

Preparation of silver sulphide (Ag₂S) thin films by chemical bath deposition for photocatalytic application

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ABSTRACT

Semiconductor silver sulphide (Ag₂S) thin films were grown on the glass substrate by chemical bath deposition (CBD). Five films deposited at the room temperature in a bath containing an aqueous solution of silver sulphide. The chemically synthesized Ag₂S films are annealed at 573K for one hour for the second sample, and two hours for the third sample. The fourth sample exposed to microwave irradiation for one hour, and two hours for the fifth sample. Surface morphology, photocatalytic, optical and structural properties of all Ag₂S samples investigated. The optical parameters such as transmittance, absorbance, absorption coefficient and energy bandgap of the films with thermal annealing and expose microwave irradiation presented. Optical measurement shows high absorbance in the ultraviolet-visible (UV-Vis) region. The difference in bandgap values of Ag₂S samples was located to be in the range of (1.5-2.05) eV. X-ray diffraction (XRD) measurements reflect the existence of polycrystalline, and the scanning electron microscopy images showed that the morphologies of Ag₂S thin films have various microspheres. The summary of the samples is in the annealing Ag₂S thin film which exhibits the best photocatalytic application.

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1. INTRODUCTION

Silver sulphide (Ag₂S) sample has a direct band gap (0.9-1.05 eV), a semiconductor with strong optical limiting, a high absorption coefficient, and robust chemical stability is desired. Ag₂S thin film sample has major use as a photocatalyst among all semiconductors [1]. Chalcogenide compounds, such as Ag₂S, have become increasingly important due to their diverse applications in various scientific and technological fields worldwide [2]. Ag₂S belongs to the I-VI compound semiconductor which has a monoclinic crystal structure.

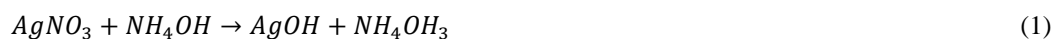
Thin films of Ag₂S are useful components in a range of modern technologies, such as photovoltaic cells, due to their functional properties [3], solar selective coatings [4], photoconductive [5], and laser recording media [6]. Chemical bath deposition is a straightforward process that offers consistent and reliable results, and inexpensive [7]. There are many techniques to fabricate samples like the sol-gel method [8], sputtering [9], solvent growth d.c. magnetron [10], PVP-assisted solvo [11], hydrothermal synthesis [12], and chemical bath deposition [13]. The best Ag₂S thin film method is prepared by chemical bath deposition on glass, silica substrate, and polyamide [14]-[17]. Numerous techniques developed to fabricate Ag₂S based on photocatalysts, including Ag₂S-ZnS microsphere composites [18], Ag₂S-ZnO photocatalysts [19], and Ni-doped Ag₂S nanoparticles [20].

The aim of the present work is to study the influence of annealing and microwave irradiation on optical, structural, surface morphology, and photocatalytic properties for Ag₂S thin films prepared by chemical bath deposition. The five samples are presented, the first sample is pure by means it is not treated with annealing or microwave irradiation, the second sample was annealed for one hour, the third sample irradiate for one hour, the fourth sample was annealed for two hours while the fifth sample irradiates for two hours only. The properties presented in this work provide an opportunity to compare the five samples.

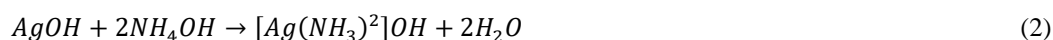
2. METHOD

Ag₂S thin films were deposited on a glass substrate at room temperature, immersed in a bath containing 0.05M silver nitrate (AgNO₃) placed in a vessel to dissolve it in distilled water. Ammonium hydroxide (NH₄OH) is added gradually with a constant magnetic stirring to form a dissolved precipitate. Sodium thiosulfate (Na₂S₂O₃·5H₂O) was added to the vessel for this stage. The substrates were supported vertically against the walls of the vessel at 50 °C. The bath was kept on a hot plate for 45 minute, as well as the deposited films for 10 minute which immersed in distilled water and then put outside to dry by air [21].

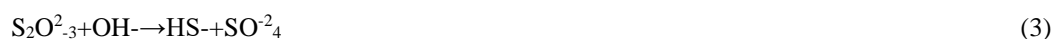
The chemical processes are considered for Ag₂S films deposition; silver ions are complexed by NH₄NO₃ as:



according to NH₄OH [22].



Thermal decomposition forms amino complex, Ag⁺ ions simultaneously released in the environment. The thiosulfate ions undergo hydrolytic decay, resulting sulphide ions in the environment, as shown in:



the final step is the combination of silver ions with the sulphide ions to form Ag₂S.



In this work, the structure of Ag₂S thin films was studied using X-ray diffraction (XRD) on a MiniFlex II Rigaku diffractometer, with a Cu K α radiation source of 1.54Å. Field emission scanning electron microscopy (FESEM) and photoluminescence (PL) were performed on a Hitachi-S4160, with a wavelength range of 220-900 nm, from Shimadzu RF-5301 pc, a gun oscillator used as a microwave source at a frequency of 9.4 MHz and a power of approximately 10 mW to study influence microwave irradiation on Ag₂S thin films.

3. RESULTS AND DISCUSSION

In this section, the results of the research are discussed in depth, providing a thorough understanding of the findings. The structural, optical, surface morphology, and photocatalytic activity of Ag₂S are shown. The figures and table are shown the milestones of the work.

3.1. Structural studies

X-ray diffraction (XRD) with a wavelength of 1.54 Å (Cu, K α) was used to analyze the structure of Ag₂S thin films using a MiniFlex II X-ray diffractometer from Rigaku (Japan). The effect of annealing and microwave irradiation on the structural properties of the Ag₂S thin films was also evaluated with x-ray diffraction. Figure 1 show XRD pattern of Ag₂S thin films. Figures 1(a) and 1(b) shows the influence of annealing, that was at 573K and microwave irradiation for one hour and two hours, respectively, on the structural properties of Ag₂S thin films. Several peaks are MO served after annealing at 573K for about an hour and after microwave irradiation exposure. The major peaks observed at 28.9° (111), 31.6° (112), 34.4° (121), 36.557(112), 36.805(121) 37.7° (103), 40.7° (031), and these peaks show the presence of Ag₂S [23].

Peak positions become sharp and small at full-width half maximum (FWHM), meaning films are polycrystalline. The peaks are indexed by comparing with JCPDS data file05—0566. Interestingly, additional peaks were found, these peaks may be due to some defects, and impurities and changed with annealing and microwave conditions. The XRD data show that the crystalline size increases with annealing temperature and microwave irradiation.

Using the Debye–Scherrer formula listed in Table 1, the average particle diameters (D) were calculated.

$$D = 0.94 \times \lambda / \beta \cos(\theta) \quad (6)$$

where λ is the wavelength of the X-ray, θ is the diffraction angle, and β is the FWHM after annealing and exposure to microwave irradiation. This equation shows an increased crystal size from 175 nm to 887 nm because of annealing and exposure to microwave irradiation. The strain and dislocation of films were calculated [24] using (7) and (8), respectively, and the results are presented in Table 1.

$$\varepsilon = \frac{\beta \cos \theta}{4} \quad (7)$$

$$\delta = \frac{1}{D^2} \quad (8)$$

Table 1. Summary of X-Ray characterization for the samples

Planes (hkl)	Annealing		Expose microwave irradiation			
	121	031	111	112	103	031
FWHM	0.331	0.2215	0.133	0.151	0.098	0.251
D(nm)	175	186	826	557	887	186
ε	33	28	15	32	13	28
δ	2.1	19	4.4	6.5	4.1	19

The quantitative analysis of Ag₂S film deposited on glass substrate was carried out using EDS technique at room temperature to study the stoichiometry of the film. The EDS was recorded in the energy region 0-20 eV. The presence of EDS peak for Ag and S are conformed from analysis and the presence of other elements like NaCl and O from the substrate as shown in Figure 1. Figure 1(a) shows a little difference in the behaviour between pure, microwave, and annealing depending on 2θ . Figure 1(b) shows the same test but after two hours of annealing and microwave irradiation and the intensity is reduced dramatically. A typical EDS pattern is shown in Figure 1(c). For clarity, the ε is multiplied by $\times 10^{14}$ lines.m⁻², while the strain is multiplied by $\times 10^{-4}$ lines⁻².m⁻⁴.

3.2. Optical properties

The optical behaviour of the presented samples is shown in Figure 2. Figure 2(a) shows the absorbance (A) pattern with wavelength (nm) for Ag₂S before and after annealing, and microwave irradiation, respectively. The high absorbance of the three films in the UV region (< 400 nm) makes them important materials for use in photovoltaic technology [25]. The increase in crystallite size and grain size improves the absorption in the visible region.

The transmittance in Figure 2(b) shows the UV-visible transmittance spectra of Ag₂S thin films deposited on a glass substrate with different time annealing and microwave irradiation in the range of 300-1,000 nm. As verified by the XRD study, the transmission of all films increased with an increase in a wavelength corresponding to improving photon dispersion due to impurities and surface roughness and an increase in the grain size of the silver sulphide (Ag₂S) process, and the light transmission of Ag₂S films improved after exposed microwave irradiation for 1h of full transmission compared to all samples. The maximum value of the transmittance greater than (45%) is obtained for the sample with one-hour microwave irradiation.

3.3. Optical energy gap (E_g)

The characteristics of $(ah\nu)^2$ and $h\nu$ (photon energy) were plotted for evaluating the band gap (E_g) of the Ag₂S thin films. Figure 3 displays the linear section close to the beginning of the photon energy axis's absorption edge. The straight-line nature of the graph suggests that Ag₂S is direct band gap material. The deposited Ag₂S thin films show the optical band gap for all sample in the range of 1.5-2.05 eV and this is agreeing with the reported data [26].

3.4. Surface morphology

Figure 4 shows a FESEM image of Ag₂S thin film deposited on the glass surface. It shows closely packed grains in different sizes. Figure 4(a) is the pure sample, Figure 4(b) is after annealing for one hour, Figure 4(c) is after annealing for two hours, Figure 4(d) is the sample exposed to microwave irradiation for one

hour, and Figure 4(e) is exposed microwave irradiation for two hours. The four films after annealing and exposure to microwave irradiation have a rough surface and irregular grain size. The annealing temperature and microwave irradiation exposure significantly altered the microstructure of the films. It is noticed the crystallite and grain size increased after annealing and exposed microwave irradiation for a one-hour sample.

The field emission scanning electron microscopy (FESEM) analysis of the Ag_2S thin films determined that the grain sizes ranged from 298 to 526 nm for the second and third samples respectively. The large grain sizes may be attributed to grain agglomeration. Figures 4(d) and 4(e) present SEM nano graphs of the annealed and irradiated Ag_2S thin films after two hours of exposure. The annealed film has some cracks due to the crystallization process during the annealing process, which causes vacancies to diffuse to the surface of the film. Subsequently, the fourth and fifth samples of the Ag_2S thin films were observed to have grain sizes of 80-120 nm. The SEM results of Ag_2S films reveal that the films formed are homogeneous and uniform.

3.5. Photocatalytic activity of Ag_2S

UV-Visible spectroscopy was used to analyze the photocatalytic performance of as-grown Ag_2S films. The films were placed in a vessel containing 50 mL of 30 ppm methylene orange (MO), which was stirred in the dark for 30 minutes. Subsequently, the absorption intensity of UV-Visible spectra of the samples before and after irradiation under natural sunlight was examined, as illustrated in Figure 5.

The photocatalytic activity of Ag_2S thin films after and before annealing and exposure to microwave irradiation is estimated by photodegrading of MO under sunlight as shown in Figure 5(a). The Ag_2S thin films after annealing as shown in Figure 5(b), and microwave irradiation as shown in Figure 5(c) present stronger MO adsorption ability than before annealing and exposure to microwave irradiation. The XRD properties and surface area of the films are responsible for the distinct character of each film, which is reflected in the results.

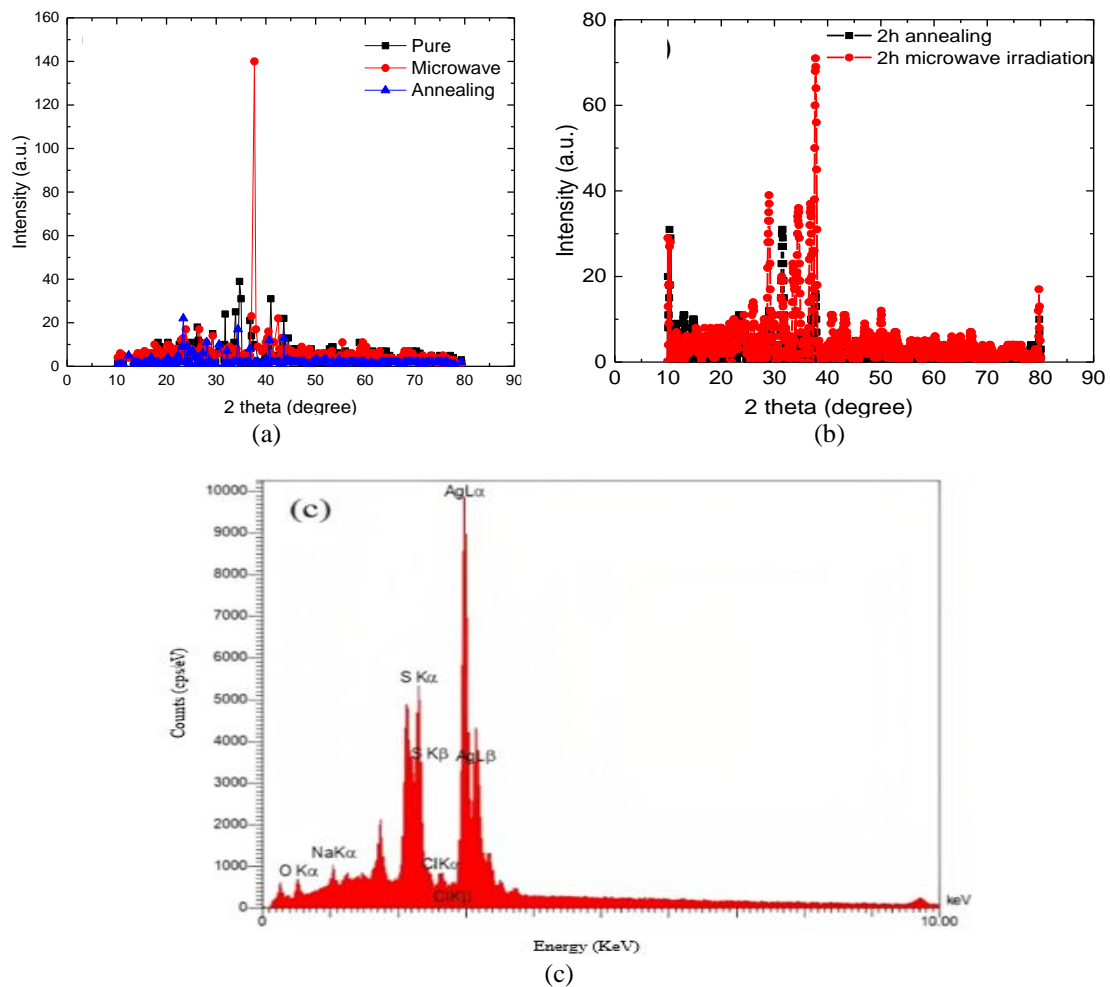


Figure 1. XRD pattern of Ag_2S thin films for (a) pure, after annealing at 573K, and after exposing microwave irradiation for one hour, (b) after exposing microwave irradiation for two hours, and (c) EDS profile at room temperature showing the Ag and S peaks

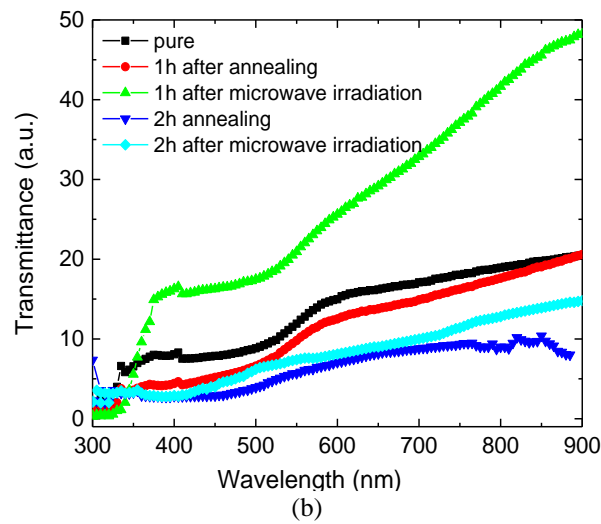
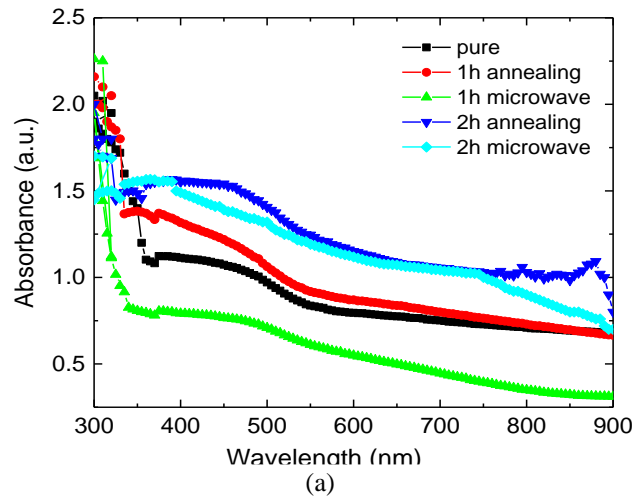


Figure 2. Optical properties as a function of wavelength for silver sulphide thin films (a) absorbance and (b) transmittance

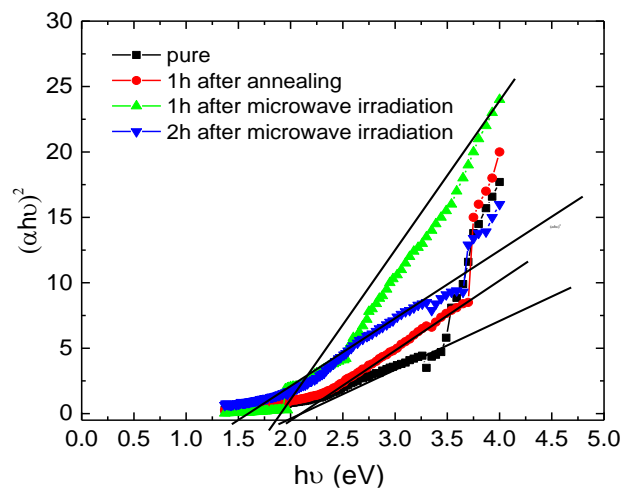


Figure 3. $(\alpha h\nu)^2$ with photon energy for silver sulphide thin films

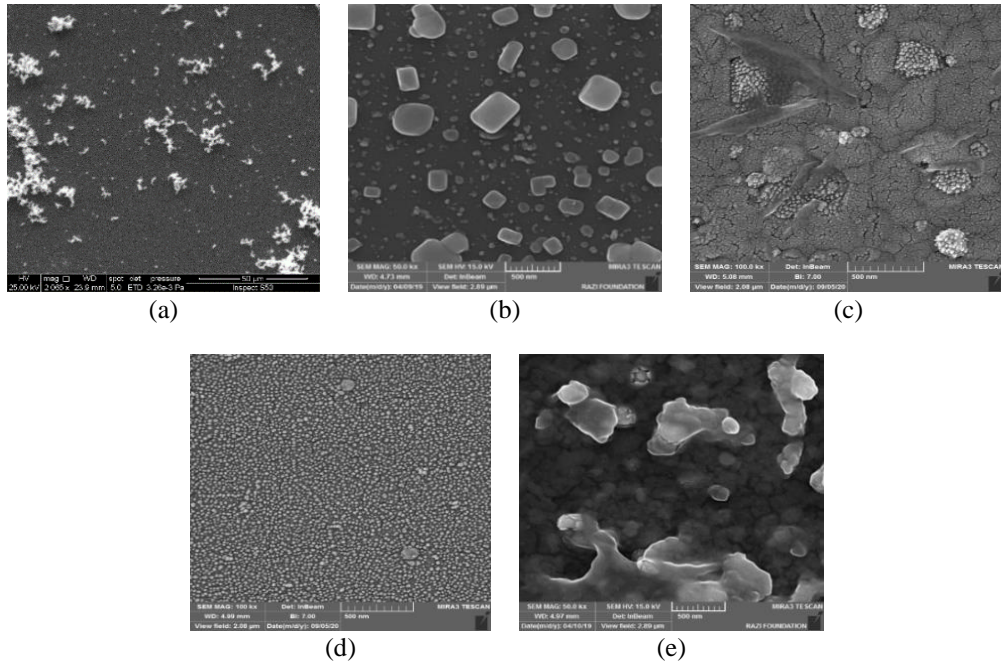


Figure 4. FESEM image of Ag_2S thin films (a) pure, (b) after annealing 1 hour, (c) after annealing 2 hour, (d) expose microwave irradiation 1 hour, and (e) expose microwave irradiation 2 hour

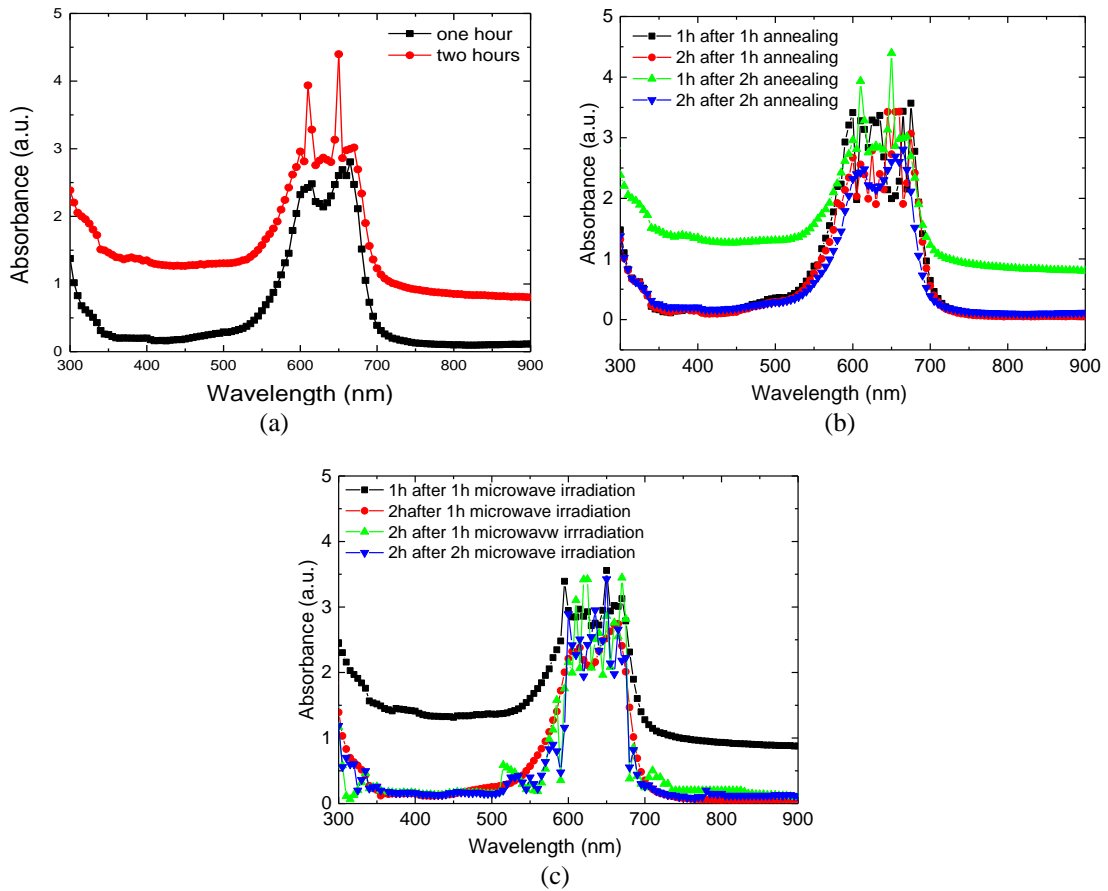


Figure 5. The UV-VIS absorption spectra demonstrate the progression of photodegradation of MO dye over time when exposed to solar radiation (a) before annealing and exposure to microwave irradiation for the pure sample, (b) after annealing, and (c) after exposure to microwave irradiation




4. CONCLUSION

In this work, silver sulphide (Ag_2S) thin films were prepared using the CBD technique with a silver acetate ammonia-thiourea system. Optical studies conducted on the films showed that the absorbance of the Ag_2S films increased steadily towards the visible region. The energy band gap of the films was determined to be 2.1 eV. It is observed from FESEM measurements that the substrate is well-covered with Ag_2S and has better uniformity in grain size. The X-Ray diffraction analysis shows that the preferential plane of silver sulphide film is (121). Ag_2S thin films annealing and microwave irradiation present stronger OB absorption ability than Ag_2S films before annealing and exposure to microwave irradiation. Thus, we conclude that the CBD method is low-cost method for the fabrication of Ag_2S thin film as a device for photocatalytic application.




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