Desalination and Water Treatment 317 (2024) 100098

Contents lists available at ScienceDirect

Desalination and Water Treatment

journal homepage: www.sciencedirect.com/journal/desalination-and-water-treatment/

# Synthesis of lead sulphide nanoparticles from egg shell membrane and its relevances

Pongayi Ponnusamy Selvi[a,*], T. Usharani[b], B. Palanisamy[c], P. Akilamudhan[b], B. Sasikumar[b], S. Gokila[b]

[a] Department of Chemical Engineering, Kongu Engineering College, Erode 638 060, India
[b] Department of Chemical Engineering, Erode Sengunthar Engineerong College, Erode 638 057, India
[c] Department of Chemistry, J.K.K.Nataraja College of Arts and Science, Namakkal, India

ARTICLE INFO

*Keywords:*
Egg shell
Nanoparticles
Mechano chemical method
Ultrasonic bath
Solar cell

This study innovatively repurposes eggshell waste for synthesizing lead sulphide nanoparticles, leveraging the sulphur-rich cysteine amino acid in the eggshell matrix. Three methods—mechanochemical, solvent precipitation, and ultrasonic precipitation—are employed, introducing variability through solvent choices. Comprehensive characterization demonstrates successful synthesis across all methods. Mechanochemical processing for 180 min and solvent selection significantly impact nanoparticle characteristics, while the ultrasonic precipitation method, using an ultrasonic bath, proves effective. Application of these nanoparticles to a solar cell reveals enhanced performance, with voltage increasing from 9.3 V to 9.7–9.9 V and current rising from 354 mA to 375 mA. This work not only addresses waste management concerns but contributes to sustainable semiconductor nanoparticle production for renewable energy technologies. The customizable solvent precipitation method and demonstrated solar cell improvement underscore the potential for broader applications. In conclusion, these findings indicate the feasibility of repurposing eggshell waste for sustainable materials development. The study's environmental impact is two fold, tackling waste concerns and contributing to green energy advancements. Further research may optimize synthesis conditions and explore additional applications for these eco-friendly nanoparticles.

## 1. Introduction

In the pursuit of advanced nanomaterials crucial for contemporary technological applications, our study focuses on the synthesis and theoretical characterization of lead sulfide (PbS) nanoparticles using eggshell membranes as a bio-template. As the demand for materials with enhanced dielectric and optoelectronic properties continues to grow, our investigation aims to leverage the unique properties of eggshell membranes for the controlled synthesis of PbS nanoparticles. The co-precipitation chemical synthesis route serves as the foundation for our study, building upon the bio-inspired mechanochemical synthesis technique utilizing eggshell membranes as a platform for material science [1,2]. This approach not only aligns with sustainable practices but also exploits the inherent nano-scale characteristics of the eggshell membrane for the controlled generation of PbS nanoparticles. To comprehend the fundamental properties of PbS nanoparticles, this study utilizes X-ray diffraction (XRD) patterns [3,4]. Scanning electron microscope (SEM) images are anticipated to reveal morphological changes, corroborating findings in the synthesis of lead sulfide nanoparticles and shedding light on the unique nanostructures formed with the eggshell membrane as a bio-template [5,6]. Theoretical examinations of optical properties draw parallels with similar studies that explore the effects of nanoparticle size on band gaps and optoelectronic behavior [7,8]. Dielectric characterizations are expected to demonstrate changes in various parameters, informed by previous investigations into the dielectric and electrical properties of PbS nanostructures [9]. This comprehensive study presents a theoretical exploration of the potential effects of the bio-inspired synthesis of PbS nanoparticles using eggshell membranes, offering valuable insights into their structural, optical, dielectric, and electrical properties. The

* Corresponding author.
*E-mail address:* chemusharani@gmail.com (P.P. Selvi).

https://doi.org/10.1016/j.dwt.2024.100098
Received 14 January 2024; Received in revised form 14 January 2024; Accepted 15 January 2024

**Fig. 1.** Collection of egg shell.

anticipated enhancements underscore the promise of PbS nanoparticles synthesized through this biomimetic approach for future applications in optoelectronics [10–12].

## 2. Material and methods

In this study, eggshell waste is acquired from a local food store (Fig. 1), with a focus on preserving the delicate protein structure within the eggshell membrane (Fig. 2). The manual removal of the membrane is meticulously undertaken to avoid compromising the integrity of the proteins through chemical treatment. The extracted membranes undergo a one-day drying process in an oven, resulting in a crisp and dry membrane subsequently finely powdered in a mortar (Fig. 3).

The milling process plays a crucial role in the synthesis of lead sulphide nanoparticles (Fig. 4). Lead acetate, a key precursor, is combined with the eggshell membrane powder in a ratio of 1:8. Given the 4% cystine content in the eggshell membrane, a substantial amount of eggshell membrane is utilized to ensure an ample supply of reactants. The milling process spans 180 min, with the first 60 min dedicated to the reduction of particle size from coarse to fine. After 120 min, sulfur atoms become available for the reaction, leading to the formation of lead sulphide nanoparticles. The synthesized nanoparticles undergo further transformation into nanofluids, a process deemed vital for subsequent evaluations. The nanofluid preparation employs an ultrasonic bath, utilizing water as a solvent, with a precisely controlled duration of one hour. This step ensures the stability and uniform dispersion of nanoparticles in the fluid medium (Fig. 5).

To assess the efficiency of the lead sulphide nanoparticles, a solar panel coating experiment is conducted (Fig. 6). The inherent semiconductor nature of lead sulphide, characterized by a small band gap, positions it favorably for optoelectronic devices. Solar panel performance is then evaluated, with the voltage increase from 9.2 to 9.6 eV being attributed to the excitation of electrons from the outer orbit of PbS molecules by incident photons containing minimal energy.

**Fig. 2.** Mechanically peeled ESM.

**Fig. 3.** Mortar for grinding dried ESM.


**Fig. 4.** Ball mill.

**Fig. 5.** PbS nanoparticle.

**Fig. 6.** Solar panel with multimeter.

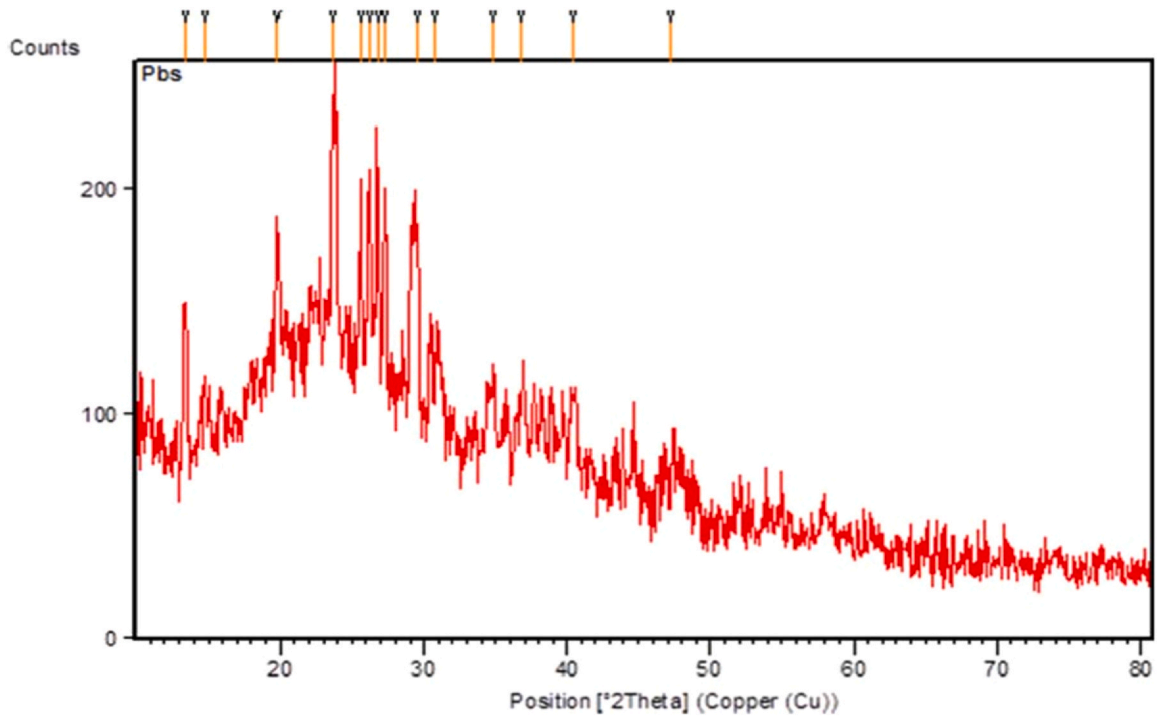


**Fig. 7.** XRD Analysis.

## 3. Results and discussion

The X-ray diffraction (XRD) analysis has elucidated compelling insights into the composition and characteristics of lead sulfide (PbS) nanoparticles within the eggshell membrane (Fig. 7 & Table 1). The XRD patterns, reflecting the crystalline structure, reveal distinct peaks with relative intensities indicative of small crystal sizes, averaging between 5 to 10 nanometers. We compared the particle size with already published work [13–19] and showed in the Table.2. This nanoscale dimension is particularly significant, as it suggests the presence of PbS nanoparticles in a quantum-confined regime, which can confer unique electronic and optical properties.

**Table 1**
Peak list - Graphical Data.

| Pos. [°2Th.] | Height [cts] | FWHM Left [°2Th.] | d-spacing [Å] | Rel. Int. [%] |
|---|---|---|---|---|
| 13.4086 | 100.81 | 0.1476 | 6.60357 | 53.66 |
| 14.7863 | 54.61 | 0.5904 | 5.99126 | 29.07 |
| 19.844 | 138.59 | 0.246 | 4.4742 | 73.78 |
| 23.6965 | 187.86 | 0.3444 | 3.75481 | 100 |
| 25.9776 | 151.63 | 0.1476 | 3.47875 | 80.72 |
| 26.2087 | 155.62 | 0.1476 | 3.40031 | 82.84 |
| 26.7659 | 145.89 | 0.1476 | 3.33078 | 77.66 |
| 27.3305 | 149.39 | 0.1968 | 3.26324 | 79.52 |
| 29.5129 | 135.94 | 0.5904 | 3.02672 | 72.36 |
| 30.0432 | 66.23 | 0.5904 | 2.90557 | 35.26 |
| 34.8818 | 62.84 | 0.5904 | 2.57218 | 33.45 |
| 36.7908 | 58.89 | 0.3936 | 2.44298 | 31.35 |
| 40.419 | 58.59 | 0.3936 | 2.23167 | 31.19 |
| 43.0552 | 23.23 | 1.968 | 1.92201 | 12.37 |

The choice of the eggshell membrane as a template for PbS nanoparticle synthesis adds another layer of importance to these findings. The biocompatible nature of the eggshell membrane implies that it provides a conducive environment for the growth and formation of nanoparticles without inducing adverse effects. This attribute opens avenues for potential biomedical applications where the biocompatibility of materials is critical. Furthermore, the biodegradability of the eggshell membrane aligns with sustainability goals, offering an environmentally friendly template compared to synthetic counterparts.The discussion on potential applications, particularly in solar cells and LEDs, underscores the versatility of PbS nanoparticles. The nanoscale size and unique properties of these particles make them promising candidates for enhancing the efficiency of solar energy conversion and for applications in optoelectronics.

Acknowledging the presence of impurities, such as calcium carbonate ($CaCO_3$) and magnesium hydroxide ($Mg(OH)_2$), in the eggshell membrane before nanoparticle synthesis demonstrates a thorough understanding of the starting material. Importantly, the assurance that

**Table 2**
Comparison of particle size in the published work.

| Author, Year of publication | Size | Analysis |
|---|---|---|
| Manthrammel et al., 2022 | 17 to 25 nm | XRD, Spectroscopy |
| Mohd Shkir et al., 2022 | 14 nm | XRD, Fourier Transform Analysis, SEM, UV-Visible Spectroscopy |
| Sivalingam Muthu Mariappan et al., 2022 | 10 – 20 nm | XRD, Raman spectroscopy |
| Mohd. Shkir et al., 2021 | 19-25 nm | XRD, SEM |
| Mohd. Shkir et al., 2020 | 20 – 40 nm | XRD, SEM, Fourier Transform Spectroscopy |
| Kamlesh V. Chandekar et al., 2020 | 13 – 15 nm | XRD, SEM, Fourier Transformation |
| Khan et al., 2022 | Film | XRD, Raman Spectroscopy |

these impurities do not compromise the overall XRD results reinforces the robustness and reliability of the study. In conclusion, this research not only identifies the presence of PbS nanoparticles in the eggshell membrane but also sheds light on the potential of using this natural template for sustainable and cost-effective nanoparticle synthesis. The combination of biocompatibility, biodegradability, and the unique properties of PbS nanoparticles positions the eggshell membrane as a promising template for various applications, marking a significant advancement in the field of nanomaterial synthesis.

## 4. Conclusion

Lead sulphide nano particles present in the residue of the ESM matrix were successfully prepared by utilizing the ESM biomaterial and lead acetate as precursors of sulphur and lead respectively. The presence of lead sulphide nano particles was identified using XRD test. The size of nanoparticle was found between 5 to 10 nm. Confirmation of lead sulphide is also done by JCPDS card specifically available for PbS. Other methods are tried to prepare nanoparticle. Solvent precipitation was carried out by trials. Solvent such as water, ethanol and acetone were used to dissolve egg shell powder and followed by adding lead acetate. The system doesn't dissolve in anyone of the solvents. Several trials were done by adding hydrochloric acid accompanied by heating. But the system showed no response. Then the system is kept in ultrasonic bath to precipitate. The temperature was varied from 30 – 40 °C with time span of one hour. Then surfactant EDTA was added to remove the resistance between hydrophobic system and water. But the powder doesn't dissolve with variables being added. This is due to the presence of disulphide bond in cystine. Nano fluid was prepared using ultrasonic bath. Obtained nanofluid is coated over solar panel. The initial current generated without coating is 354 mA whereas current obtained after coating is 375 mA. Results shows that efficiency of the solar panel is increased. The process involving the preparation of Lead sulphide nanoparticles shows that the mechanochemical synthesis is efficient when compared with the other two methods. Mechanochemical synthesis produces nanoparticles with uniform size which is important factor in case of photo electronic devices. Thus, nanofluid is produced by using water as a solvent after undergone several trials. Results shows that the efficiency of solar panel was increased when nanofluid is coated on solar panel.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## References


[1] Uhuegbu Chidi C. Growth and characterization of lead sulphide thin film for solar cell fabrication. Cana J Sci Ind Res 2011;2:230–41.

[2] Balaz Matej, Balaz Peter, Sayagues MariaJ, Zorkovska Anna. Bio–inspired mechanochemical synthesis of semiconductor nanomaterial using eggshell membrane. Matrl Sci Semi Process 2013;16:1899–903.

[3] Matej Balaz Eggshell. membrane bio material as a platform for application in material science. Acta Biomater 2014;10:3827–43.

[4] Rath NC, Liyanage R, Makkar SK, Lay Jr JO. Protein profiles of hatchery egg shell membrane, Rath et al. Proteome Sci 2017;15:1–9.

[5] Naresh BKotadiya, Anjana JKothari, Devendra Tiwari K, Chaudhur Tapas. Photoconducting nanocrystalline lead sulphide thin films obtained by chemical bath deposition. Appl Phys A 2012;7:819–24.

[6] Shukla PK, Kumar Tomar Sandeep, Bhattacharya Bhaskar, Singh Pramod K. Synthesis of lead sulphide nanoparticles for electrode application of dye synthezied solar cells. Nanosci Nanotechnol Lett 2014;6:31–6.

[7] Su Huilan, Han Jie, Wang Na, Dong Qun, Zhang Di, Zhang Chunfu. In situ synthesis of lead sulfide nanoclusters on eggshell membrane fibers by an ambient bio-inspired technique, Smart. Mater Struct 2008;17:015–45.

[8] Kull Sascha, Heymann Leonard, Hungria AnaB, Klinke Christian. Synthesis of single-crystalline lead sulfide nanoframes and nanorings. Chem Mater 2019;31:5646–54.

[9] Wang Qi, Ma Chunlei, Tang Jianke, Zhang Cuihong, Ma Lihua. Eggshell membrane templated MnO2 nanoparticles: facile synthesis and tetracycline hydrochloride decontamination. Nanosca Res Let 2018;13:15–31.

[10] Liang Miao, Su Rongxin, Qi Wei, Yu Yanjun. Synthesis of well-dispersed Ag nanoparticles on eggshell membrane for catalytic reduction of 4- nitrophenol. J Mater, Sci 2014;49:1639–47.

[11] Chung Sheng-Heng, Manthiram Arumugam. Carbonized eggshell membrane as a natural polysulfide reservoir for highly reversible Li-S batteries. Adv Mater 2014;26:1360–5.

[12] Devi Parukuttyamma Sujatha, Banerjee Suparna, Roy Chowdhury Sebanti, opinatha G, Kumar Suresh. Eggshell membrane: A natural biotemplate to synthesize fluorescent gold nanoparticles. RSC Adv 2012;2:11578–85.

[13] Muthu Mariappan Sivalingam, Jun Hong Sung, Han Byungchan, Shkir Mohd, Vinoth Elangovan, Mary Stella, Janani K, Archana, Karthikeyan Balasubramanian, Algarni Hamed, AlFaify Salem. Slow excitonic carrier cooling in Sr-doped PbS. nanocrystals hot Carr Device: Integr Exp first-Princ Approach J Mater Chem *C* 2023;10:6634.

[14] Shkir Mohd, Chandekar Kamlesh V, Hossain MdMilon, Palanivel Baskaran, Ahmad Nafis, Ashraf IM, Somaily HH, Algarni H, AlFaify S. Enhanced dielectric and electrical properties of PbS nanostructures facilely synthesized by low-cost chemical route: an effect of Ce doping concentrations. Mater Chem Phys 2022;278:125626.

[15] Khan ZR, Shkir Mohd. Improved opto-nonlinear and emission properties of spray pyrolysis grown Nd:PbS nanostructured thin films. Phys B: Condens Matter 2022;627:413612.

[16] Aslam Manthrammel M, Muthu Mariappan Sivalingam, Shkir Mohd, Alfaify S. A facile microwave assisted synthesis of La@PbS nanoparticles and their characterizations for optoelectronics. J Inorg Organomet Polym Mater 2022;32:469–77.

[17] Shkir Mohd, Palanivel Baskaran, Chandekar KamleshV, Khan Aslam, Ahmed M, Anees ElToni, Ansari A, Ahmad Zargar Rayees, Sayed MA, AlFaify S. Microwave-assisted synthesis of Cu doped PbS nanostructures with enhanced dielectric and electrical properties for optoelectronic applications. Mater Sci Eng: B 2021;271:115268.

[18] Mohd. Shkir, Chandekar Kamlesh V, Alshahrani T, Kumar Ashwani, Khan Aslam, AlFaify S. An impact of La doping content on key physical properties of PbS spherical nanoparticles facilely synthesized via low temperature chemical route. Eur Phys J 2020;135:816.

[19] Chandekar Kamlesh V, Alshahrani T, Ben Gouider Trabelsi A, Alkallas FH. Mohd.Shkir and S. AlFaify, Novel rare earth yttrium doping effect on physical properties of PbS nanostructures: facile synthesis and characterization. J Mater Sci 2021;56:4763–81.