JOURNAL OF NANO- AND ELECTRONIC PHYSICS
Vol. 13 No 1, 01027(4pp) (2021)

ЖУРНАЛ НАНО- ТА ЕЛЕКТРОННОЇ ФІЗИКИ
Том 13 № 1, 01027(4cc) (2021)

Synthesis and Characterization of Multiwalled Carbon Nanotubes (MWCNTs) Dispersed ZnS Based Photocatalytic Activity

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(Received 10 January 2021; revised manuscript received 13 February 2021; published online 25 February 2021)

Zinc Sulfide (ZnS) based photocatalytic activity has been focused in solar hydrogen production and water treatment process because to their very strong redox reaction. Due to wide visible light range, ZnS becomes a promising semiconductor in formation of photocatalysts. The bandgap energies (E_g) of all prepared samples ZnS NCs and MWCNTs/ZnS nanocomposites were evaluated and Methylene Blue (MB) degradation study occurring of ZnS NCs and MWCNTs/ZnS nanocomposites were evaluated under visible light using UV-visible spectroscopy. The author found that removal rate of MB is greater than 95 percentage in the presence of MWCNTs/ZnS composites photocatalysts after 50 min. Crystalline grain size and structure of photocatalyst were characterized by X-ray Diffraction (XRD) spectroscopy. The enhancement of photocatalytic activity can be associated by many factors like a suitable band gap in visible region, crystalline structure of nanocomposites and particle size in nanometer (nm) of the MWCNTs/ZnS nanocomposites. The suitable photocatalytic reaction and mechanisms of MB degradation also included in this article.

Keywords: Photocatalytic activity, Degradation of MB, Band gap, MWCNT/ZnS.

DOI: 10.21272/jnep.13(1).01027 PACS numbers: 61.48.De, 42.70.Qs

1. INTRODUCTION

ZnS semiconductor is found II-VI group in the periodic table. ZnS nanocrystals (NCs) has been used in multiple purposed in research because of excellent morphologies show in nanoscale and effective photocatalytic properties show due to strong redox reaction [1-3]. ZnS semiconductor has been focused much attention because of different important applications like light-emitting diodes (LEDs), luminescence devices, flat panel displays, electronic sensors, infrared windows and lasers [1]. In addition, ZnS was used excellent charge carrier transportation properties, higher stability, excellent electronic mobility and low cost semiconductor [1, 6]. ZnS NCs forms two types of crystalline structure. The first is cubic and is also known as sphalerite and the other one is hexagonal also known as wurtzite structure. In both cubic and hexagonal structure the expectation value of band gap energy (E_g) is 3.71 eV and 3.78 eV, respectively [1]. Photocatalysts demonstrate absorption bands at longer wavelengths are highly desirable for solar light efficiency [7, 8]. Several experiments have been conducted in the formation of solar energy conversion by visible light activation. In addition, during visible light activation must has been focused that photocatalyst is stable under solar visible light irradiation [9]. Researchers used several methods in formation of photocatalyst like transition metal doping, composite semiconductor and dye sensitization for development of higher photocatalytic activity [10]. Moreover, ZnS NCs crystalline size, crystal structure and large volume to surface ratio play an important role in photocatalytic activity like charge carrier transportation and semiconductor surface reactions [11, 12]. Photocatalytic activity of ZnS NCs depends on: (1) separation rate of charge carriers (electron/holes), (2) photocorrosion (3) electron/hole recombination rate [13]. The energy conversion of chemical-to-solar is controlled by the interfacial interaction between charge carriers and kinetic reactions of semiconductor surface.

Multiwalled carbon nanotubes (MWCNTs) have an excellent electron conductivity, strong mechanical, thermal stability and high surface area. Due to this properties MWCNTs makes most common solid phase material used for the removal of organic and inorganic compounds and it has been adsorbed on the outer surface of ZnS NCs. However, because of good electronic conductivity of MWCNTs can significantly promote the interfacial electron transfer from photocatalysts surface to MWCNTs, then reduce the charge recombination of electron/hole pair, therefore also reduce the photocorrosion of charge carriers on photocatalysts surface as a result MWCNTs could enhanced the photocatalytic activity [14-19].

1.1 Photocatalytic Mechanism

Fig. 1 represents the possible photocatalysis mechanism of MWCNTs/ZnS composites. MWCNTs and ZnS NCs were shows strong interaction between them represents that MWCNTs are strongly adsorbed on ZnS NCs. In the presence of environmental air and oxygen, light particle ($h\nu$) activated the MWCNTs/ZnS nanocomposites then electron/holes pair produces by strong oxidization and reduction process, respectively:

$$\text{MWCNTs/ZnS} + h\nu \rightarrow h^{+} + e^{-}, \quad (1)$$

$$OH^{-} + h^{+} \rightarrow OH \text{ and } O_2 + e^{-} \rightarrow O_2^{-}. \quad (2)$$

The residual radicals emerge out during oxidation and reduction reaction in degradation of MB. After a complete reaction CO_2 and H_2O produces as a final products [20, 21]:

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The results were presented at the International Conference on Multifunctional Nanomaterials (ICMN2020)

$$MB + OH \rightarrow \text{products } (CO_2 + H_2O + NH_4^+ + NO_3^- + SO_4^{2-} + Cl^-), \quad (3)$$

$$MB + O_2 \rightarrow \text{products } (CO_2 + H_2O + NH_4^+ + NO_3^- + SO_4^{2-} + Cl^-). \quad (4)$$

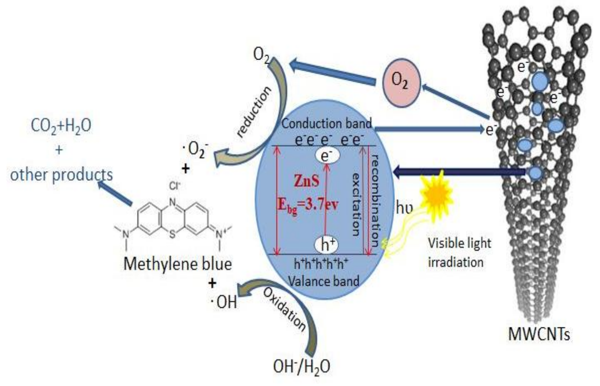

Fig. 1 – Schematic diagram of a possible photocatalysis mechanism

1.2 Methylene Blue

The molecular formula of methylene blue (MB) is C16H18N3SCl and for structure see Fig. 2. Methylene blue is a dark green powder, when it is mixed in water, it turn blue solution and provide absorbance peak at 664 nm. When methylene blue added in photocatalyst, it affected the photocatalytic activity of photocatalyst.

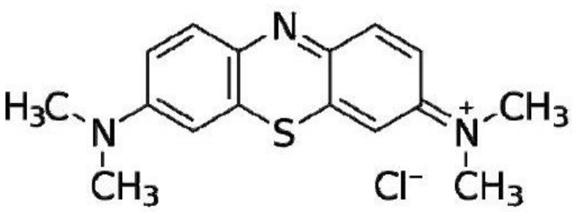

Fig. 2 – Structure of methylene blue (MB)

2. EXPERIMENTAL METHODS

2.1 Synthesis and Characterization of MWCNTs/ ZnS Composites

MWCNTs (multiwalled carbon nanotubes) were purchased from the Helix Company, China. Methylene blue (aqueous) was purchased from Merck chemicals and zinc sulphide (ZnS) 98 % extra pure was purchased from Loba chemical Pvt. Ltd. The solution was prepared in deionized double distilled water. All chemicals were purchased from credible suppliers and used without purification, purity of these chemicals was verified by reactions.

The prepared solutions were characterized by a UV-visible absorption spectroscopy with complete scale 200 to 800 nm on a Shimadzu UV-visible spectroscopy manufacturing in Japan. The reaction among ZnS NCs and MWCNTs/ZnS nanocomposites was evaluated in aqueous solution of MB using UV-visible spectroscopy and absorption peak found of MB at 664 nm. The X-ray diffraction spectroscopy (XRD) spectra study of Bruker-AXS D8 ADVANCE with scanning rate 0.01 steps from 20-80 degree with CuK$_\alpha$ radiation(λ = 0.1542 nm).

2.2 Photocatalytic Activity Measurement

Degradation rate of MB (dye) in the presence of synthesized photocatalysts ZnS NCs and MWCNT/ZnS composites were investigate by simulated solar irradiation. ZnS NCs of 50 mg and 50 mg MWCNTs/ZnS composites were added into the photocatalytic reactor containing 1000 ml aqueous solution of MB (concentration 1 mg/l) separately. After that for complete mixing of composites aqueous solution of photocatalyst was performed on magnetic agitation for 60 min and ultrasonic cleaner for 30 min, respectively. Oxygen was providing to the aqueous solution by environmental air such that oxygen increase to help in the formation of photocatalyst during reaction. During photoreaction temperature maintained by water cooling and experiment were carried out at room temperature about 25 °C.

Percentage degradation of MB can be determined by using Beer-Lambert law [22, 23]:

$$R = \frac{Co - C}{Co} \times 100\% = \frac{Ao - A}{Ao} \times 100\%, \quad (5)$$

where C, C_0 and A, A_0 are the concentration and absorbance of MB at reaction times t and 0, respectively.

3. RESULTS AND DISCUSSION

3.1 X-ray Diffraction (XRD)

Fig. 3 shows XRD spectrum of MWCNTs, ZnS NCs and MWCNTs/ZnS composites. X-ray diffraction peaks of hexagonal MWCNTs recorded at 25.07° and 43.19° can be assigned to the (002) and (100) crystalline planes (JCPDS card no. 89-8487), respectively.

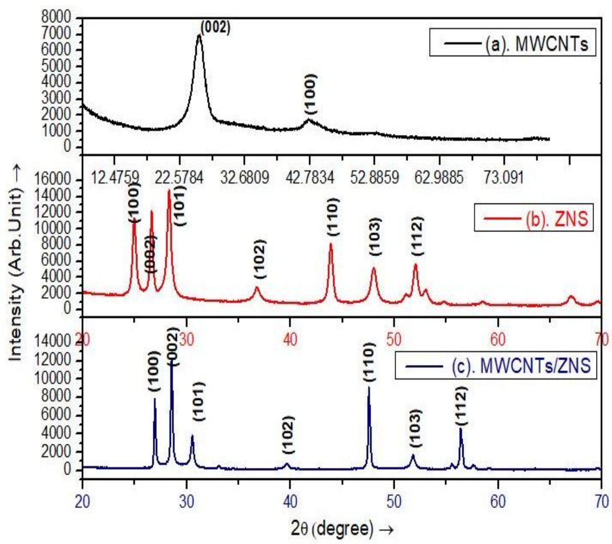

Fig. 3 – XRD patterns of (a) MWCNTs, (b) ZnS NCs and (c) MWCNTs/ZnS nanocomposite

ZnS crystal structure with seven predominant characteristics X-ray diffraction peaks obtained at 2θ is equal to 24.9°, 26.6°, 28.3°, 36.7°, 43.8°, 47.9°, 51.15° can be assigned to the hexagonal crystalline phase of ZnS (100), (002), (101), (102), (110), (103) and (112), respectively (JCPDS card number 36-1450). It has been observed from the spectra that the peak height increases in composite system and shifted to higher angles.

Crystalline grain size has been determined using the Scherrer equation:

$$D = \frac{k\lambda}{\beta cos\theta}, \quad (6)$$

where $k = 0.94$ (shape factor constant), β is the FWHM value (full width at half maximum).

The crystalline grain size was found to be high height peaks for ZnS nanoparticles having the value of FWHM is 0.46773 and 2θ is 28.309 degree and obtained crystalline size of ZnS by Scherrer formula is 28.30 nm and crystalline size of MWCNTs/ZnS nanocomposites is 13.18 nm. This result shows that after doping of MWCNTs the particle size is reduced attributed MWCNT is a good catalyst.

3.2 Photocatalytic Activity of MWCNTs/ZnS Composites

To find the efficiency of photocatalyst the authors researched on degradation study of dye in the presence of photocatalyst ZnS NCs and MWCNTs/ZnS nanocomposites and also checked role of MWCNTs in photocatalytic efficiency.

Fig. 4 shows Tauc plot for ZnS NCs and MWCNTs/ZnS composites. The light absorption of MB is controlled by charge carriers (electron/holes), which study is depending on optical properties. A strong visible light absorbance was observed in spectra of both ZnS NCs and MWCNTs/ZnS composites, respectively.

The value of optical band gap was calculated using Tauc relation:

$$(\alpha h\nu)^2 = A(h\nu - E_g)^n, \quad (7)$$

where $n = 0.5$ (for direct allowed transition), A is a constant, h is the Planck constant, E_g is the band gap energy, $h\nu$ is the photon energy and ν is the frequency of incident radiation. Using Tauc relation, we obtained E_g for ZnS NCs and MWCNTs/ZnS composites which are 3.3 eV and 3.12 eV, respectively.

Fig. 5 and Fig. 6 represent the visible light degradation spectra of dye in the presence of photocatalysts ZnS NCs and MWCNTs/ZnS composites for several exposure times. Degradation study shows the absorption curves of Methylene Blue slightly decreases with increasing of reaction time. The author have found that methylene blue is overall degrade greater than 95 % under visible light, degradation time for ZnS NCs was in 100 min and for MWCNTs/ZnS was observed in only 50 min. Therefore, we conclude that MWCNTs enhance the photocatalytic activity of photocatalyst and increase the reaction rate. Fig. 7 represents the comparative result of photocatalytic activity between ZnS NCs and MWCNTs/ZnS composites. Comparative results of composites show that MWCNTs/ZnS composite shows higher photocatalytic activity in comparison of ZnS NCs. Fig. 8 shows the bar study of composites ZnS and MWCNTs/ZnS composites for 50 min. This results shows that MWCNTs increase the reaction rate in MWCNTs/ZnS composites.

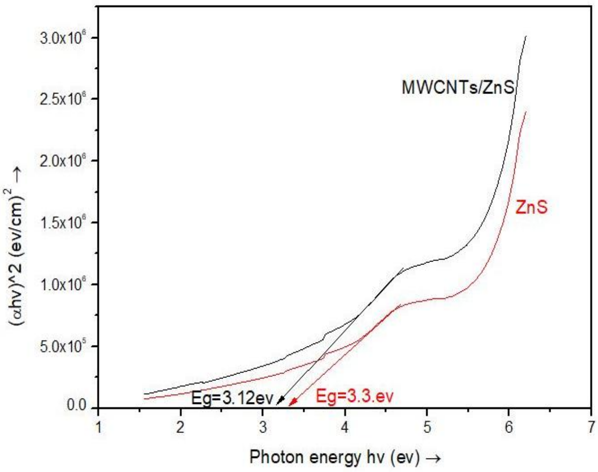

Fig. 4 – Tauc plot of pure ZnS NCs and MWCNTs/ZnS composites

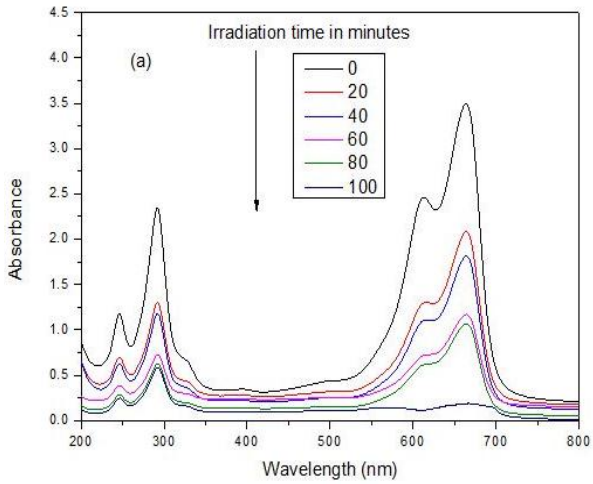

Fig. 5 – UV-visible spectra of MB (aqueous solution 1 mg/l) for ZnS NCs (50 mg)

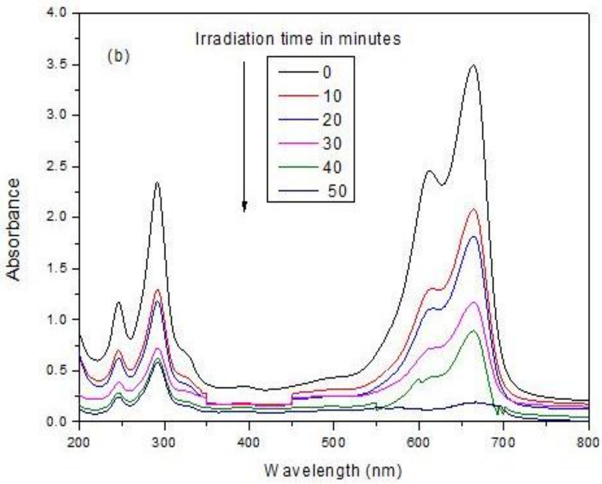

Fig. 6 – UV-visible spectra of MB (aqueous solution 1 mg/l) for MWCNTs/ZnS composites (50 mg)

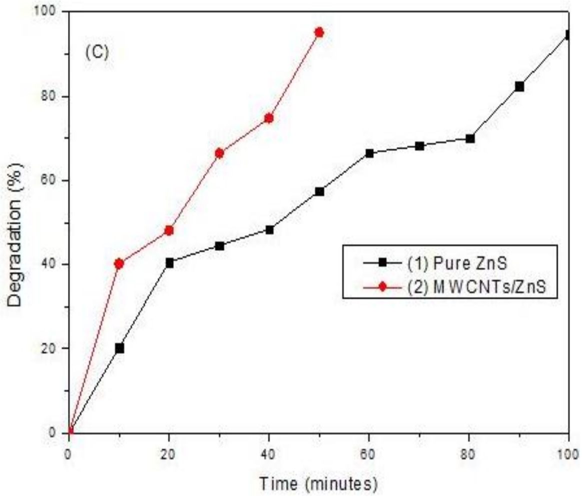

Fig. 7 – Percentage (%) degradation of MB (aqueous solution concentration 1 mg/l) with pure ZnS NCs and MWCNTs/ZnS composites under visible light

The interaction process between them is following: In visible light, the ground state electrons of ZnS NCs are moves in excited state and increasing the regeneration of charge carriers (electron/holes). The excited electrons of ZnS NCs can move towards to MWCNTs. All excited electron capturing by MWCNTs, therefore reducing the recombination of charge carriers (electron/holes), and so we conclude that MWCNTs boost the dispersion of MB and enhance the photocatalytic activity of ZnS NCs.

4. CONCLUSIONS

MWCNTs/ZnS composites photocatalyst were synthesized by chemical and eco-friendly method. Its morphology and structural effect characterized by X-ray diffraction (XRD) and crystalline grain size calculate using Scherrer equation. Crystalline grain size shows that MWCNTs reduced particle size of ZnS NCs. Therefore, it was concluded that MWCNTs are a good cocatalyst for photocatalytic activity. Optical, degradation and band gap study characterized by UV-visible absorption spectroscopy. Bandgap of prepared sampled were calculated using Tauc relation and percentage degradation of MB calculated using Beer-Lambert law. Degradation results shows the MWCNTs/ZnS composites shows higher photocatalytic activity and degradation rate in comparison of pure ZnS. Kinetics study shows the successfully synthesis of all photocatalytic composites.

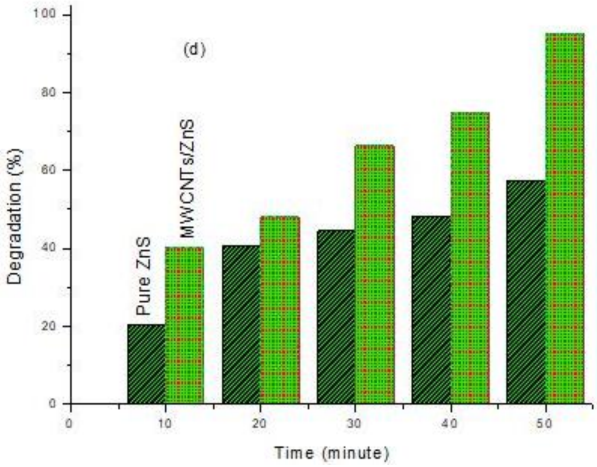

Fig. 8 – Bar chart of MB (aqueous solution 1 mg/l) with ZnS NCs and MWCNTs/ZnS nanocomposites for 50 min

ACKNOWLEDGEMENTS

This study is supported by the Central Analytical Facilities of Manipal University Jaipur. The authors gratefully thank to vice chancellor of Manipal University Jaipur for their support and constant encouragement.

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