords: **semiconductor, dichalcogenide material, multiple band gap, photocatalysis**.

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I. INTRODUCTION

Molybdenum disulfide is an inorganic TMD compound having very exciting electronic as well as optical properties. Being semiconductor compound, its finite BG energy provides an important application in energy-related matters [1-5]. MoS_2 can also be used as a catalyst material harvesting solar energy in photocatalytic reaction. The BG energy value of this material lies in the visible range which is a promising part to apply it as a photocatalyst. In many applications, for example, textile industries, paper industries, rubber industries, food industries etc. several dye materials are used out of which some are very toxic and harmful to the environment [6-8]. Such dyes create pollution when exposed to the environment directly or indirectly. The wastage and drainage system of such industries directly pollute the water bodies of our ecosystem. In order to cease the effect of toxic dyes, they are to be decomposed before releasing into the ecosystem. MoS_2, being nontoxic can be used as a good material to degrade such dye by using solar energy through a photocatalytic activity which is an eco-friendly and cheaper way [9,10]. In few reports, H_2 evolution using MoS_2/CdS photocatalyst, composite of TiO_2 NPs and MoS_2/graphene cocatalyst have been performed [11, 12]. But very few works on the degradation of polluting dye using MoS_2 NPs have been reported to date. In this work, we have synthesized MoS_2 NPs to investigate the photocatalytic behavior using methyl orange (MO) as a model dye. MoS_2 NPs are superior to bulk one in the sense that they have wide BG which corresponds to more intense visible light and the increase in surface area which favor one important criterion for an efficient photocatalytic process. MO is a toxic dye used in different laboratory activity as well as an industry which can cause a hazard to living organisms. This may cause skin irritation, respiratory tract irritation if inhaled and harmful to body tissues. A large amount of such kind of toxic dyes is drained out into our ecosystem which causes pollution. Since MoS_2 is nontoxic solid, insoluble in water and dilute acids, can be used as a catalyst material. We have observed that MoS_2 NPs are very efficient photocatalyst which can degrade MO within few hours. Also the reusability of such catalyst makes the photocatalytic process much cheaper and advantageous.

II. EXPERIMENTAL SECTION

2.1 Material Synthesis and Characterization

MoS_2 NPs are synthesized using solid-state reaction between molybdic acid and excess Thiourea (1:48 molar ratio) in N_2 gas environment at 500º C [13, 14]. After synthesis, the material is cleaned using warm distilled water to remove soluble impurities and dried followed by centrifugation and filtration.

The material is further ground gently into powder form by mortar and pestle. The morphology of the sample is characterized by X-ray diffractometer (XRD) (make: RIGAKU MINIFLEX) with Cu-Kα radiation (λ= 1.5405 Å) and Scanning Electron Microscope (SEM) (make: make: JEOL JSM-6390LV). The composition of the material is studied using energy dispersive X-ray spectrometer (EDX). Photocatalytic activity is performed using a xenon arc lamp (Make: Xenon Lamp Zolix SLH- X500 Xenon Arc Light Source) as visible light source and UV-Visible spectroscopy (make: UV 2450, SHIMADZU CORPORATION).

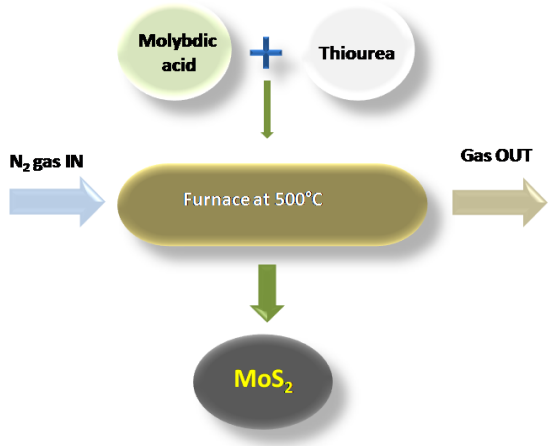

Figure 1: Schematic of material synthesis set up

2.2 Photocatalytic activity measurement

In order to measure the photocatalytic activity of the as-synthesized material, a 10μM solution of MO is prepared. The as-synthesized MoS_2 NPs are added to the solution in 1mg/ml and 0.5mg/ml amount and stirred for few hours to attain absorption-desorption equilibrium in the dark. After that, the solution mixture is exposed to visible light radiation. For irradiation, a xenon arc lamp of output intensity 12,000lux when the sample is kept at 8cm below the source light is used. 10ml of the sample is taken out at an interval of half an hour. Then the samples are centrifuged at 7000rpm for 12 min. 4ml of the aliquot from each sample is taken out which is then analyzed by UV-Vis absorption spectroscopy.

III. RESULTS AND DISCUSSION

The XRD plot (figure 2a) of the as-synthesized NPs confirms the formation of MoS_2 when compared with JCPDS software (card no. 1999 JCPDS No. 75-1539). The characteristic peaks (002), (004), (100), (102), (006) and (008) are observed for the MoS_2 NPs. SEM micrograph (figure 2b) reveals that the particles are in nanoscale dimension having broad size distribution from about 50nm to 100nm, however, most of them get agglomerated. It is found from EDX spectrum (figure 2c) that the as-synthesized material is mainly composed of Mo and S, S being most abundant. From the UV-Visible reflection spectrum, the optical BG of the sample is obtained by using Kubelka-Munk (KM) plot (figure 2d) and found to have multiple BG in the range of visible light energy [15,16].

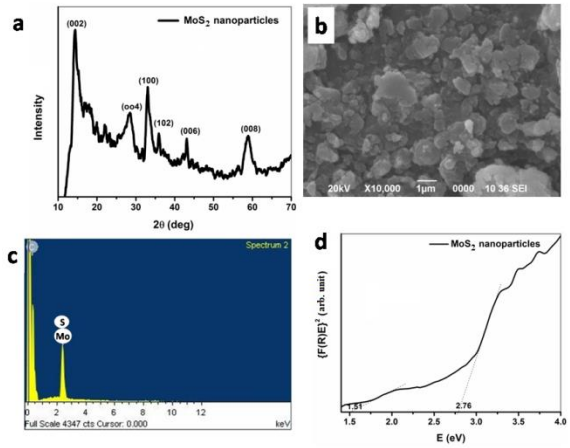

Figure 2: a.XRD plot, b. SEM micrograph, c. EDX spectrum and d. KM plot of the as-synthesized MoS_2 NPs.

The photocatalytic activity measurement is evaluated by observing the degradation of UV-Vis absorption peak of MO due to the influence of MoS_2 NPs after irradiation. The formula used to calculate the percentage degradation is [15,17]

$$\%D=\left(\frac{A_0-A_t}{A_0}\right)\times 100\% \qquad (1)$$

where A_0 is the absorbance before radiation and A_t is the absorbance after radiation time 't'. The degradation rate constant can be calculated by plotting $\ln(A_0/A_t)$ vs t using equation 2 [18].

$$\ln\left(\frac{A_0}{A_t}\right)=kt \qquad (2)$$

where k is the rate constant.

From plot 3a and 3b it has been observed that the intensity of absorption peak of MO gradually decreases with time due to the radiation exposure. Nearly 98% degradation of the MO peak is observed at about 1.5h to 2h. Considering these to have first-order kinetics, the degradation rate constants are calculated using equation 2 and determined to be $0.027min^{-1}$ for 1mg/ml catalyst and $0.022min^{-1}$ for 0.5mg/ml catalyst [15]. The degradation is faster when MoS_2 NPs catalyst is used in amount 1mg/ml than 0.5/ml as obtained from the plot for the rate constant of the two catalytic activities. This is because when the number of catalyst particles increases the number of electron-hole (e^- -h^+) pairs

generated becomes more which are responsible for the activation of the catalytic degradation process. Also, due to the nanoscale dimension of the particles, more surface area of the catalyst is exposed to light radiation which in turn leads to generate more

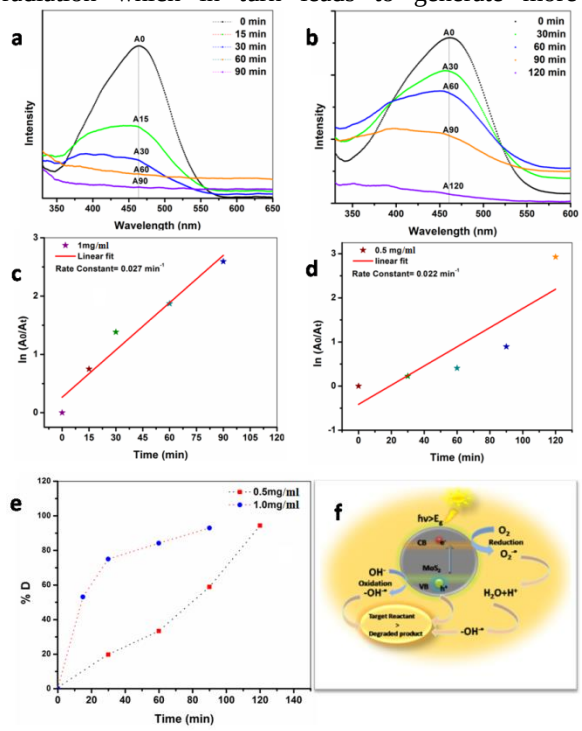

Figure 3: (a) and (b) show the degradation of absorption peak for MO by MoS_2 catalyst using amount 1mg/ml and 0.5mg/ml respectively, (c) and (d) represent the corresponding rate constants measurement plot, (e) represents the amount of percentage degradation of the UV-Vis absorption peak with time and (f) a schematic of photocatalysis mechanism.

photoexcitons. The mechanism is that when visible light is incident on the MoS_2 NPs, due to its multiple BG values, a broad range of light is absorbed and more e^- -h^+ pairs are generated. These exciton pairs before got recombined react with water and oxygen molecule, which are absorbed in water, to produce hyperactive hydroxyl(-OH^-•) ion. These –OH^-• and h^+ further react with the target dye molecules and degraded them. MoS_2 being layered semiconductor have BG value approximately 1.3eV in bulk form. As the dimension decreases BG of MoS_2 increases and reaches 1.9eV at monolayer [1,19]. The high value 2.76eV of BG in NP form is due to quantum confinement effect. Also, different phases and defects of the material give rise to multiple BG. This leads to absorb light in the different wavelength range. The multiple BG values thus enhance the efficiency of photocatalytic activity by providing more solar energy to be utilized to generate more exciton pairs. The degradation of the dye is due to the photocatalytic activity via effective charge separation and transfer in MoS_2. Thus increased number of exciton pairs enhances the catalysis process and degrade the dye molecule more effectively and efficiently.

IV. CONCLUSIONS

In this work, MoS_2 NPs are successfully synthesized. From the photocatalytic activity, it is observed that MoS_2 is a promising material for photocatalysis and can be used as dye-pollution controlling material in future. As the catalyst is insoluble in water, it can be easily removed from the solution mixture and reusable. Also the catalyst molecules, being solid, insoluble to water and dilute acids and also stable can be reused again and again which reduces the overall cost of the synthesis process. Thus MoS_2 NPs are happened to be very good photocatalyst which can degrade polluting dyes very efficiently keeping the environment free from pollution which may occur due to the exposure of such kind of dyes.

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