RESEARCH PAPER

Photocatalytic Activity to Remove the Effect of Methylene Blue Dye by Using CdS Nanocrystalline under Visible Light

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ABSTRACT

Porous CdS nanocrystalline thin film was synthesized via chemical bath deposition. The XRD (X-ray diffraction) pattern of the porous shows the cubic structure. FESEM (Field emission scanning electron microscopy) analysis shows that the surface of Cadmium sulfide (CdS) is a porous shape. The EDX (energy dispersive X-ray spectroscopy) Technique assures the presence of Cd and S elements in the sample. To determine the band gap energy of porous CdS, UV-visible absorption spectra were analyzed, revealing an estimated value of approximately 2.39 eV. Subsequently, the photocatalytic degradation of methylene blue was using porous CdS as the catalyst. This degradation process took place under visible light irradiation from a 200-W xenon lamp. The utilization of porous CdS in this photocatalytic reaction demonstrates its potential as an effective catalyst for the degradation of methylene blue, a commonly used dye in various industries. To our knowledge, there is no previous study about porous CdS acting as catalysis to remove methylene blue dye. In seven hours, porous CdS removed 72% of methylene blue.

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INTRODUCTION

Photocatalysis is a highly effective process utilized in the treatment of colored dye wastewater. It involves the utilization of a semiconductor material that absorbs light energy equal to or greater than its band gap. This absorption triggers the excitation of valence band electrons, causing them to move to the conduction band. As a result, electron-hole pairs are formed, which play a crucial role in generating

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free radicals within the system. These free radicals, including hydroxyl (•OH), exhibit exceptional oxidizing capabilities, particularly when it comes to organic materials. Consequently, these radicals facilitate the degradation of pollutants present in the wastewater, contributing to the overall decoloration process [1]. The textile, paper, and certain industrial processes generate large quantities of colored dye wastewater that is both highly toxic and resistant to biodegradation. When

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this wastewater is discharged into natural water runoff, it poses a significant threat to the entire ecosystem by interfering with the photosynthetic activity of aquatic plants. Over the past few decades, researchers and scientists have dedicated their efforts to developing a range of physical, chemical, and biological techniques to tackle the decoloration of dye effluents. However, it is crucial to acknowledge that conventional treatments, including coagulation, flocculation, absorption, adsorption, ultrafiltration, reverse osmosis, and membrane technologies, primarily concentrate on transferring or moving organic compounds from one phase to another. Although conventional methods can reduce the visible presence of colored dyes in wastewater, they do not adequately address the toxicity and non-biodegradability of the pollutants. As a result, there is a need for further advancements and innovations to develop sustainable and efficient solutions that can effectively degrade or remove colored dyes from wastewater. These advancements are crucial to ensure the protection and preservation of the ecosystem [2-6]. Traditional methods just concentrate organic substances or move them through one state to the next. Although disruptive methods like chemical oxidation and advanced oxidation processes (AOPs) could be able to solve such issues, they still have high prices and insufficient deterioration [7]. Among AOPs, Since visible light is the predominant component of both indoor illumination and the solar spectrum, photocatalysis under visible-light irradiation is without a doubt one of the most successful and inexpensive approaches [5]. Cadmium sulfide (CdS) in a nanosize is considered one of the best photocatalytic because of characteristics like inexpensive price, high stability, safety, and great photoactivity [8,9]. absorption of light by a semiconductor material occurs when the energy of the incident light is greater than or equal to the band gap, valence electrons in the ground

Fig. 1. Flowchart and the preparation steps of porous CdS.

state band are activated and can recombine or dissociate at the material's surface [10,11]. As potential photocatalysts, a variety of materials including TiO₂, ZnO, and SnO₂ have attention to the degradation of organic dye causing water waste [12,13].

This research focuses on using the photocatalytic properties of a porous CdS nanocrystalline thin film, which is irradiated with visible light to oxidatively destroy aqueous source pollutants and highly colored dyes like methylene blue.

MATERIALS AND METHODS

Synthesis of porous CdS nanocrystalline thin film

In brief, Chemical bath deposition was used to create the porous CdS. A suitable amount of Thiourea CH₄N₂S and cadmium nitrate Cd(NO₃)₂ were dissolved in 100ml of s distilled water. Then the beaker containing a solution was placed in a hotplate at 70±5°C to deposit a thin film [14]. All procedures are shown in the following flowchart.

RESULTS AND DISCUSSION

Structural Studies

Nondestructively revealing a material's crystal structure, physical properties, and chemical make-up, XRD (X-ray diffraction) analysis is a key

technique. Fig. 2 shows the XRD diffractograms obtained for porous CdS nanocrystalline thin film. The main peaks (2 0 0), (2 2 0) and (1 1 1) confirm the cubic structure type. At $2\theta^{\sim}33^{\circ}$, the (511) plane was discovered to dominate the tiny peak crystalline of sulfur. The other peaks return to a glass substrate [15].

Surface characterizations

Macropores are defined as being larger than 50 nm, micropores are defined as being smaller than 2.0 nm and mesopores are between 2 and 50 nm [16]. Fig. 3 (A) is a FE-SEM micrograph displaying the CdS in a porosity state. It can be seen that CdS was formed in the macropores type with an average distribution porous size between 200-300nm as depicted in (B). The EDX (energy-dispersive x-ray) spectroscopy technique is important to estimate the chemical composition of the material. Fig. 3(C) displays a typical EDX spectrum for a CdS film placed on glass with a high porosity. The results indicate the existence of both Cd and S peaks, with a ratio of 16.3 for Cd to S.

Optical properties

Absorbance spectra from 200-800nm for a nanocrystalline porous CdS sheet, as well as

Fig. 2. XRD patterns of porous CdS.

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Fig. 3. FE-SEM of porous CdS (A), Distribution porous siz (B) and EDX spectra (C)

methylene blue dye are displayed in Fig. 4(A). By creating a Tauc plot of (hvα)2 versus (hv), and then projecting the linear sections of the curves to the energy axis, the band gap energy (Eg) of porous CdS was derived from the UV-Vis spectra through calculation[17].

$$
(\alpha h\nu)^{1/n} = (h\nu - Eg) \tag{1}
$$

where, α is denoted by absorption coefficient, The optical band gap of porous CdS is denoted by Eg, h v is the photon energy, and The value of the exponent (n) varies depending on the kind of transition being considered. Fig. 4(B) shows that it determined the energy gap of porous CdS thin

films is 2.39eV, There is a redshift from the spectra that can be observed compared with a bulk CdS (2.42 eV).

Photoluminescence (*PL*)

The photoluminescence spectral analysis was used to detect the formation defect of Cd and S [18-20]. The PL spectra of the nanocrystalline CdS thin films are shown in Fig. 5. The figure depicting the two peaks, The first one has its center near 461nm and is associated with emission resulting from the recombination of electron-hole pairs occurring close to the band gap ,whereas the second one has a significant shift towards 620nm. The red band emission may be attributed to the increase in sulfur vacancies [21].

Fig. 4. UV–Vis spectra (A) and Tauc plot of the porous CdS(B).

Photocatalytic activity

In this work, MB (methylene blue) dye was used as a target pollutant to assess the real performance of the as-prepared catalyst porous CdS under visible-light illumination with power 200W (Xenon) as depicted in Fig. 6.

Photocatalytic degradation of MB was studied using UV-Vis spectral analysis scanned in the range of 200-900nm. The sample was centred directly at the circular spot of light for continued times 0-7

$CdS + h\theta \rightarrow h^+ + e^-$	porous thin film	(2)	
$OH^- + h^+ \rightarrow OH$	hydroxyl radical	(3)	
$O_2 + e^- \rightarrow O_2$	superoxide radical	(4)	
$MB + OH$	$\rightarrow (CO_2 + H_2O + NH_4^+ + NO_3^- + SO_4^{2-} + Cl^-)$	products	(5)

Fig. 6. Schematic diagram of photocatalytic activity

Fig. 7. Photodegradation of MB dye by porous CdS.

hours. Upon photon (hυ) activation of porous CdS, highly reactive electron-hole pairs are released, which can be written as equqtions 2-5 [22,23]

The photodegradation rate estimate using the formula [24]:

$$
D(\%) = \frac{A_0 - A}{A_0} \times 100\%
$$
 (6)

where A_{\circ} , and A represent the absorbance value before and after exposure, respectively.

Fig. 7 shows that the presence of porous CdS led to the obvious breakdown of MB dye. The degradation rate efficiency has reached 72% after 7h of exposure to visible light.

CONCLUSION

In conclusion, an easy and low-cost method named chemical bath deposition was employed to prepare CdS in form porous. Porous-CdS was confirmed by FE-SEM analysis. The optical bandgap of porous CdS was evaluated using Tauc's relationship and it's about 2.39eV. EDX analysis confirms that the compound form was CdS. The XRD pattern shows a cubic structure for porous CdS. After a continuous illumination period of 7 hours, the photocatalyst porous demonstrated a degradation efficiency of approximately 72%. This indicates that the POROUS photocatalyst effectively facilitated the breakdown and removal of pollutants present in the colored dye wastewater. The high degradation efficiency achieved within this timeframe highlights the effectiveness of the photocatalytic process in treating such wastewater and reducing its environmental impact.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

REFERENCES

- 1. [Pouretedal HR, Norozi A, Keshavarz MH, Semnani A.](http://dx.doi.org/10.1016/j.jhazmat.2008.05.128) [Nanoparticles of zinc sulfide doped with manganese, nickel](http://dx.doi.org/10.1016/j.jhazmat.2008.05.128) [and copper as nanophotocatalyst in the degradation of](http://dx.doi.org/10.1016/j.jhazmat.2008.05.128) [organic dyes. J Hazard Mater. 2009;162\(2-3\):674-681.](http://dx.doi.org/10.1016/j.jhazmat.2008.05.128)
- 2. [Jiang R, Zhu H, Li X, Xiao L. Visible light photocatalytic](http://dx.doi.org/10.1016/j.cej.2009.05.037) [decolourization of C. I. Acid Red 66 by chitosan capped CdS](http://dx.doi.org/10.1016/j.cej.2009.05.037) [composite nanoparticles. Chem Eng J. 2009;152\(2-3\):537-](http://dx.doi.org/10.1016/j.cej.2009.05.037) [542.](http://dx.doi.org/10.1016/j.cej.2009.05.037)
- 3. [Sharma M, Jain T, Singh S, Pandey OP. Photocatalytic](http://dx.doi.org/10.1016/j.solener.2011.11.006) [degradation of organic dyes under UV–Visible light using](http://dx.doi.org/10.1016/j.solener.2011.11.006) [capped ZnS nanoparticles. Solar Energy. 2012;86\(1\):626-](http://dx.doi.org/10.1016/j.solener.2011.11.006) [633.](http://dx.doi.org/10.1016/j.solener.2011.11.006)
- 4. [Torres-Martínez CL, Kho R, Mian OI, Mehra RK. Efficient](http://dx.doi.org/10.1006/jcis.2001.7684) [Photocatalytic Degradation of Environmental Pollutants](http://dx.doi.org/10.1006/jcis.2001.7684) [with Mass-Produced ZnS Nanocrystals. Journal of Colloid](http://dx.doi.org/10.1006/jcis.2001.7684) [and Interface Science. 2001;240\(2\):525-532.](http://dx.doi.org/10.1006/jcis.2001.7684)
- 5. [Zhu H, Jiang R, Xiao L, Chang Y, Guan Y, Li X, Zeng G.](http://dx.doi.org/10.1016/j.jhazmat.2009.04.037) [Photocatalytic decolorization and degradation of Congo](http://dx.doi.org/10.1016/j.jhazmat.2009.04.037) [Red on innovative crosslinked chitosan/nano-CdS](http://dx.doi.org/10.1016/j.jhazmat.2009.04.037) [composite catalyst under visible light irradiation. J Hazard](http://dx.doi.org/10.1016/j.jhazmat.2009.04.037) [Mater. 2009;169\(1-3\):933-940.](http://dx.doi.org/10.1016/j.jhazmat.2009.04.037)
- 6. [Hussain AA, Abdulelah H, Amteghy AH, Dheyab RA, Hamdan](http://dx.doi.org/10.1155/2023/7998917) [AlMulla B. Effect of Multilayers CdS Nanocrystalline Thin](http://dx.doi.org/10.1155/2023/7998917) [Films on the Performance of Dye-Sensitized Solar Cells.](http://dx.doi.org/10.1155/2023/7998917) [Journal of Nanotechnology. 2023;2023:1-7.](http://dx.doi.org/10.1155/2023/7998917)
- 7. [Rayaroth MP, Aravindakumar CT, Shah NS, Boczkaj G.](http://dx.doi.org/10.1016/j.cej.2021.133002) [Advanced oxidation processes \(AOPs\) based wastewater](http://dx.doi.org/10.1016/j.cej.2021.133002) [treatment - unexpected nitration side reactions - a](http://dx.doi.org/10.1016/j.cej.2021.133002) [serious environmental issue: A review. Chem Eng J.](http://dx.doi.org/10.1016/j.cej.2021.133002) [2022;430:133002.](http://dx.doi.org/10.1016/j.cej.2021.133002)
- 8. [Abdulelah H, Ali B, Mahdi MA, Hassan JJ, Al-Taay HF,](http://dx.doi.org/10.1016/j.physe.2017.03.019) [Jennings P. Fabrication and characterization of nanowalls](http://dx.doi.org/10.1016/j.physe.2017.03.019) [CdS/dye sensitized solar cells. Physica E: Low-dimensional](http://dx.doi.org/10.1016/j.physe.2017.03.019) [Systems and Nanostructures. 2017;90:104-108.](http://dx.doi.org/10.1016/j.physe.2017.03.019)
- 9. [Zhang Q, Zhang Y, Huang S, Huang X, Luo Y, Meng Q, Li D.](http://dx.doi.org/10.1016/j.elecom.2009.12.032) [Application of carbon counterelectrode on CdS quantum](http://dx.doi.org/10.1016/j.elecom.2009.12.032) [dot-sensitized solar cells \(QDSSCs\). Electrochem Commun.](http://dx.doi.org/10.1016/j.elecom.2009.12.032) [2010;12\(2\):327-330.](http://dx.doi.org/10.1016/j.elecom.2009.12.032)
- 10. [Warrier M, Lo MKF, Monbouquette H, Garcia-Garibay MA.](http://dx.doi.org/10.1039/b408152h) [Photocatalytic reduction of aromatic azides to amines](http://dx.doi.org/10.1039/b408152h) [using CdS and CdSe nanoparticles. Photochemical &](http://dx.doi.org/10.1039/b408152h) [Photobiological Sciences. 2004;3\(10\):859-863.](http://dx.doi.org/10.1039/b408152h)
- [11.Giribabu K, Suresh R, Manigandan R, Vijayaraj A, Prabu](http://dx.doi.org/10.5012/bkcs.2012.33.9.2910) [R, Narayanan V. Cadmium Sulphide Nanorods: Synthesis,](http://dx.doi.org/10.5012/bkcs.2012.33.9.2910) [Characterization and their Photocatalytic Activity. Bull](http://dx.doi.org/10.5012/bkcs.2012.33.9.2910) [Korean Chem Soc. 2012;33\(9\):2910-2916.](http://dx.doi.org/10.5012/bkcs.2012.33.9.2910)
- [12.Diebold U. The surface science of titanium dioxide. Surf Sci](http://dx.doi.org/10.1016/s0167-5729(02)00100-0) [Rep. 2003;48\(5-8\):53-229.](http://dx.doi.org/10.1016/s0167-5729(02)00100-0)
- 13. [Zhang M, An T, Hu X, Wang C, Sheng G, Fu J. Preparation and](http://dx.doi.org/10.1016/j.apcata.2003.10.025) photocatalytic properties of a nanometer ZnO–SnO₂ coupled [oxide. Applied Catalysis A: General. 2004;260\(2\):215-222.](http://dx.doi.org/10.1016/j.apcata.2003.10.025)
- 14. [Abdulelah H, Ali B, Mahdi MA, Abdullah AQ, Hassan JJ,](http://dx.doi.org/10.1155/2016/1093821) [Al-Taay HF, Jennings P. Fabrication and Characterization](http://dx.doi.org/10.1155/2016/1093821) [of Porous CdS/Dye Sensitized Solar Cells. Journal of Solar](http://dx.doi.org/10.1155/2016/1093821) [Energy. 2016;2016:1-7.](http://dx.doi.org/10.1155/2016/1093821)
- 15. [Abdul-Manaf NA, Weerasinghe AR, Echendu OK,](http://dx.doi.org/10.1007/s10854-015-2700-5) [Dharmadasa IM. Electro-plating and characterisation of](http://dx.doi.org/10.1007/s10854-015-2700-5)

[cadmium sulphide thin films using ammonium thiosulphate](http://dx.doi.org/10.1007/s10854-015-2700-5) [as the sulphur source. Journal of Materials Science:](http://dx.doi.org/10.1007/s10854-015-2700-5) [Materials in Electronics. 2015;26\(4\):2418-2429.](http://dx.doi.org/10.1007/s10854-015-2700-5)

- 16. [Zdravkov B, Čermák J, Šefara M, Janků J. Pore classification](http://dx.doi.org/10.2478/s11532-007-0017-9) [in the characterization of porous materials: A perspective.](http://dx.doi.org/10.2478/s11532-007-0017-9) [Open Chemistry. 2007;5\(2\):385-395.](http://dx.doi.org/10.2478/s11532-007-0017-9)
- 17. [Simmons BA, Li S, John VT, McPherson GL, Bose A, Zhou](http://dx.doi.org/10.1021/nl010080k) [W, He J. Morphology of CdS Nanocrystals Synthesized in a](http://dx.doi.org/10.1021/nl010080k) [Mixed Surfactant System. Nano Lett. 2002;2\(4\):263-268.](http://dx.doi.org/10.1021/nl010080k)
- 18. [Chen W, Wang Z, Lin Z, Lin L. Absorption and luminescence](http://dx.doi.org/10.1063/1.366152) [of the surface states in ZnS nanoparticles. J Appl Phys.](http://dx.doi.org/10.1063/1.366152) [1997;82\(6\):3111-3115.](http://dx.doi.org/10.1063/1.366152)
- 19. [Arai T, Yoshida T, Ogawa T. Photoacoustic and Luminescence](http://dx.doi.org/10.1143/jjap.26.396) [Spectra of CdS Fine Particles. Jpn J Appl Phys.](http://dx.doi.org/10.1143/jjap.26.396) [1987;26\(3R\):396.](http://dx.doi.org/10.1143/jjap.26.396)
- 20. [Agata M, Kurase H, Hayashi S, Yamamoto K.](http://dx.doi.org/10.1016/0038-1098(90)90084-o) [Photoluminescence spectra of gas-evaporated CdS](http://dx.doi.org/10.1016/0038-1098(90)90084-o) [microcrystals. Solid State Commun. 1990;76\(8\):1061-1065.](http://dx.doi.org/10.1016/0038-1098(90)90084-o)
- 21. [Venkatesu P. Doping effect of Mn on structural optical](http://dx.doi.org/10.1109/icanmeet.2013.6609255) [magnetic and electrical properties of CdS nanoparticles.](http://dx.doi.org/10.1109/icanmeet.2013.6609255) [International Conference on Advanced Nanomaterials and](http://dx.doi.org/10.1109/icanmeet.2013.6609255) [Emerging Engineering Technologies; 2013/07: IEEE; 2013.](http://dx.doi.org/10.1109/icanmeet.2013.6609255)
- 22. [Zhao J, Yang X. Photocatalytic oxidation for indoor air](http://dx.doi.org/10.1016/s0360-1323(02)00212-3) [purification: a literature review. Building and Environment.](http://dx.doi.org/10.1016/s0360-1323(02)00212-3) [2003;38\(5\):645-654.](http://dx.doi.org/10.1016/s0360-1323(02)00212-3)
- [23.Das DP, Biswal N, Martha S, Parida KM. Solar-light induced](http://dx.doi.org/10.1016/j.molcata.2011.08.012) [photodegradation of organic pollutants over CdS-pillared](http://dx.doi.org/10.1016/j.molcata.2011.08.012) [zirconium–titanium phosphate \(ZTP\). J Mol Catal A: Chem.](http://dx.doi.org/10.1016/j.molcata.2011.08.012) [2011;349\(1-2\):36-41.](http://dx.doi.org/10.1016/j.molcata.2011.08.012)
- 24. [Bechambi O, Chalbi M, Najjar W, Sayadi S. Photocatalytic](http://dx.doi.org/10.1016/j.apsusc.2015.03.049) [activity of ZnO doped with Ag on the degradation of](http://dx.doi.org/10.1016/j.apsusc.2015.03.049) [endocrine disrupting under UV irradiation and the](http://dx.doi.org/10.1016/j.apsusc.2015.03.049) [investigation of its antibacterial activity. Appl Surf Sci.](http://dx.doi.org/10.1016/j.apsusc.2015.03.049) [2015;347:414-420.](http://dx.doi.org/10.1016/j.apsusc.2015.03.049)