THIRD ORDER NONLINEAR OPTICAL, ELECTROCHEMICAL, CATALYTIC AND ANTIBACTERIAL PROPERTIES OF GREEN SYNTHESIZED $BaSnO_3$ NANOPARTICLES

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Abstract

Perovskite materials are widely studied for their super-conducting, magnetic, catalytic and electro-optic properties. Among them, barium stannate ($BaSnO_3$) finds applications in dielectric and optically active devices, thermally stable capacitors, humidity and gas sensors. This research compared the electrochemical, third-order nonlinear, dye-deactivation and bacterial growth inhibition capabilities of $BaSnO_3$ produced by chemical (CBS) and greener (GBS) methods. Decreased crystallite size was realized for the green synthesized $BaSnO_3$. Energy band gaps were 3.23 and 3.04 eV for CBS and GBS, respectively. The GBS sample exhibited increased specific capacitance value. Photocatalytic degradation efficiencies were 78.4%and 89.7%, respectively for $BaSnO_3$ synthesized by normal and greener approach against methyl violet after 90 min of UV light irradiation. Enhanced nonlinear optical parameters were obtained for the GBS sample. Excellent antibacterial efficacy against *Proteus vulgaris* bacteria was realized for GBS thanks to the domination of phytochemicals of *M. olifera* leaf extract.

Keywords

$BaSnO_3$ perovskite; bacteria suppression; green synthesis; specific capacitance

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1. Introduction

Perovskite materials with super-conducting, magnetic and electro optic properties [1] finds applications as catalysts, proton and oxygen-ionic conductors, electrochemical and magnetic devices, etc. [2]. Amongst the perovskite materials, earth alkaline stannate with chemical formula $MSnO_3$ (M = Ba, Sr and Ca) which forms a component of dielectric materials are used in thermally stable capacitors, photoelectron-chemical energy conversion, gas sensors, etc. [3]. Barium stannate ($BaSnO_3$), being stable up to 1000°C exhibits n-type conductivity with a band gap of 3.4 eV which makes it suitable for applications in dielectric devices, thermally stable capacitors, humidity and gas sensors, optical applications, ceramic boundary layers, etc. [4, 5]. However, the insulating behaviour of $BaSnO_3$ at room temperature limits its viability for various technological applications. To utilize $BaSnO_3$ for optoelectronic, catalytic, magnetic and bio medical applications, its band gap must be lowered which is achievable through doping with impurities. James et al. [1] observed improved optical and magnetic properties for Fe-doped $BaSnO_3$ nanopowders. An electrical resistivity of 2.43 Ω-cm has been realized for $BaSnO_3$ through Sb doping [6]. $BaSnO_3$'s band gap influenced by splitting of energy levels was procured through Mn doping [7].Improved crystalline quality through Au doping was quoted for $BaSnO_3$ by Athawale et al. [4]. Besides doping, reduced band gap is also possible by green synthesizing $BaSnO_3$ using plant leaf extracts which acts as reducing, stabilizing and capping agents [8]. Decreased band gap was reported for CeO_2/ZrO_2 core nanoparticles (NPs) biosynthesized using *Justiciaadhatoda* by Pandiyan et al. [9]. ZnO and NiO NPs green synthesized using *M. Oleifera* and neem leaves displayed reduced band gaps [10, 11].

Herein *Moringa oleifera (M. oleifera)* leaf extract is adapted to green synthesized $BaSnO_3$ NPs as it contains rich phytochemicals which reduce metal ions to nanoparticles in the chelating process. Various fatty acids, vitamins, aminoacids and nutrients, glucosinolates and phenolics such as flavonoids, anthocyanins, proanthocyanides and micronutrients such as Cu, Mn, Fe, Co and Ni are also present in *M.oleifera* extract [12]. In literature, silver and zinc oxide NPs for antibacterial application was green synthesized using *M. oleifera* by Irfan et al. [13]. *M. oleifera* mediated Ni-doped Fe_3O_4exhibited excellent catalytic skill [14]. Super-paramagnetic behaviour was reported for iron oxide nanoparticles capped with *M. Oleifera* extract by Aisida et al. [15]. MgO [16] and TiO_2

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[17] NPs were green synthesized using *M. oleifera* for antibacterial applications. To ascertain the dominance of phytochemicals of *M. oleifera*, in this work $BaSnO_3$ was green synthesized using it, characterized and compared with the results obtained for chemically synthesized $BaSnO_3$.

2. Experimental Procedure

2.1 Materials

Barium chloride [$BaCl_2.2H_2O$] and tin (II) chloride [$SnCl_2.2H_2O$], both of analytical reagent (AR) grade obtained from Rankhem chemicals, India with 99.8% assay are the precursor salts used to synthesize $BaSnO_3$ NPs by chemical and greener methods.

2.2 Preparation of *M. oleifera* leaf extract

Fresh *M. Oleifera* leaves after cleaned with water were shade dried and powdered. Then, 25 g of the powder was dissolved in a reaction mixture of ethanol (5 mL), water (25 mL) and kept in soxhlet apparatus for two hours at 60°C. The resultant was filtered to get *M. Oleifera* leaf extract.

2.3 Chemical synthesis of $BaSnO_3$ (CBS) NPs

Barium chloride and tin (II) chloride each of 0.1 M were dissolved in a reaction mixture containing de-ionized water (135 mL), dilute HCl (5 mL) and liquid ammonia (10 mL), stirred and aged for two hours. The settled precipitates were washed, dried, calcined at 400°C for 1 h and crushed to form chemically synthesized $BaSnO_3$ which is designated as CBS.

2.4 Green synthesis of $BaSnO_3$ (GBS) NPs

To green synthesize $BaSnO_3$, the precursor salts were dissolved in a reaction mixture containing 115 mL de-ionized water, 5 mL dilute HCl and 30 mL leaf extract. By repeating the above procedure (Section 2.3) greener $BaSnO_3$ was synthesized which is designated as GBS. To avoid agglomeration, heat treatment was done at 200°C for 1 h [18].

2.5 Characterization

XRD, SEM, XPS, UV-Vis-NIR, FTIR and PL details used to characterize the CBS and GBS samples are displayed in Table 1.

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2.6 Electrochemical test

CV curves was acquired using scanning potentiostat/galvanostat (EG & G, model: 273 A) with a standard three electrode configuration: CBS & GBS - Working electrode, conventional saturated calomel electrode (SCE) - Reference electrode and platinum - Counter electrode. 2 mg of the synthesized samples dissolved in ethylene glycol were brushed and coated on the surface on the glass substrates to use as working electrode.

2.7 NLO studies

The third order NLO studies were performed using a 532 nm diode pumped CW Nd:YAG laser (coherent compass TM215 M – 50), which was focused by a 3.5 cm focal length lens.

2.8 Catalytic activity

The photocatalytic activity was evaluated by monitoring the deactivation of 0.05 M methyl violet dye under 60 W UV light irradiation. 10 mg of CBS and GBS NPs was added to 100 mL aqueous solution containing the dye separately. Before light exposure, the dye solution with the catalysts was stirred to reach the absorption/desorption equilibrium.

The degradation efficiency (η) and rate constant (k) were calculated using the dye concentrations in dark (C_0) and light (C) conditions:

$$\eta = \left(1 - {}^{C}/_{C_0}\right) \times 100\ \% \qquad (1)$$

$$k = \frac{ln(C_0/C)}{t} \qquad (2)$$

2.9 Antibacterial activity

Antibacterial activity was analyzed by well diffusion method against *Proteus vulgaris* bacteria. *Proteus vulgaris* strains were swapped in petriplates containing Mueller–Hinton agar medium in which 6 mg sample was placed in wells (6 mm diameter) and incubated for 24 h at 37 ± 2°C. By measuring the inhibition zones, the bacterial suppression ability was evaluated.

2.10 *In-vitro cytotoxicity activity*

HepG2 human liver cancer cells were used for anticancer studies. Incubation at 37ºC was performed after seeding the cells in 10% Dulbeccos Modified Eagle Medium (DMEM) added

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to 96 well plates. At 80% confluence, the cells treated with different concentrations of the synthesized GBS NPs (10 µL, 20 µL, 30 µL, 40 µL and 50 µL) were incubated for 24 h. After photographing, the cells are washed with 1xPBS and evaluated for cytotoxicity using MTT (Thiazolyl Blue Tetrazolium Bromide) and incubated for 4 hr in dark, after which MTT is reduced into purple colored formazan crystals which were mixed with dimethyl sulfoxide (DMSO) for complete solubility and absorbance spectra was taken at 570 nm.

3. Results & Discussion

3.1 XRD studies

XRD patterns (Fig. 1(a, b)) indicate the cubic structural nature of both CBS and GBS NPs (JCPDS card No. 15-0780). Reduction in peaks intensities and amorphous quality is noticed for the GBS sample due to bioactive active elements in the extract [12]. The crystallite sizes were 63±2 nm and 49±2 nm, respectively for the CBS and GBS samples, respectively.

3.2 SEM analysis

The SEM images and histographs of a) CBS and b) GBS are pictured in Fig.2 which showed grains with different sizes and shapes. More agglomeration occurred for the GBS sample with many empty sites. The average grain sizes from the histograms were 84 ± 3 nm and 77 ± 3 nm, respectively for CBS and GBS which is in consistent with the XRD results.

3.3 EDS and mapping

Fig. 3 shows the EDS spectra of a) CBS and b) GBS nanoparticles, which affirmed the presence of Ba, Sn, and O. The atomic percentage compositions of the elements are displayed in the inset pie diagrams.

Fig. 4 shows the mapping images of Ba, Sn, O of a) CBS and b) GBS. Uniform distribution of elements slightly deviates for the greener sample owing to the capping of $BaSnO_3$ by the bioactive elements in the extract.

3.4 XPS studies

Survey scan spectrum (Fig.5 (a)) of GBS marks the residence of Ba, Sn, and O. The C1s signal located at 281.2 eV might have resulted from CO_2 absorbed [19]. The 792.8 and 777.8 eV

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peaks (Fig. 5(b)) assigned to Ba $3d_{3/2}$ and Ba $3d_{5/2}$ spin states coincides to Ba^{2+} [20]. The Sn $3d_{3/2}$ and $Sn3d_{5/2}$ peaks observed at 492.7 and 484.4 eV (Fig. 5(c)) corresponds to Sn^{2+} in $BaSnO_3$ [21]. The core spectra for O1s (Fig. 5(d)) has a single peak at 529 eV attributed to O^{2-} ions in $BaSnO_3$ [22].

3.5 FTIR studies

Fig. 6 shows the FTIR spectra of a) CBS and b) GBS samples. The OH stretching vibration related peaks were observed between 3040 to 3860 cm^{-1} for both the samples [23], at 2808 cm^{-1} for CBS and at 2812 cm^{-1} for GBS. The band at 1996 cm^{-1} corresponds to S–O bending vibration [24]. Deformation mode of OH group resulted in bands at 1751, 1636, 1605 cm^{-1} for CBS and at 1755, 1611 cm^{-1} for GBS [25]. The 1402 cm^{-1} peak corresponds to C=O stretching [26]. C–O single bond stretching and OH bending mode vibrations are observed respectively at 1256 and 1032 cm^{-1} for GBS [27]. The SnO_6 stretching vibration peak at 679 cm^{-1} is connected to the barium ion [28]. The ν_{Sn-O} stretching appears at 565 cm^{-1} for CBS and at 561 cm^{-1} for GBS [4]. Metal-oxygen related peak occurs at 415 cm^{-1} for the CBS sample.

3.6 DRS studies

Fig. 7 shows the transmittance spectra of a) CBS and b) GBS NPs. Even though high transparency occurs for the greener sample in 900 – 1400 nm region, remarkable drop is experienced in 400 – 900 nm range due to increased absorption (Inset Fig). For the greener $BaSnO_3$, strong surface plasmon resonance peaks occur at 420 and640 nm in the wavelength region 300 – 700 nm, which highlighted that *M. oleifera* extract have dominated its optical absorption ability and agrees with earlier reports [29, 30]. The energy gap values of the CBS and GBS samples were estimated by calculating the Kubelka–Munk function (K_M) from the diffuse reflectance (R) values using the relation [31]:

$$K_M = \frac{(1-R)^2}{2R} \qquad (3)$$

Using the K_M values, plots were drawn between $(K_M h\nu)^2$ vs $h\nu$ (Fig. 8) and the band gap (E_g) values were calculated to be 3.23±0.01 eV and 3.04±0.01 eV, respectively for CBS and GBS NPs. The obtained band gap value for the CBS sample agrees with the value reported earlier [1]. The

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reduced E_g value for the GBS sample is due to phytochemicals in the leaf extract which acts as reducing agent [32].

3.7 PL studies

In the PL spectra (Fig. 9(a, b)) emission peaks were observed at 361, 380, 412 and 490 nm for both the samples. Radiative recombination of free excitons emits the NBE ultra-violet emission at 361 and 380 nm, respectively [33]. Oxygen vacancies correspond to 412 nm band for both the samples and at 437 nm for the greener sample [34]. The size-dependent excitonic transition peak is seen at 490 nm [35]. The decreased PL intensities realized for the GBS sample might be responsible for its enhanced photogenerated electron-hole pair separation which enhances its bacterial suppression (Section 3.11). The decreased intensity might be attributed to the decreased crystallite size due to increased number of defects [36]. Decrease in crystallite size increases non-radiative oxygen vacancies and photoexcited electrons are trapped within those vacancies, thereby decreasing their recombination with holes [37].

3.8 Electrochemical studies

Fig. 10 shows the cyclic voltammetric curves of CBS and GBS NPs. The CV curves reveal two distinct redox couples (oxidation and reduction process) supporting pseudocapacitive behaviour [38]. Increased peak area with increased peak current realized for the greener $BaSnO_3$ confirmed its superior electrochemical behaviour. The specific capacitance (C_S) values calculated by the relation, $C_S = \frac{I\Delta t}{m\Delta V}$ are 29±0.05 and 46±0.05 F/g, respectively for the chemical and greener $BaSnO_3$. The higher C_S value obtained for the greener sample favours for its improved electrochemical behaviour [39]. In order to understand the interfacial charge transfer process between the electrode and electrolyte, EIS measurements were performed and shown in Fig. 11. In the high frequency domain, both CBS and GBS samples demonstrate a semicircular pattern and in the low frequency domain they reveal a linear segment [40]. The decreased diameter observed for the GBS sample promotes reduced polarization and low charge transfer resistance which facilitates accelerated ion diffusion in the electrolyte. The R_{ct} values were 5330 and 3185 ohms for the CBS and GBS

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samples, respectively. The GBS sample's potential as a supercapacitor was validated by its lowest charge transfer resistance value.

3.9 Z-scan studies

Figs. 12 shows the Z-scan (a) closed, (b) open and (c) closed-to-open aperture curves of CBS and GBS nanoparticles. Pre-focal peak along with post-focal valley in the closed-aperture curve indicates negative non-linearity revealing that the nonlinear refraction is positive due to thermo-optic or thermal defocusing effect [41].

The nonlinear refractive index n_2 values are 5.24 x 10^{-9} cm^2/W and 6.16 x 10^{-9} cm^2/W respectively for the CBS and GBS NPs. The open aperture curves confirmed that both the samples displays a reverse saturation absorption (RSA) process by stout nonlinear absorption at the origin (Z=0) which occurs either from single photon absorption or multi photon absorption [42]. The nonlinear absorption coefficient (β) values of the CBS and GBS NPs are 3.26 x 10^{-4} cm/W and 3.26 x 10^{-4} cm/W, respectively. The third order nonlinear optical susceptibility values are compiled in Table 2. The GBS sample possesses high third order NLO susceptibility due to more electron cloud movement from the donor to the acceptor confirming its utility for photonic applications.

3.10 Photocatalytic test

Methyl violet was tested under UV light to justify the dye deactivation ability of CBS and GBS catalysts. Fig. 13 shows the absorption spectra of the catalysts measured at 587 nm. For both the catalysts, absorbance decreased with increased in irradiation time, confirming their degrading nature. The degradation efficiencies calculated using Eqn. (1) is compiled in Table 3. The maximum degradation efficiencies achieved for CBS and GBS catalysts after 90 min light irradiation were 78.4% and 89.7%, respectively. The photoefficiency depends on the charge transfer, electron-hole recombination and light absorption properties. When light falls on CBS and GBS catalysts (Fig. 14), electrons in their valence bands are excited and move to their conduction bands; leaving holes in VB. The electrons reacts with surrounding oxygen and reduce to O_2^{*-}; whereas holes left in the VB oxidize OH- derived from adsorbed water to form OH^*. The O_2^{*-} and OH^* radicals have a strong oxidative ability and decompose MV dye into CO_2, H_2O and small molecules [43]. The increased degradation

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efficiency observed for the GBS catalyst might be due to the easy excitation of phytochemicals present in the leaf extract which are loaded on $BaSnO_3$ which creates more mobile electrons and hence more O_2^{*-} radicals are produced [44]. Also, the photo-excited electrons of the phytochemicals are easily transferred to the conduction band of GBS which creates more active sites, which enhances the electron-hole separation thereby improving the degradation efficiency [45].

The apparent rate constants (k) estimated from the slopes of the plots of $ln(C_0/c)$ vs. irradiation time was 0.01907 min^{-1} and 0.02685 min^{-1} for CBS and GBS, respectively. Higher value of k obtained for the GBS sample favours for its higher degradation efficiency.

3.11 Bacterial suppression

The antibacterial activity of the CBS and GBS samples is shown in Fig. 15 (a, b). The greener sample showed higher antibacterial activity (Fig. 15(b)) against the tested bacteria. The bacterial suppression of the CBS and GBS NPs rely on their contact with the bacterial membrane which collapse and rupture it thereby leaks bacterial cytoplasm [46]. When the bacterial cells and NPs interacts, reactive oxygen species (ROS) are generated which tear down the bacterial membrane [47]. ROS generation inhibits the protein synthesis, DNA replication and metabolism cycle damaging the bacterial cell [48]. Also, the release of constituent metal ions from the surface contributes to the antibacterial activity. These ions which are in direct contact with the bacteria are absorbed by its outer membrane. They react with this membrane according to the electronegative tendencies of the element which creates hole in the bacterial membrane, ultimately leading to its demise [49]. More ROS are generated for the greener sample due to decreased crystallite size which makes it more effective in resisting the bacterial growth. Also the hydroxyl group related phenols in the extract exhibits better scavenging ability and hence enhanced bacterial suppression was realized for the greener $BaSnO_3$.

3.12 *Anticancer activity*

The extract mediated $BaSnO_3$ effectively resisted the tested HepG2 cancer cells; on the other hand, the control and the chemically synthesized $BaSnO_3$ showed no sign of resistance (Fig. 16(a-e)). From the graph between cell viability and the concentration of the sample (Fig. 17), the sample with 40 µL concentration exhibited better cytotoxicity against the tested cells. The effective cytotoxicity

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realized for the extract mediated sample might be due to smaller crystallite size, larger surface area, electrostatic fascination between +vely charged GBS NPs and –vely charged cells which demise the HepG2 cell by membrane leakage, ROS generation and induction of apoptosis which cause the death of the cells. Eicosane in an appreciable quantity in the leaf extract might have dominated the anticancer ability of the green synthesized $BaSnO_3$.

4. Conclusion

Comparison on the electrochemical, nonlinear optical, catalytic, antimicrobial and anticancer properties of chemical and green synthesized $BaSnO_3$ perovskite. Decreased crystallite size and increased specific capacitance was achieved for the greener $BaSnO_3$. The greener $BaSnO_3$exhibited remarkable third order NLO properties and it degraded 89.7 % of methyl violet dye within 90 min under UV light irradiation. Excellent bacterial suppression and anticancer activity was observed for the greener sample. The obtained results endorsed that the *M. oleifera* leaf extract mediated greener $BaSnO_3$ perovskite which was synthesized without employing toxic solvents was facile, green and suitable for large area production to be used as efficient electrode materials in pseudo capacitors, optical switching, catalytic and biomedical applications.

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Figure captions

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Table 1
Instruments used to characterize CBS and GBS NPs

Instrument	**Model**
XRD	PW 340/60 diffractometer
SEM	HITACH S-3000H
FTIR	Perkin Elmer RX - 1
UV-Vis	LAMBDA - 35
XPS	K - alpha^{TM}
PL	Varian Cary Eclipse spectrometer

Table 2
Third order nonlinear optical susceptibility values of CBS and GBS NPs

Sample	**Optical susceptibility**		
	Real part (R_e) $\chi^{(3)}$ x 10^{-6} esu	**Imaginary part (I_m) $\chi^{(3)}$ x 10^{-6} esu**	**Absolute value χ^3 x 10^{-6} esu**
CBS	5.48	2.12	5.87
GBS	6.03	2.27	6.45

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Table 3
Photodegradation efficiencies of CBS and GBS catalysts

Sample	Photodegradation efficiency (%)					
	Irradiation time (min)					
	15	**30**	**45**	**60**	**75**	**90**
CBS	9.5	20.3	37.8	52.7	68.4	78.4
GBS	19.1	36.8	52.9	69.1	79.4	89.7

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