Research Article

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Morphology-controlled $BaSO_4$ Nanostructures by Solvents and Molar Concentrations

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ABSTRACT

The aim of the present work is to synthesize environmentally friendly nanomaterials, which are viable and better alternative method for distinct applications. The co-precipitation method is used for the preparation of $BaSO_4$ nanostructures with the influence of *Azadirachta indica* leaf extracts as organic stabilizing agents. For the synthesis of nanostructures, two solvents (ethanol and deionized water) and different molar concentrations (0.05 and 1.0 M) were investigated using various characterization techniques. The XRD pattern confirmed an orthorhombic phase, in good agreement with the JCPDS reference file. FTIR spectra verified the presence of Ba and SO_4 stretching vibrations. SEM analysis (at 1–2 µm scale) revealed the successful formation of rice-grain or nanorod-like nanostructures with average diameters of ~73.5 nm (ethanol) and 222 nm (DI water). Elemental composition was further confirmed by EDX analysis. The study indicates that DI water and higher molar concentration significantly influence the morphology and particle size of $BaSO_4$ nanostructures. These nanocrystalline materials may find potential applications in antimicrobial fields.

Keywords: Green synthesis; *Azadirachta indica*; $BaSO_4$; Antimicrobial; Nanostructures.

1. INTRODUCTION

Nowadays, science and technology have been garnering great attention at nanoscale level. Also, the production and control of nanostructure size and shape have become remarkable research subjects for various applications. It is a known fact that materials could have various unique structural, electronic, optical, magnetic, physical, and chemical properties because of their size changes from bulk materials at the nanoscale level. The preparation of organic or inorganic powders ($BaSO_4$) by controlling size and morphologies is attracting and increasing interest due to its whiteness, inertness, and high specific gravity. This $BaSO_4$ nanostructure is useful as a filler and additive in paints, thin film coatings, plastics, and pharmaceutical applications (Wu *et al*. 2007; Shen *et al*. 2007; Kucher *et al*. 2008). Many researchers have reported the synthesis of $BaSO_4$ nanostructures using various additives and methods, including co-precipitation, sol–gel, microemulsion, membrane separation, and microchannel reactors (Jones *et al*. 2004; Wang *et al*. 2005; Adityawarman *et al*. 2005; Nagaraja *et al*. 2007; Wang *et al*. 2009). Amiri *et al*. (2022) presented the enhanced piezocatalytic activity of $BaSO_4$ by doping it with different materials ($BaTiO_3$, Cu: $BaTiO_3$, Fe: $BaTiO_3$, S: $BaTiO_3$).

Jha *et al*. (2019) demonstrated the green synthesis of barium sulfate nanoparticles using *Azadirachta indica* leaf extract via a sonochemical method. The prepared nanoparticles were characterized for their structural, morphological, functional, and elemental properties. These results strongly confirm the thermally stable and highly crystalline $BaSO_4$ nanoparticles. Emel Akyol and Murat Alper (2016) experimentally investigated the size and morphology of barium sulfate nanostructures by using various crystal growth modifiers such as polyacrylic acid, polyvinyl sulfonic acid, and ethylenediaminetetraacetic acid. They reported that additive concentration and pH play a pivotal role in the effect of morphology and size on $BaSO_4$ nanostructures. Furthermore, the organic and inorganic materials that incorporated $BaSO_4$ were reported by various researchers (Yu *et al*. 2005; Bala *et al*. 2006; Wang *et al*. 2006; Shen *et al*. 2007; Zhao *et al*. 2007; Jones *et al*. 2007; Gupta *et al*. 2010; Nandakumar and Kurian 2012). Mochahari (2024) proposed the influence of molar concentrations and studied their structural, morphological, optical and luminescence of polyvinyl alcohol-capped nanostructures ZnS films.

Koao *et al*. (2018) investigated the effect of octadecyl ammine molar concentration (0.3 to 15%) on the structural, morphological and optical properties of ZnO nanostructures which was prepared by precipitation

method. Similar work carried out by Chand *et al*. (2015) explored the morphology, optical and ferroelectric properties of CuO nanostructures by influence of various NaOH concentrations. With the effect of these molar concentrations, the optical band gap reduced from 3.55 to 2.95 eV with the increase of molar concentration. Despite these literature reports, the development of $BaSO_4$ nanostructures using green leaf extracts remains limited, highlighting the need for eco-friendly and cost-effective synthesis approaches. In this context, the synthesized $BaSO_4$ nanostructures are systematically investigated and compared with respect to different solvents (ethanol and deionized water) and molarity using various optical, structural, morphological, functional, and elemental characterization techniques.The selection of the solvents plays a crucial role for the preparation of nanostructures. There are several advantages and disadvantages like good solvency, low toxicity with environmental impact and volatility are more concerns.

2. EXPERIMENTAL SECTION

2.1 Materials

Azadirachta indica fresh leaves were collected from Sri YN College campus, Narsapur, West Godavari (District), Andhra Pradesh. $BaCl_2.2H_2O$ and anhydrous Na_2SO_4 were procured from commercial suppliers. Ethanol and distilled water were used as solvent.

2.2 Preparation Method

Fig. 1 indicates the procedural steps for the preparation of $BaSO_4$ nanostructures. The nanostructures were obtained with the green leaves extracted. Initially, *Azadirachta indica* (*A. indica*) leaves were washed with distilled water several times to move the unwanted dirt. Then, 30 g of the leaves were boiled in 80 mL of ethanol and distilled water for 2 hours individually. $BaCl_2.2H_2O$ and Na_2SO_4 were used as precursor materials for the synthesis of $BaSO_4$ nanostructures (0.05 M and 0.1 M). *Azadirachta indica* leaf extract was added to the reaction solution as a green reducing and stabilizing agent. The solution was thoroughly mixed using a magnetic stirrer, resulting in the formation of a white precipitate. Subsequently, the mixture was transferred to a hot-air oven for further processing at 100 °C for 2 hours. The dried $BaSO_4$ powders were collected and named Sample B (0.05 M) and Sample C (0.1 M).

2.3. Characterization Techniques

The samples were characterized for their structural, functional, morphological and elemental properties by using X-ray diffraction (XRD, Rigaku Mini flex, Japan), Fourier transform infrared (FTIR, JASCO FT/IR 6600, Japan) spectroscopy, scanning electron microscopy (SEM, TESCAN VEGA3, Czech Republic) and energy dispersive X-ray (EDX, Genesis, US) spectroscopy.

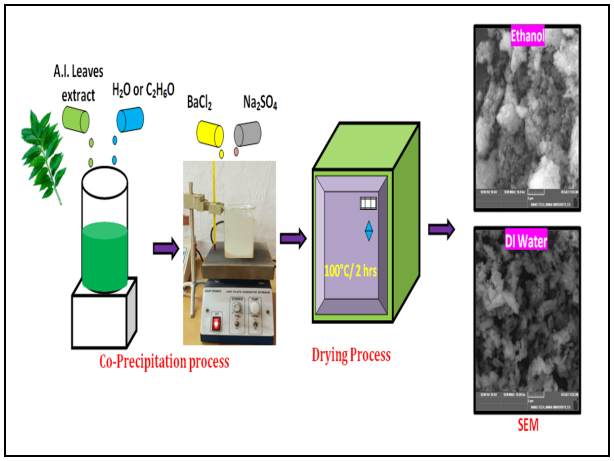


Fig. 1. The synthesis process of $BaSO_4$ nanostructures

3. RESULTS AND DISCUSSION

The XRD patterns of $BaSO_4$ nanostructure samples are shown in Fig. 2 (a) and (b). The indexed XRD pattern of $BaSO_4$ synthesized using de-ionized water and ethanol solvents along with various molar concentrations. Compared to deionized (DI) water, the ethanol-based sample exhibited sharper and more intense diffraction peaks at 24.39° (021), 28.9° (121), 32.2° (002), and 46.7° (212), indicating improved crystallinity. However, these peaks of both synthesized nanoparticles are well matched with JCPDS (2017) and 0020-024 (Kipp *et al*. 1996) JCPDS 1997 (Meagher *et al*. 2013). Also, XRD pattern exhibited the orthorhombic phase and nanoparticles are pure, with all the intense peaks according to the JCPDS file.

This indicates that the prepared sample possesses good purity and a well-crystalline structure. However, as shown in Fig. 5, a few impurity elements such as C, Na, S, and Cl were detected, which may have originated from the calcination process in the muffle furnace or from the testing atmosphere. The $BaSO_4$ nanostructures were characterized by the FTIR technique to determine the functional groups of the samples (organic and inorganic). Fig. 3(a) and (b) shows the FTIR transmittance spectrum of green synthesized $BaSO_4$ nanostructures. The characteristic peaks located around 1224-1208 cm^{-1} are assigned to the plane bending vibrations of the sulphate ion (Manteghian and Sameni, 2019). The absorption peaks at ~3400 and 1500 cm^{-1}

confirm the presence of water molecules (Chen *et al*. 2016; Saravanan *et al*. 2024).

Sample B exhibits broader peaks compared to sample C, which can be attributed to the influence of the solvents used. The choice of solvent, such as distilled water or ethanol, can significantly affect the growth of $BaSO_4$ nanoparticles by influencing reaction kinetics, particle size, and crystal morphology. In this case, deionized water, being a highly polar solvent, may preferentially stabilize certain crystal facets, whereas ethanol, with lower polarity, can alter nucleation and growth behavior, leading to distinct structural features and diffraction patterns. Additionally, solvent properties can impact the solubility of reactions, and the nucleation processes can also affect nanostructure size distributions. However, the selection of solvents should align with the desired properties of $BaSO_4$ nanoparticles. The SEM morphological studies are shown in Fig. 4 (a)-(d). For Sample B, synthesized using ethanol as the solvent, the SEM micrographs (Fig. 4a) reveal rod- or rice-like structures at the 2 µm scale. From the corresponding higher-magnification image (Fig. 4b, 1 µm scale), the average particle diameter is estimated to be around 73 nm, with some degree of agglomeration observed.

The morphological images of $BaSO_4$ structures prepared in water are shown in Fig. 4(c). An increase in particle size and changes in morphological structure were observed when deionized water was used as the solvent. Generally, increasing molar concentration ratio can lead to increased particle nucleation growth, potentially yielding larger or more numerous nanostructures. It's crucial to consider the reaction kinetics, solubility and other factors that can influence the sample's properties and nature. Also, adjusting the concentration ratio should be done cautiously, as it might also impact the stability and uniformity of the prepared nanostructures. However, in the morphological images at 1 µm, the diameter of nanorods around 222 nm which is very clear, as shown in Fig. 4(d). These selections of the solvents play key role in nano and microstructures. With respect the solvents, nanomaterials size and shape could be controlled as reported by various research groups (Gholami *et al*. 2024). They experimentally demonstrated that ethanol as a solvent promotes faster diffusion, leading to the formation of smaller nanostructures, whereas water enhances interparticle attraction, resulting in larger aggregates (Abdulkareem *et al*. 2023).

Fig. 5 (a) and (b) show the EDX spectra of $BaSO_4$ nanoparticles. These elemental spectra confirm the presence of Ba, O and S in both samples. Impurity elements were observed, which may be introduced during the calcination process. However, the peak intensity increased considerably due to the higher weight percentage (wt%) and atomic percentage (at%). The EDX analysis shows that the DI water–based sample exhibits strong peaks corresponding to Ba, S, and O elements. The use of DI water as a solvent plays a key role in the formation of free-standing $BaSO_4$ nanostructures, which may be useful for various biomedical applications.

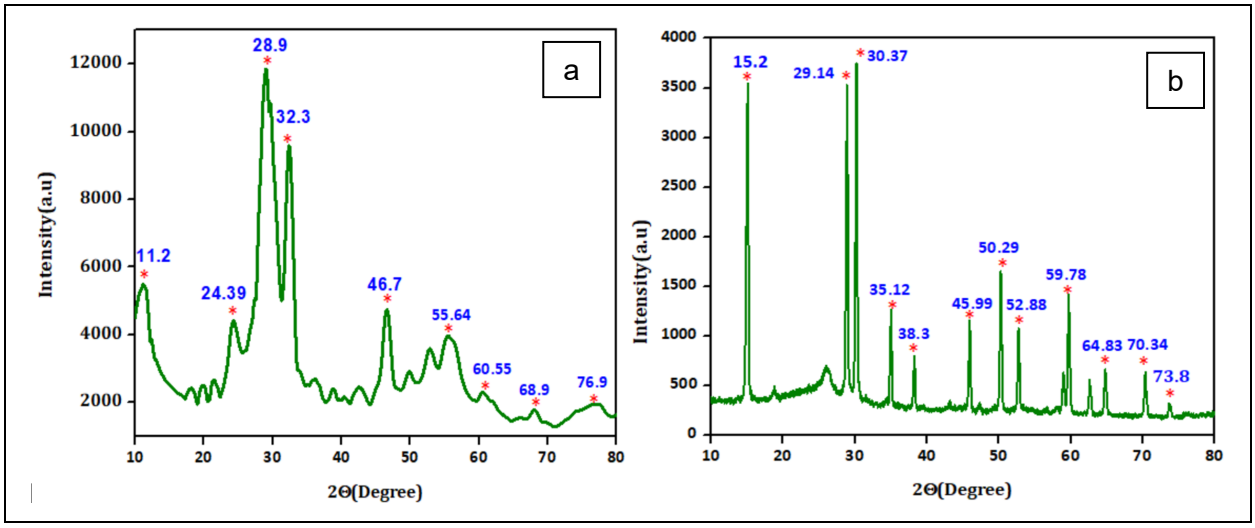


Fig. 2: XRD diffraction pattern of $BaSO_4$ nanostructures

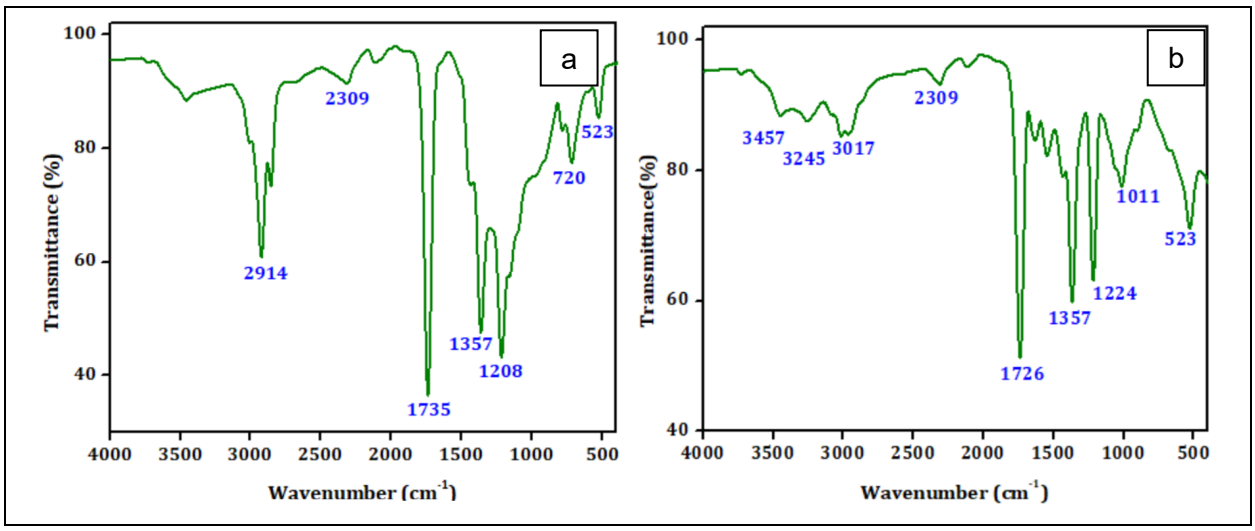


Fig. 3: FTIR transmittance spectra of $BaSO_4$ with ethanol (a) and Deionized water (b)

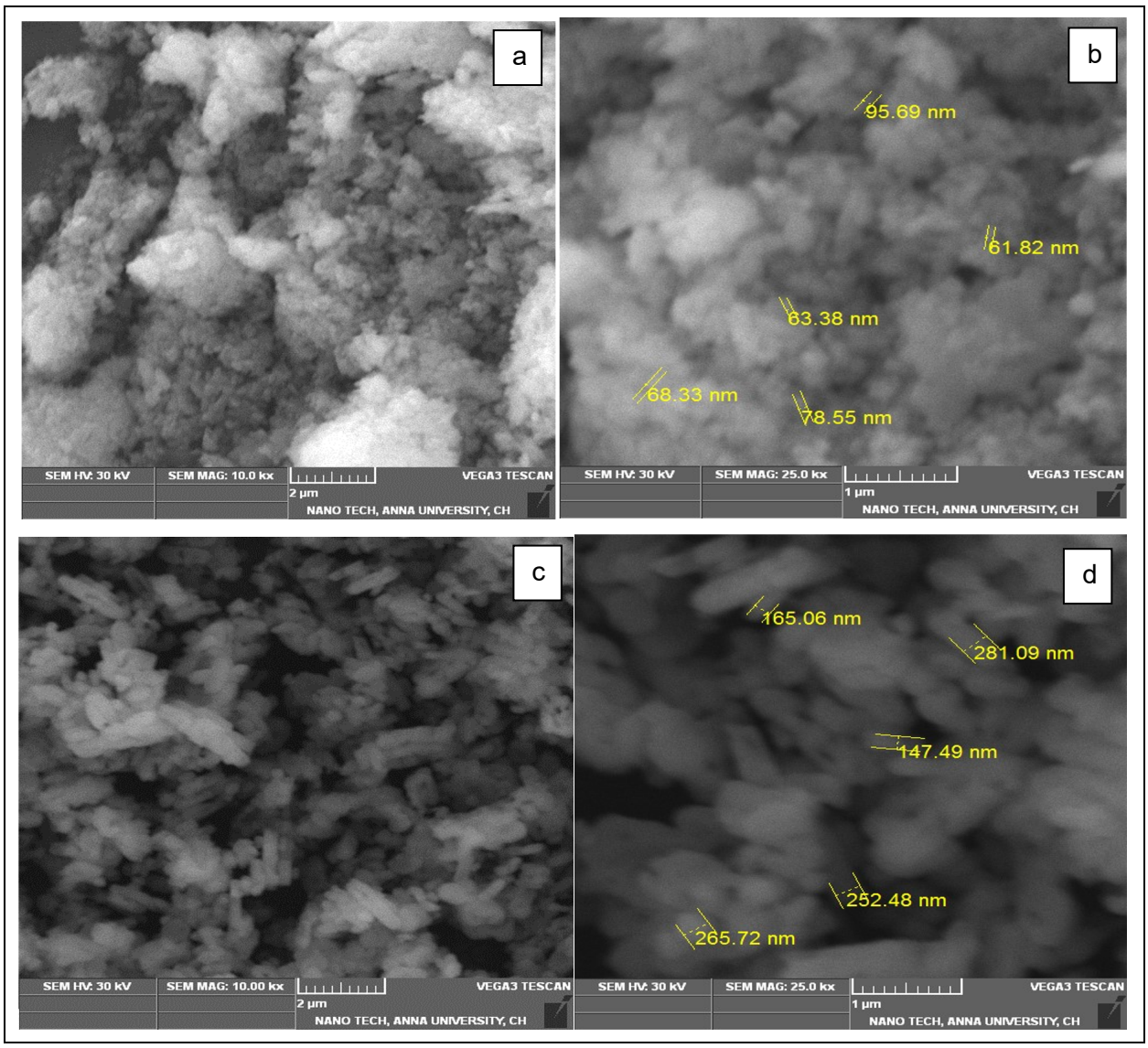


Fig. 4: SEM morphological images of $BaSO_4$ nano and microstructures, ethanol (a)-(b), Deionized water (c) -(d) solvent

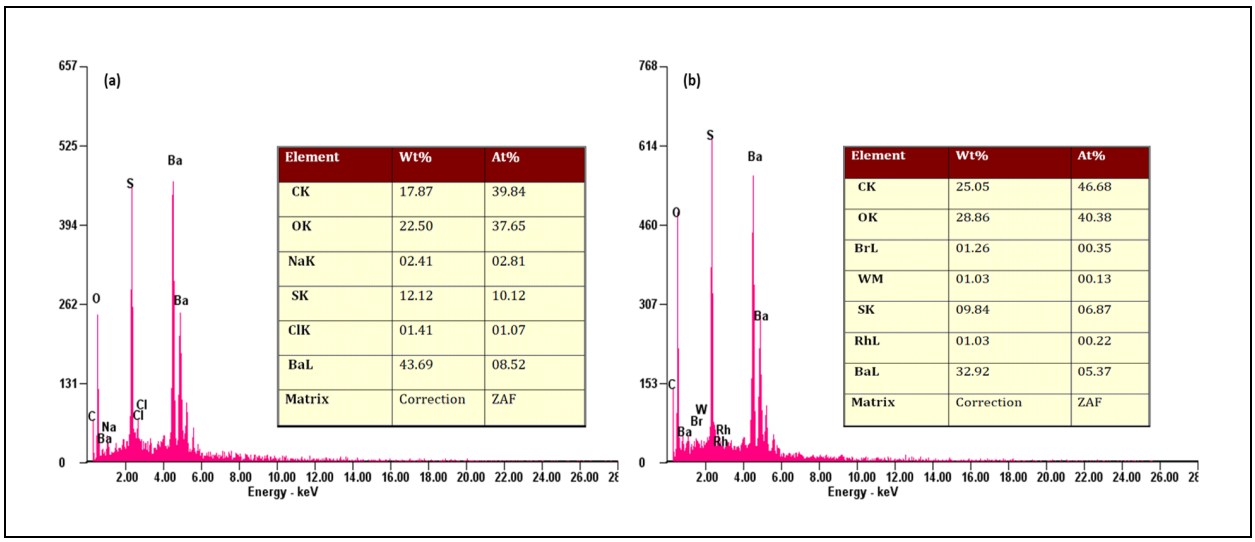


Fig. 5: EDX elemental images of $BaSO_4$ nanostructures based on ethanol (a) and deionized water (b)

4. CONCLUSIONS

$BaSO_4$ nanorods were successfully synthesized using different molar concentrations (0.05 M and 0.1 M) and solvents (ethanol and deionized water) via the co-precipitation method with *Azadirachta indica* leaf extract as a natural stabilizing agent. X-ray diffraction confirmed an orthorhombic phase structure, while Fourier transform infrared spectroscopy indicated characteristic Ba–O and sulfate vibrations. Scanning electron microscopy revealed well-defined nanorod morphology with effective control under different synthesis conditions, with improved resolution observed at 0.1 M compared to 0.05 M, supporting nucleation behavior studies. Elemental composition was confirmed by energy-dispersive X-ray analysis. Further optimization of molar concentration and solvent selection may enable the development of well-crystallized nanostructures for antimicrobial applications.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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