Novel sonochemical green approach for synthesis of highly crystalline and thermally stable barium sulphate nanoparticles using *Azadirachta indica* leaf extract

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Abstract. Nanomaterial synthesized using plant extract is a viable and better alternative to chemical synthesis methods. A simple, nontoxic and inexpensive strategy, which meets the standard of green chemistry, has been introduced for the synthesis of highly crystalline and thermally stable barium sulphate (BaSO_4) nanoparticles. This work reports ultrasonic-assisted green synthesis of BaSO_4 nanoparticles using *Azadirachta indica* leaf extract at room temperature. The as-synthesized BaSO_4 nanoparticles were subjected to various physiochemical characterization using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), field emission gun-scanning electron microscopy (FEG-SEM), thermogravimetric analysis (TGA) and energy-dispersive X-ray spectroscopy (EDX). XRD explored orthorhombic, highly crystalline and pure BaSO_4 (JCPDS: 24-1035) with average crystallite size of 55.6 nm. FEG-SEM study revealed about size (>80 nm) of BaSO_4 nanoparticles. Co-precipitation method was also employed to synthesize BaSO_4 for comparison between biogenic and chemical methods. The size of BaSO_4 nanoparticles obtained using co-precipitation method was very large with rod shape morphology. Novel sonochemical green method is preferable because of its control over particle size as well as morphology. FTIR study confirmed the formation of BaSO_4 nanoparticles. High thermal tolerance and stability of BaSO_4 nanoparticles was evidenced from single step weight loss in TGA. In addition, strong characteristic signals of barium, sulphur and oxygen in EDX confirmed the purity of ultrasonic-assisted green synthesized BaSO_4 nanoparticles. Overall, this one pot, inexpensive and green sonochemical approach is a promising method for the synthesis of BaSO_4 nanoparticles, which might be used for various commercial applications.

Keywords. *A. indica*; BaSO_4 nanoparticles; XRD; TGA; FEG-SEM.

1. Introduction

Recently, synthesis of efficient nanomaterials with colossal applications is emerging and crucial to meet increasing demand for advanced materials. Fabrication of industrially important materials has rapidly developed into a promising field in materials science. The prospect of commercial application has drastically accelerated the growing demand of multifunctional barium sulphate (BaSO_4) nanoparticles. BaSO_4 is important in various applications such as catalyst carrier, adsorbent materials, biomedical devices, engineering plastics and so on [1–3]. Due to its ability to increase the density of fluid and hydrostatic pressure of a well it reduces blowout and applied as a drilling fluid in off-shore oil production [4]. The white transparent colour of BaSO_4 is extensively applied in white pigment, printing ink and cosmetics. A high burning point and water insoluble nature makes it suitable as a coating material and is mostly used in paper brighteners. Its opaque nature towards X-rays is useful in medical imaging

to visualize the intestinal tract. Hence it is recommended to drink a cocktail containing BaSO_4 and its progress through digestive organs can be scanned by X-rays. Furthermore, it is used as a filler to enhance density and used in root-canal filling, plastic, paint and rubber industry. Other applications include soil testing (soil pH), as a catalyst support (Rosenmund reduction), in pyrotechnics, in colorimetry, in glass, TV screens, car filters, ceramics and electronics. Bhide *et al* have investigated photoluminescence properties of U_6^{+} doped BaSO_4 [5]. Esen *et al* have studied the X-rays and radioisotope energy absorption capacity of heavyweight concrete containing barite aggregate [6]. Practically, synthesis of BaSO_4 is beneficial for lots of commercial applications.

Various researchers have reported a number of synthetic strategies such as precipitation [7–9], microemulsion [10], organic modification [11], membrane separation [12] for BaSO_4 fabrication. Bala *et al* have synthesized BaSO_4 through a precipitation reaction using octadecyl dihydrogen phosphate (ODP; $n\text{-C}_{18}\text{H}_{37}\text{OPO}_3\text{H}_2$) as a modifier.

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Sun *et al* have also synthesized BaSO_4 nanoparticles in the presence of sodium polyacrylate by simple precipitation [13]. Adityawarman synthesized BaSO_4 nanoparticles *via* a non-ionic microemulsion synthetic method [14], Gupta used sodium hexametaphosphate as a stabilizer to obtain BaSO_4 nanoparticles [7]. Some other approaches used for BaSO_4 synthesis include microchannel reactor [15], two phase flow microreactor [16], membrane microreactor [17], rotating liquid film reactor [18], spinning disc reactor [19] and T-mixture reactor [20]. These methods for BaSO_4 fabrication are expensive and energy intensive and inflict environment risk by using noxious and persistent reagents. To overcome these problems, new emerging nanotechnology, green nanotechnology provides an eco-friendly and cost-effective solution by utilizing plant extract as a reducing and stabilizing agent without consuming or generating toxic chemicals and its by-products [21–24]. Previously, our research group synthesized various nanomaterials (ZnO , $n\text{-BaCO}_3$, CaCO_3 , CaSO_4 , TiO_2 , AgNPs and $\text{Mg}(\text{OH})_2$) using chemical as well as bio-inspired green methods [25–33].

Present work reports reliable, bioinspired, eco-friendly green sonochemical route for BaSO_4 synthesis using *Azadirachta indica* leaf extract (*A. indica* LE), which works as a bio-reducing, capping and stabilizing agent. Synergic coupling of sonochemistry and green chemistry protocol contributes to innovative and attractive advances in terms of low-cost, non-toxic processing, high reaction rate, less time and energy consuming, controlled size and morphology etc. *A. indica* is also known as neem tree (figure 1). Taxonomic classification of *A. indica* is provided as – Kingdom, Order: Plantae, Sapindales; Family, subfamily: Meliaceae, Melioiae; Tribe, Genus, species: Melieae, *Azadirachta*, *A. indica*.

Figure 1. Schematic representation of synthetic procedure followed during ultrasonic-assisted green synthesis of BaSO_4 with probable mechanistic path.

This is generally grown in tropical and semi-tropical regions. Phytocomponents of *A. indica* leaf extract includes alkaloids, flavonoids, reducing sugar, tannin, saponin, triterpenoid, carbohydrates and protein. As per the literature data available, this is the first ever report on ultrasonic-assisted green synthesis of BaSO_4 using *A. indica* LE. This report is significant for bioinspired low-cost protocol for multifunctional inorganic (BaSO_4) nanomaterial development. The novelty of proposed synthesis lies predominantly in its simplicity of the experimental process (without inert conditions, high temperature, pressure, surfactant and is less time consuming). Development of novel synthetic strategy using efficient green precursor and non-toxic solvent as well as rapid, one-pot, less energy intensive synthesis, could provide significant environmental and economic advantages. This paper unveils a green approach designed for the synthesis of BaSO_4 and its physiochemical properties have been investigated.

2. Experimental

2.1 Chemicals and characterization

Anhydrous sodium sulphate (Na_2SO_4) and barium chloride dihydrate ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) were procured from S. D. Fine-Chem Limited, Mumbai (India). Cetyltrimethylammonium bromide (CTAB, $\text{C}_{19}\text{H}_{42}\text{BrN}$, 99%, Fluka) was used as a stabilizer without further purification. Ethanol and deionized water were used throughout the experimentation. *A. indica* fresh leaves were collected from University campus, Kalina, Mumbai. Glassware was thoroughly washed using aqua regia and rinsed using distilled water and acetone, prior to synthesis.

Ultrasonic cell with processor (SJIA-250 W) (Unigenetics Instruments, New Delhi) was used for the synthesis of BaSO_4 nanoparticles. Fourier transform infrared spectroscopy (FTIR) was performed on Perkin-Elmer Frontier, Private Limited (India) in the range of $4000\text{--}400\text{ cm}^{-1}$ at a resolution of 4 cm^{-1} to identify functional groups present in *A. indica* LE and BaSO_4 . Crystalline nature and crystallographic phase were identified using X-ray diffractogram Shimadzu XRD 7000 with operating voltage 40 kV, $\text{CuK}\alpha$ radiation ($\lambda = 1.54060\text{ \AA}$), current 30 mA and scan range $15\text{--}80^\circ$, count time 0.60 s. Diffraction peaks of crystalline phases were compared with standard JCPDS data. Thermal stability and weight loss of BaSO_4 were studied on a thermal gravimetric analyser at $30\text{--}1000^\circ\text{C}$. The sample was kept in an aluminium pan sample holder and exposed to heating under continuous nitrogen purging (20 ml min^{-1}). SEM was performed on JEOL JSM-7600F (USA) combined with energy-dispersive X-ray (EDX) spectroscopy to study the size, shape and elemental composition of BaSO_4 nanoparticles. SEM imaging was performed with an accelerating voltage of 15 kV. Platinum sputtering was applied before SEM imaging.

2.2 Extract preparation and synthesis of BaSO₄

Fresh leaves of *A. indica* were washed several times with double distilled water along with deionized water to remove contaminants from the surface and shade dried at room temperature. After 7 days, the dried leaves were crushed in a grinder. Thirty gram of fine *A. indica* powder was added in 300 ml of water–ethanol mixture and refluxed at 30°C for 60 min. After cooling, the leaf extract was filtered through Whatman filter paper and cooled for 30 min. Further, 20 ml of filtrate was taken in an ultrasonic probe sonicator and 40 ml of 0.05 mol l⁻¹ BaCl₂ solution was added dropwise during sonication. After 5 min, with continuous sonication 40 ml of 0.05 mol l⁻¹ Na₂SO₄ was added dropwise and a white precipitate was obtained. The reaction mixture was incubated at

37°C for 24 h for complete growth of BaSO₄ nanoparticles. Afterwards, the white precipitate was separated by centrifugation (6000 rpm, 25 min) and washed thrice with deionized water and ethanol. The obtained precipitate was vacuum dried to obtain a final mass of BaSO₄. In another experiment, BaSO₄ was synthesized using a co-precipitation technique in the presence of CTAB as a surfactant. The intention behind using a co-precipitation method for BaSO₄ synthesis was for a comparative study of size and shape, with that obtained using the ultrasonic-assisted green method.

3. Results and discussion

3.1 Mechanistic path of BaSO₄ nanoparticle synthesis using ultrasonic-assisted green method

Synthesis of BaSO₄ followed green synthetic approach coupled with ultrasonic-assisted mixing of reagents BaCl₂ and Na₂SO₄ and *A. indica* LE. Proposed mechanistic aspects can be explained in the following terms. Initially both BaCl₂ and Na₂SO₄ get reduced and then the reaction of barium ions (Ba²⁺) and sulphate ions (SO₄²⁻) generates BaSO₄

Figure 2. UV-Vis absorbance spectra of BaSO₄ nanoparticles.

Figure 3. FTIR spectrum of (a) *A. indica* LE, (b) green synthesized BaSO₄ and (c) chemically synthesized BaSO₄.

Figure 4. (a) X-ray diffractogram of BaSO₄ synthesized using *A. indica* LE (JCPDS card no. 241035). (b) XRD of crystalline BaSO₄ nanoparticles synthesized using chemical co-precipitation method.

precipitate in the reaction mixture. As BaSO_4 is insoluble in water, its precipitate settles at the bottom and NaCl remains in the solvent mixture. Figure 1 shows the mechanistic path of nanoparticle synthesis. Probably in reaction mixture, Ba^{2+} makes a complex with phytocomponents and after that the entrapped Ba^{2+} reacts with SO_4^{2-} generating BaSO_4 . Here phytocomponents of the leaf extract act as a nucleator and growth modifier. Some consequent secondary processes such as capping, ageing, agglomeration, ripening and breakage might occur depending upon the nature of

interaction of phytocomponents and the reaction process. Mostly, the nucleation rate is governed by temperature, degree of supersaturation, phytocomponent encapsulation and surface energy. Size control is governed by these factors to a large extent. Increment in supersaturation decreases surface energy and consequently increases nucleation rate which leads ultimately to small sized nanoparticles. Moreover, the exact phenomenon involved in ultrasonication is acoustic cavitation which produces high energy shock waves and increases nucleation rate and a simultaneous collapse of

Table 1. Details of diffraction pattern, d -spacing, lattice strain, crystallite size and average size of BaSO_4 nanoparticles.

2θ ($^\circ$)	d ($\text{\AA}$)	hkl	FWHM (β)	Lattice strain	Crystallite size (nm)	Average size (nm)
20.45	4.3386	101	0.14670	0.0035	57.5	55.6
22.79	3.8978	111	0.14200	0.0031	59.62	
25.84	3.4443	021	0.14930	0.0028	57.04	
28.74	3.1031	121	0.14790	0.0025	57.94	
31.53	2.8345	211	0.17030	0.0026	50.63	
32.78	2.7291	002	0.18800	0.0028	46.01	
36.17	2.4813	221	0.13310	0.0018	65.61	
38.73	2.3228	022	0.18170	0.0023	48.42	
40.79	2.2102	122	0.15500	0.0018	57.14	
42.59	2.1206	140	0.15220	0.0017	58.54	
44.00	2.0559	041	0.16560	0.0018	54.06	

Figure 5. TGA thermogram of BaSO_4 synthesized using *A. indica* LE.

Figure 6. (a) TGA thermogram of *A. indica* LE and (b) supporting derivative curve.

fast bubble turn out a high rate of temperature decrease which stops agglomeration and organization of particles, leading to small size nano-crystal formulation. Figure 2 shows the absorbance of BaSO₄ nanoparticle in the UV-Vis spectrum. The result confirms the purity of the as-synthesized nanoparticles.

3.2 FTIR analysis

Figure 3a shows the functional group of reducing and stabilizing agents available in *A. indica* LE. Band at 3278 cm⁻¹ depicts intermolecular bonded -OH group (polyphenol or flavonoid). Observed transmittance peaks at 2921 and 2852 cm⁻¹ correspond to alkane group. Band at 1725 and 1602 can be assigned to aromatic C=O and C=C stretchings. Band at 1163 cm⁻¹ represents tertiary alcohol and

Figure 7. FEG-SEM of BaSO₄ nanoparticle synthesized using *A. indica* (under magnification of 1 μm (a, b) and 100 nm (c)). The frequency (%) vs. particle size histogram corresponding to (c) is presented in (d) showing nanoparticles > 80 nm.

1024 cm^{-1} displays anhydride. These functional groups are actively involved in reduction, capping and stabilization. From the graph it appears that vibrational group at 3278 cm^{-1} is very much shifted (completely participated) and actively involved in the reduction of Na_2SO_4 and BaCl_2 in the prepared sample.

Figure 3b represents the FTIR spectra of ultrasonic-assisted green synthesized BaSO_4 . Characteristic transmittance peaks

at 1192 , 1064 and 980 cm^{-1} correspond to symmetric vibrational stretching of SO_4^{2-} , whereas a peak at 604 cm^{-1} is attributed to out-of-plane bending of sulphate (SO_4^{2-}) group [34]. According to Alder and Kerr, sulphur–oxygen (S–O) stretching of inorganic sulphate is found in the characteristic region of $1192\text{--}1072\text{ cm}^{-1}$ [35]. FTIR results are in complete agreement with successful formation of BaSO_4 using *A. indica* LE. Figure 3c demonstrates FTIR of BaSO_4

Figure 8. FEG-SEM images of powdered BaSO_4 (without sonication) synthesized using chemical route under different magnifications (a–h).

synthesized using the co-precipitation method. Peaks were completely tuned with each other and confirmed the purity of synthesized BaSO₄.

3.3 X-ray diffraction (XRD) study

Microstructural characteristics of cryo ground BaSO₄ nanoparticles were investigated using XRD pattern (figure 4a). A sharp and intense diffraction peak reveals the highly crystalline nature of BaSO₄ synthesized using *A. indica* LE. The absence of impurity peaks confirms high purity of the as-synthesized BaSO₄. Reflection planes were completely matched with standard JCPDS card no. 24-1035 (see Supporting information) having a typical orthorhombic structure of BaSO₄. The average crystallite size was calculated by applying Debye Scherrer equation [36]:

$$d = \frac{K\lambda}{\beta \cos \theta},$$

where d represents crystallite size in nanometre, K is Scherrer constant (0.94), λ is the wavelength of CuK α radiation with a value 0.154 nm, β is full width at half maximum (FWHM) in radian and θ is Bragg diffraction angle.

By using above data, the crystallite size from eleven prominent peaks was calculated and their average crystallite size was found to be 55.6 nm (table 1). Figure 4b presents the XRD pattern of freshly prepared BaSO₄ using the chemical co-precipitation technique. The diffraction pattern was found to be more intense with a crystalline nature. The average crystallite size was found to be ~98.12 nm. The results indicate that ultrasonic-assisted green method provides good control over size as compared to the chemical co-precipitation method.

3.4 Thermogravimetric and differential thermal analysis

Figure 5 presents thermogravimetric analysis (TGA) of BaSO₄ nanoparticles exhibiting high thermal stability. Organic decomposition at temperature 310°C was observed from derivative weight loss curve, which corresponds to mass loss of 7.69%, this behaviour was most likely a consequence of the surface desorption of the bio-organic compounds present in *A. indica* LE getting involved in capping of BaSO₄. Single weight loss in TG thermogram, single derivative formation in derivative weight loss curve and 92.30% residue of pure BaSO₄ strongly evidences high thermal stability of BaSO₄ nanoparticle synthesized using *A. indica* LE. Figure 6a and b shows TGA and derivative curve of *A. indica* LE, where only 4.9% residue remained after two successive weight losses (66.04 and 28.46%), which was observed as a consequence of surface desorption of bio-organic moiety acted as reducing and stabilizing agent during synthesis of BaSO₄.

3.5 Morphological study

Figure 7 displays the field emission gun-scanning electron microscopy (FEG-SEM) images of BaSO₄. Figure 7a and b displays FEG-SEM under magnification of 1 μ m, while figure 7c presents nanoparticles on a 100 nm magnification scale. Figure 7d presents the frequency (%) vs. particle size distribution diagram. Result reveals the influence of *A. indica* LE on the morphology of BaSO₄. FEG-SEM reveals rod-like BaSO₄ nanoparticles with size >80 nm. Previous reports have shown larger particle size of BaSO₄ synthesized using chemical route. Hopwood and Mann have reported synthesis of BaSO₄ in DDAB microemulsion and

Figure 9. EDX spectra of BaSO₄ with characteristic signals of Ba, S and O.

nanoparticles were of 200 nm in size [37]. Liu and Wu reported biomimetically synthesized BaSO₄ nanotubes with length 1.5–2.5 μm. According to the report, synthesized nanotubes had an external diameter and inner diameter with size range 90–140 and 73–122 nm, respectively [38]. Cofiero *et al* had synthesized BaSO₄ using a spinning disc reactor and found nanoparticles in size range 3–0.7 μm [39]. Sun *et al* reported PAAS modified BaSO₄ in the size range of 100–300 nm diameter [13]. In this report also, BaSO₄ synthesized using chemical method (co-precipitation technique) showed a large particle size (~80–600 nm) under magnification of 1 and 2 μm scale in SEM analysis. The SEM images were taken without ultrasonication. Figure 8a–h displays morphology of chemically synthesized BaSO₄ which is rod shaped hierarchical architectures with some agglomeration. Overall, *A. indica* green LE has proved to be an efficient size controller and ultrasonic-assisted green method provided small sized BaSO₄ nanoparticles for several commercial applications.

3.6 EDX analysis

To further study the chemical composition and purity of as-synthesized BaSO₄, EDX measurement was performed. EDX study of BaSO₄ explored the strong signal of Ba, S and O. The inset represents the area selected for elemental mapping of present elements (figure 9). All characteristic signals reveal that sample possess Ba, S and O elements only. Another less intense signal appeared due to platinum coating during SEM analysis. The weight percentage of elements in the sample was 60.81% Ba, 14.47% S and 21.71% O. The weight of elements in EDX confirms that sample contains BaSO₄ nanoparticles.

4. Conclusion

The present work reports a sustainable, less energy intensive, novel and rapid synthetic technique for the synthesis of stable and size controlled BaSO₄ nanoparticles using *A. indica* LE. The synthesis was conducted without any additive or surfactant. Green protocol facilitates to obtain highly pure, orthorhombic, crystalline and thermally stable BaSO₄ nanoparticles. XRD revealed high purity and crystalline nature of the as-synthesized BaSO₄ with average crystallite size 55.6 nm. FEG-SEM images confirmed about rod morphology with particle size range >80 nm. The presence of vibrational stretching of SO₄²⁻ group in FTIR confirmed the formation of BaSO₄ nanoparticles without any surfactant or stabilizer. High consistency in elemental presence was confirmed by EDX analysis which explored the presence of characteristic strong signals of Ba, S and O elements. TGA study strongly evidenced the high thermal stability of BaSO₄ nanoparticles, it was completely stable up to 310°C and a single weight loss of 7.69% was observed with 92.30% residue. The above results strongly confirmed the formation of the thermally stable and highly crystalline BaSO₄

nanoparticles using this novel ultrasonic-assisted green synthetic approach. This green synthetic approach may be extended to other noble material synthesis. Sustainable non-toxic biocompatible precursor of green methodology provided reduced particle size of BaSO₄ as compared to previously reported and chemically synthesized method. Small sized nanoparticles can be employed for possible pharmaceutical applications as a potential contrast agent for X-ray examinations without any side effects. In addition, physiochemical properties such as excellent stability, inertness, whiteness, high specific gravity and outstanding optical property makes it suitable for various industrial, medicinal and technological applications.

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