Transdisciplinary Insights in Life Sciences

ISSN: 2584-2161(Online)
Journal Homepage: www.panainool.com

RESEARCH ARTICLE

Photocatalytic activity of CMC capped Zinc Indium Selenide nanoparticles under UV Light Irradiation using Methyl Red Dye

Anantha Kumar Thangaiya[1]*, & Mariselvi Perumal[2]

[1]*Department of Chemistry, Merit Arts and Science College, Idaikal, Tirunelveli, Tamil Nadu, India.*

[2]*PG and Research Department of Chemistry, Rani Anna Govt. College for Women, Abishekapatti, Tirunelveli, Tamil Nadu, India.*

ARTICLE HISTROY

Received 08 March 2024

Revised 18 March 2024

Accepted 20 March 2024

Keywords

ZIS nanoparticles
Carboxy methyl cellulose
SEM
EDX
TEM
Crystallinity

ABSTRACT

In the present study, polymer-capped zinc indium selenide (ZIS) nanoparticles are synthesized and characterized by means of a range of analytical techniques, such as atomic force microscopy (AFM), transmission electron microscopy (TEM), scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDX), and X-ray diffraction (XRD). The ZIS nanoparticles were produced using a simple chemical process, and their size and shape were regulated by the use of a polymer capping agent. Carboxymethyl cellulose, or CMC, functions as a polymer. The synthesized nanoparticles' rhombhohedral crystal structure is shown by the XRD. The SEM revealed that the nanoparticles' surface had a consistent dispersion. TEM microscopy was used to confirm that the $ZnIn_2Se_4$ nanoparticles were spherical. Additionally, CMC-capped zinc indium selenide nanoparticles were used to photocatalytically degrade methyl red in an aqueous solution while being exposed to UV radiation.

✉ Anantha Kumar Thangaiya
ananthspkc@gmail.com

Introduction

In recent times, there has been a growing interest among researchers in a ternary compound belonging to the II-III-VI group, mostly due to its potential applications in optoelectronic devices and solar cells (Choe et al., 1995; Mahalingam et al., 2005; Tenne et al., 1985). The chemical formula for zirconium selenide is AIBII2CIV4, and it is an n-type ternary chalcogenide semiconductor. In this compound, A represents Zn, Cd, or Hg, B represents In or Ga, and X represents Se, S, or Te (Yadav et al., 2008). At ambient temperature, the crystal exhibits direct energy gaps of 1.82 eV (Choe, 2009).

Zinc indium selenide (ZIS) nanoparticles are an interesting group of semiconductor materials that have gotten a lot of attention in many fields, such as sensing, photovoltaics, optoelectronics, and catalysis. The nanoparticles commonly consist of zinc (Zn), indium (In), and selenium (Se) atoms, which are organized in a crystalline configuration. These nanoparticles possess distinctive characteristics that make them well-suited for a diverse array of applications. ZIS nanoparticles can be made using a variety of methods, such as chemical vapor deposition, sol-gel, hydrothermal, and co-precipitation. These methods allow for precise control over their size, shape, and chemical make-up. Nanoparticles frequently have adjustable optical and electrical properties, which are primarily dependent on their size and makeup. This characteristic renders them highly promising for applications that necessitate customized attributes (Sundarrajan et al., 2012). This study presents the photocatalytic performance of CMC-capped ZIS nanoparticles when exposed to UV light using methyl red dye. The fabrication and characterization of zinc indium selenide nanoparticles coated with CMC were disclosed in our previous publication (Qu & Luo, 2022). Thus, the present aimed to investigate the polymer-capped zinc indium selenide (ZIS) nanoparticles are synthesized and characterized by means of a range of analytical techniques.

Materials and Methods

Preparation of polymer solutions

The preparation of the CMC solution involved the dissolution of 1.5 grams of CMC in 100 millilitres of distilled water while maintaining continuous stirring at ambient temperature.

Synthesis of CMC capped Zinc Indium Selenide ($ZnIn_2Se_4$) nanoparticles

The experimental procedure involved the combination of a 90-mL polymer solution at room temperature with $ZnCl_2.2H_2O$ (AR), $InCl_3$ (absolute AR), and selenium dioxide (SeO_2, AR) in a molar ratio of 1:2:4. We rapidly agitated the mixture to ensure the formation of a homogenous solution. The resultant solution mixture was subsequently transferred into a 100-mL autoclave lined with Teflon. Following a period of nearly 12 hours at a temperature of 180 °C, the autoclave underwent automatic cooling to reach the surrounding temperature. Following the collection of the precipitate and subsequent washing with distilled water and ethanol, it was subjected to a four-hour drying process at a temperature of 60 °C. We then gathered the resulting powders for subsequent analysis (Qu & Luo, 2022).

Photocatalytic Activity

The photocatalytic activity of CMC-capped zinc indium selenide nanoparticles was evaluated by subjecting methyl red (MR) textile dye to photodegradation. The investigation was carried out within a cylindrical hollow photoreactor, including two walls and a water circulation system. We attached a UV bulb to the reactor. The catalytic tests were done using 20 mg of the catalyst and a 100 mL solution of MR [$5^2 10-5$ M], with continuous stirring. Periodically, a volume of 3 mL of the aliquot solution was extracted from the reaction mixture and subjected to centrifugation, and the absorbance value was measured in order to evaluate the extent of its reduction. A control experiment was conducted using commercial MR without catalyst under identical experimental circumstances.

$$\% \text{ Decolourization} = [(Co - C) \div Co] \times 100$$

Where,

C_0, is the initial concentration of dye solution and

C, is the concentration of dye solution after photocatalytic degradation.

Results and Discussion

XRD analysis

The X-ray diffraction pattern of ZIS is depicted in Figure 1. The XRD spectra of all the CMC-capped ZIS nanoparticles exhibited a rhombohedral crystal shape and nanocrystalline nature. The lattice constants a = 4.05 κ and c = 52.29 κ indicate the production of $ZnIn_2Se_4$ nanoparticles. The primary peak, located at about 27, and its corresponding interplanar separation of 3.279 κ, can be attributed to the reflection originating from the (112) plane of the rhombohedral system. These findings indicate that the nanocrystallines have a natural inclination towards (112) planes that are parallel to the substrate. The average particle size of the zinc indium selenide nanoparticle capped with CMC was calculated to be 49 nm using the widely recognized Debye-Scherrer formula. It corresponds to the previous results (Calì et al., 2001; Zeyada et al., 2009).

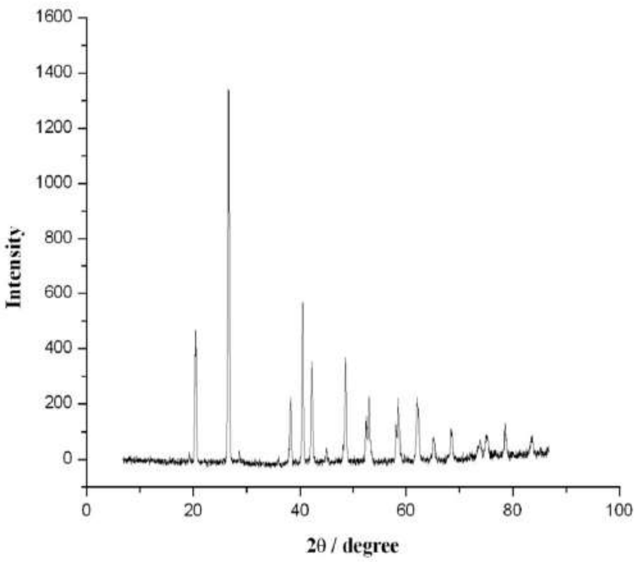

Fig 1. XRD pattern of CMC capped zinc indium selenide nanoparticles

SEM with EDAX Analysis

The SEM micrographs were utilized to examine the surface morphology of the $ZnIn_2Se_4$ nanoparticles capped with CMC, as depicted in Figure 2. With respective magnifications of 58.44 Kx and 34.03 Kx, the microscopic images provided evidence of the homogeneity, uniformity, and dispersion of spherical particles on the polymer sample. The SEM micrographs clearly reveal the rhombhedral crystal structure of the synthesized CMC-capped $ZnIn_2Se_4$ nanoparticles. The confirmation of the elements of the CMC-topped ZIS was established through the observation of distinct peaks corresponding to each element. The EDAX spectra, as depicted in Figure 3, exhibit distinct peaks that correspond to the elements Zn, In, and Se, as well as oxygen. The presence of zinc, indium, and selenide nanoparticles may be attributed to the incorporation of oxygen during the growth process of the nanomaterial, which is facilitated by the utilization of aqueous solutions. Cheng et al., (2012) previously documented the presence of zinc indium selenide.

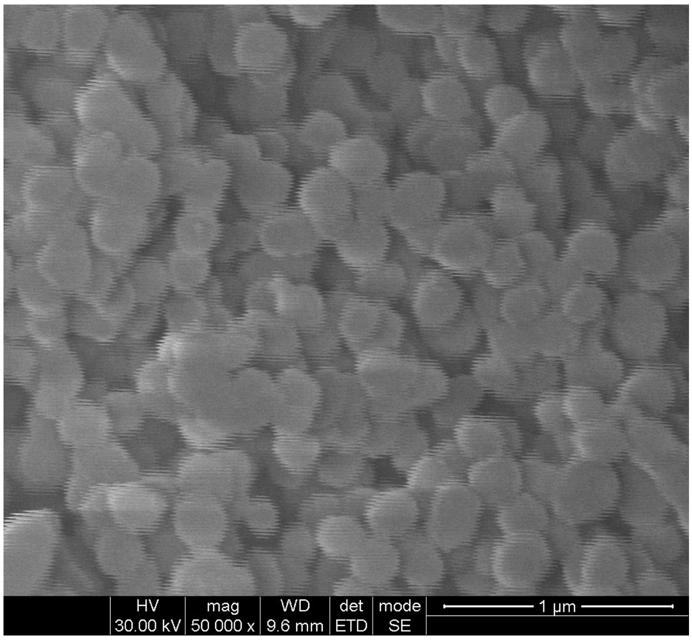

Fig 2. SEM image of CMC capped Zinc Indium Selenide nanoparticles

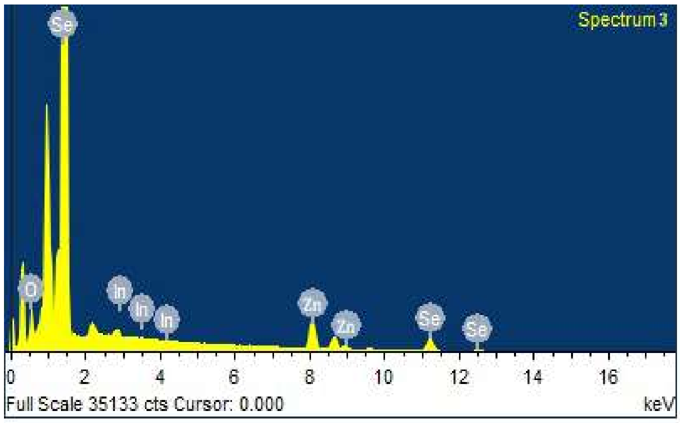

Fig 3. EDAX spectrum of CMC capped Zinc Indium Selenide nanoparticles

AFM Analysis

AFM measurements can yield insights into the particle's surface morphology, enabling investigations into the nanoparticles' characteristics, such as surface roughness and particle size. A meticulous examination of the roughness of nanoparticles can provide insights on the specific type of growth occurring during their formation (Adamczyk et al., 2023; Sitterberg et al., 2010). The micrograph, measuring 3.45 μm × 3.45 μm, reveals that the surface of the $ZnIn_2Se_4$ material exhibits non-uniform mountainous characteristics characterized by distinct domes.

Figure 4 yielded an average cluster size of 50 nm. The XRD pattern clearly agrees with this value.

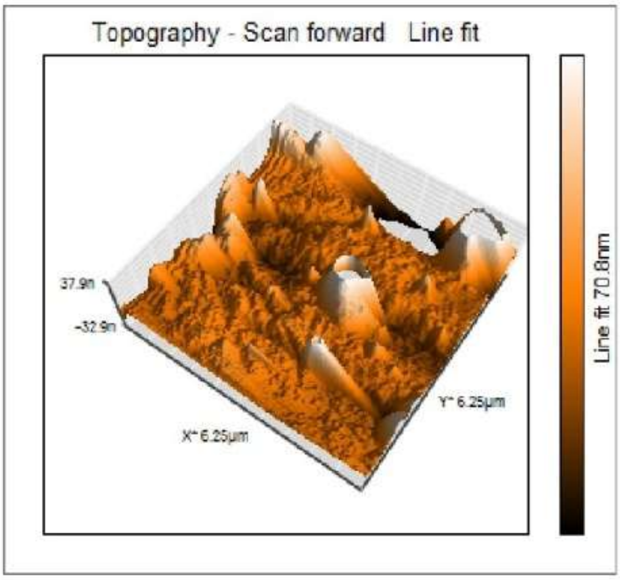

Fig 4. AFM 3D image of CMC capped Zinc Indium Selenide nanoparticles

Transmission Electron Microscopy analysis

Figure 5 displays the transmission electron microscopy (TEM) image of $ZnIn_2Se_4$ nanoparticles capped with CMC. This image confirms the distinct size and nearly spherical shape of the nanoparticles. The diameter of ternary semiconductor nanoparticles typically falls within the range of 30 to 50 nm. The results of XRD, SEM, and AFM morphological examinations strongly align with this. Furthermore, it revealed the nanocrystalline nature of zinc, indium, and selenide nanoparticles, which are indistinguishable from each other. The trend in the grain size of zinc indium selenide thin films is directly related to the annealing temperature, as shown by the results of the study that was already published (Somaghian et al., 2024).

Photocatalytic Activity

Effect of Contact time

To find out how useful the catalyst might be, we used the synthesized photocatalyst in adsorption and photocatalytic experiments on MR dye. We conducted the experiments under UV light irradiation in a dark atmosphere. The study of dye photodegradation included measuring how much the dye's absorbance dropped when it was exposed to the man-made nanomaterials. The dye solution's absorbance exhibited a negative correlation with the duration of exposure, suggesting a decline in the concentration of MR dye. Figure 6 illustrates the loss of MR over time for the samples subjected to UV light irradiation. Pseudo-first-order kinetics was employed (Meena et al., 2016).

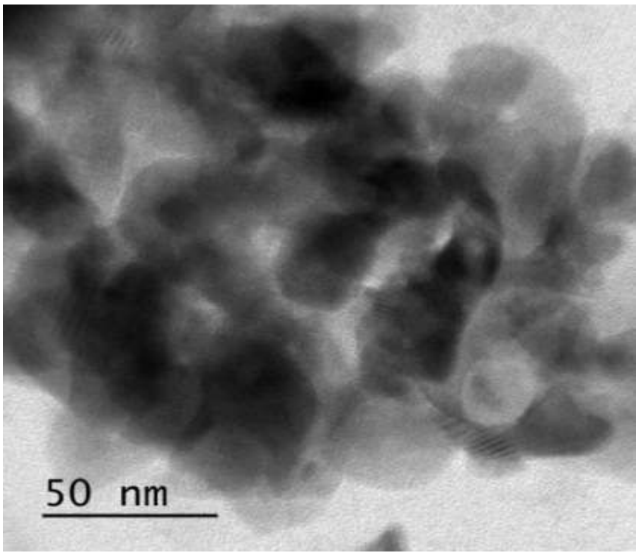

Fig 5. TEM image of CMC capped Zinc Indium Selenide (ZnIn2Se4) nanoparticles

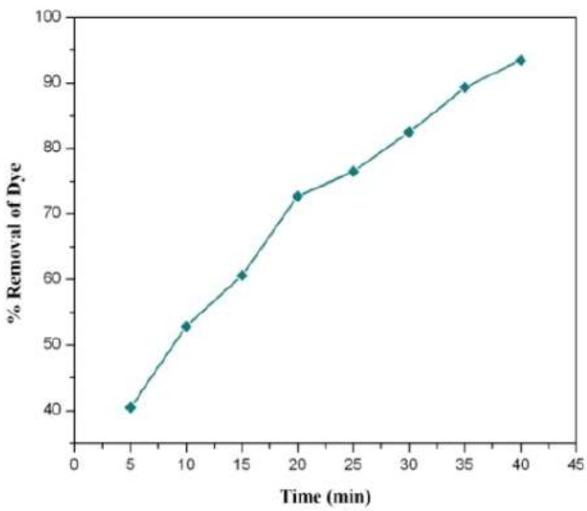

Fig 6. Effect of contact time in presence of UV light Irradiation

Effect of Dosage

Most photocatalytic investigations have observed a direct proportionality between the initial rate of photodegradation and the catalyst dosage.

Nevertheless, once the catalyst dosage exceeds a specific threshold, the rate of the reaction diminishes due to the phenomenon of light scattering and screening (Lathasree et al., 2004). As the dosage of the photocatalyst increases, there is a corresponding increase in the propensity of solid catalyst particles to aggregate. This phenomenon leads to a decrease in the effective surface area of the catalyst, which is crucial for light absorption. As a result, the rate of photocatalytic degradation decreases. Selecting the appropriate catalyst dosage is crucial to prevent excessive catalyst usage and minimize energy dissipation throughout the degradation process. We conducted the UV irradiation for 40 minutes using a polymer-capped photocatalyst, with dosages ranging from 10 to 20 mg. Figure 7 illustrates the results. The overall deterioration of MR exhibited a positive correlation with the dosage of zinc and indium selenide. Typically, in heterogeneous photocatalytic degradation a process, an initial slow increase in degradation occurs as the catalyst dose increases, followed by a subsequent drop at higher catalyst doses. Nitin Kumar Singh & Pal, (2015) reported a comparable outcome.

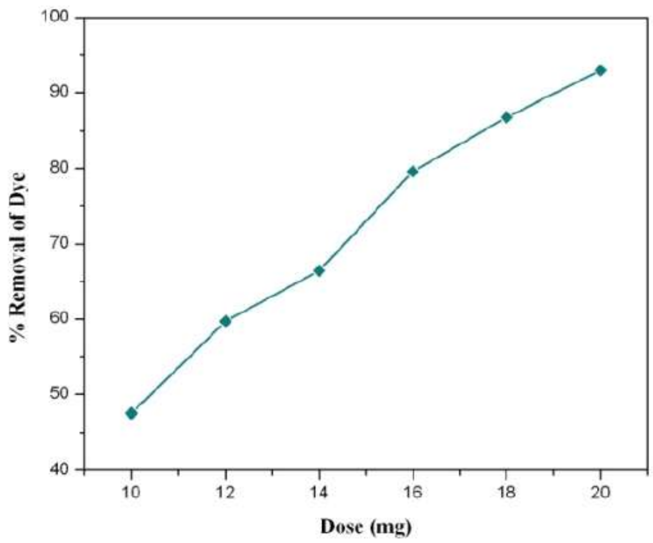

Fig 7. Effect of dosage in presence of UV light Irradiation

Effect of Initial Concentration of Dye

The impact of the initial concentration (10–50 ppm) of MR on its photocatalytic degradation under UV light. The results showed a decrease in overall deterioration as the concentration of MR increased, as depicted in figure 8. One factor contributing to this phenomenon is the heightened concentration of MR, which hinders the transmission of UV light through the solution. Another possible explanation could be the decrease in the concentration of radicals compared to the specific pollutant on the catalyst's surface (Pavel et al., 2023). It is evident that an increase in the concentration of MR leads to a corresponding rise in the reactive oxygen species (ROS), such as OH and O_2- that are necessary for the breakdown of MR. Nevertheless, the generation of reactive oxygen species (ROS) on the surface of the catalyst remains consistent within a predetermined parameter (Khan et al., 2022).

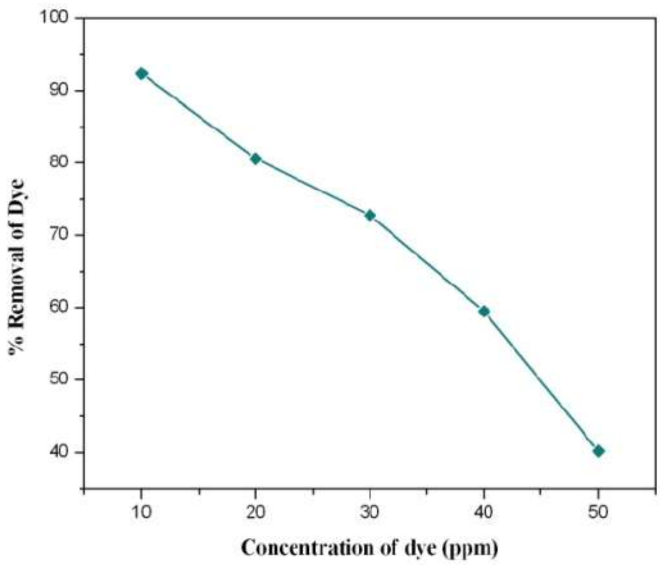

Fig 8. Effect of Initial Concentration of dye in presence of UV light Irradiation

Conclusion

The confirmation of the production of a nanoparticle of CMC-capped $ZnIn_2Se_4$ was achieved by XRD, SEM, and EDAX, AFM, and TEM techniques. The X-ray diffraction (XRD) signal provides evidence that the nanoparticles synthesized possess a rhombhohedral crystal structure. The scanning electron microscopy (SEM) analysis revealed a homogeneous dispersion of the nanoparticles on their surface. The TEM microscopy confirmed the spherical morphology of the $ZnIn_2Se_4$ nanoparticles. The sizes of these nanoparticles span a range of 30 to 50 nm. We conducted the analysis of methyl red elimination percentage using several experimental parameters, such as contact time, dosage, and beginning dye concentration. The investigation indicates that the produced materials possess significant utility in the field of water treatment.

Acknowledgement

The authors thankful to Department of Chemistry, Merit Arts and Science College, Idaikal, Tirunelveli, Tamil Nadu, India for carrying out this work.

Conflict of interest

All authors declare that there is no conflict of interest in this work.

References

Adamczyk, Z., Sadowska, M., & Nattich-Rak, M. (2023). Quantifying Nanoparticle Layer Topography: Theoretical Modeling and Atomic Force Microscopy Investigations. *Langmuir : The ACS Journal of Surfaces and Colloids*, *39*(42), 15067–15077. https://doi.org/10.1021/acs.langmuir.3c02024

Calì, C., Mosca, M., & Targia, G. (2001). A simple apparatus for the determination of the optical constants and the thickness of absorbing thin films. *Optics Communications*, *191*(3), 295–298. https://doi.org/10.1016/S0030-4018(01)01123-3

Cheng, K.-W., Cheng, Y.-H., & Fan, M.-S. (2012). Photoelectrochemical study of ZnIn2Se4 electrodes fabricated using selenization of RF magnetron sputtered Zn–In metal precursors. *International Journal of Hydrogen Energy*, *37*(18), 13763–13769. https://doi.org/10.1016/j.ijhydene.2012.03.087

Choe, S.-H. (2009). Optical energy gaps of undoped and Co-doped ZnIn2Se4 single crystals. *Current Applied Physics*, *9*(1), 1–3. https://doi.org/10.1016/j.cap.2007.10.083

Choe, S.-H., Park, B.-N., Yu, K.-S., Oh, S.-J., Park, H.-L., & Kim, W.-T. (1995). Optical properties of undoped and Co-DOPED CdIn2Se4 single crystals. *Journal of Physics and Chemistry of Solids*, *56*(1), 89–92. https://doi.org/10.1016/0022-3697(94)00140-5

Khan, I., Saeed, K., Zekker, I., Zhang, B., Hendi, A. H., Ahmad, A., Ahmad, S., Zada, N., Ahmad, H., Shah, L. A., Shah, T., & Khan, I. (2022). Review on Methylene Blue: Its Properties, Uses, Toxicity and Photodegradation. *Water*, *14*(2). https://doi.org/10.3390/w14020242

Lathasree, S., Rao, A. N., SivaSankar, B., Sadasivam, V., & Rengaraj, K. (2004). Heterogeneous photocatalytic mineralisation of phenols in aqueous solutions. *Journal of Molecular Catalysis A: Chemical*, *223*(1), 101–105. https://doi.org/10.1016/j.molcata.2003.08.032

Mahalingam, T., Kathalingam, A., Velumani, S., Lee, S., Lew, K. S., & Kim, Y. D. (2005). Characterization of electrodeposited Zn1−xHgxSe thin films. *Semiconductor Science and Technology*, *20*(8), 749. https://doi.org/10.1088/0268-1242/20/8/017

Meena, S., Vaya, D., & Das, B. K. (2016). Photocatalytic degradation of Malachite Green dye by modified ZnO nanomaterial. *Bulletin of Materials Science*, *39*(7), 1735–1743. https://doi.org/10.1007/s12034-016-1318-4

Nitin Kumar Singh, S. S., & Pal, A. (2015). Methyl red degradation under UV illumination and catalytic action of commercial ZnO: a parametric study. *Desalination and Water Treatment*, *56*(4), 1066–1076. https://doi.org/10.1080/19443994.2014.942380

Pavel, M., Anastasescu, C., State, R.-N., Vasile, A., Papa, F., & Balint, I. (2023). Photocatalytic Degradation of Organic and Inorganic Pollutants to Harmless End Products: Assessment of Practical Application Potential for Water and Air Cleaning. *Catalysts*, *13*(2). https://doi.org/10.3390/catal13020380

Qu, B., & Luo, Y. (2022). Preparation and characterization of carboxymethyl cellulose capped zinc oxide nanoparticles: A proof-of-concept study. *Food Chemistry*, *389*, 133001. https://doi.org/10.1016/j.foodchem.2022.133001

Sitterberg, J., Özcetin, A., Ehrhardt, C., & Bakowsky, U. (2010). Utilising atomic force microscopy for the characterisation of nanoscale drug delivery systems. *European*

Journal of Pharmaceutics and Biopharmaceutics, *74*(1), 2–13. https://doi.org/10.1016/j.ejpb.2009.09.005

Somaghian, S. A., Mirzaei, S. Z., Shakib, M. E. K., Marzban, A., Alsallameh, S., & Lashgarian, H. E. (2024). Biogenic zinc selenide nanoparticles fabricated using Rosmarinus officinalis leaf extract with potential biological activity. *BMC Complementary Medicine and Therapies*, *24*(1), 20. https://doi.org/10.1186/s12906-023-04329-6

Sundarrajan, P., Eswaran, P., Marimuthu, A., Subhadra, L. B., & Kannaiyan, P. (2012). One Pot Synthesis and Characterization of Alginate Stabilized Semiconductor Nanoparticles. *Bulletin of the Korean Chemical Society*, *33*(10), 3218–3224. http://inis.iaea.org/search/search.aspx?orig_q=RN:45096364

Tenne, R., Mirovsky, Y., Sawatzky, G., & Giriat, W. (1985). Ternary Chalcogenide-Based Photoelectrochemical Cells .7. Analysis Of The Chemical Processes Occurring At The Cdin2se4 Surface During Photoelectrochemical Operation. *Journal of the Electrochemical Society*, *132*(8), 1829–1835. https://doi.org/10.1149/1.2114226

Yadav, S. P., Shinde, P. S., Rajpure, K. Y., & Bhosale, C. H. (2008). Photoelectrochemical properties of spray deposited n-ZnIn2Se4 thin films. *Solar Energy Materials and Solar Cells*, *92*(4), 453–456. https://doi.org/10.1016/j.solmat.2007.10.008

Zeyada, H. M., Aziz, M. S., & Behairy, A. S. (2009). Structure formation and mechanisms of DC conduction in thermally evaporated nanocrystallite structure ZnIn2Se4 thin films. *Physica B: Condensed Matter*, *404*(21), 3957–3963. https://doi.org/10.1016/j.physb.2009.07.132