

Soft chemical synthesis and characterization of BaWO₄ nanoparticles for photocatalytic removal of Rhodamine B present in water sample

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Abstract In recent years, the use of metal oxides as photocatalysts for degradation of organic substances has attracted the attention of the scientific community. Metal oxide nanoparticles have been studied due to their novel optical, electronic, magnetic, thermal and potential applications as catalysts, gas sensors, photo-electronic devices, etc. In this research work, we report a simple, soft chemical route for synthesizing BaWO₄ nanoparticles using cheap chemicals such as barium nitrate (precursor salt) and sodium tungstate (precipitating agent). The final product was dried at room temperature overnight and calcined at 400 °C and 800 °C for 2 h to get phase-pure product. The prepared nanoparticles (as prepared and heat-treated samples) were characterized by X-ray powder diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy, energy dispersive X-ray analysis and UV–Vis spectroscopy techniques. Photocatalytic degradation characteristics of Rhodamine B in water using BaWO₄ nanoparticles were studied and reported.

Keywords BaWO₄ nanoparticles · Soft chemical method · Characterization · Photocatalytic studies

Background

Water pollution is one of the worldwide problems nowadays and this can directly affect the health of living organisms. Because of the industrialization, effluents from most of the industries are discharged directly or indirectly into water sources without treating the harmful or dangerous compounds present in it and this may lead to water pollution. There are wide varieties of water pollutants available, which include waste chemicals, waste organic matter, presence of harmful pathogens, etc. Water pollution is a burning global problem; hence development of suitable eco-friendly treatment procedures is a mandatory requirement at present [1]. One of the most harmful pollutants present in industrial waste water is organic dyes. Organic dyes are used for various industrial applications such as paper, leather, cosmetics, drugs, electronics, plastics, textiles, etc. From among these, it was reported that the textile industry alone utilizes 80 % of the synthetic dyes for printing purpose [2]. Most of the dyes have non-biodegradable compounds [3]. Recently, researchers have developed methods for the treatment of waste water especially for the removal of dyes using techniques based on chemical, physical and biological means [4]. However, these treatment methods are not suitable for large scale due to their high cost. Therefore, alternative treatment methods, which are financially viable and green-chemical in nature, are required by the industrial sectors. Photocatalysis technology is one of the best water treatment technologies, since it is an economically viable and environment-friendly technique for the purification of waste water; it removes all kinds of organic and inorganic pollutants and contaminants present in waste water [5].

Barium tungstate (BaWO₄) is the heaviest member of the family of the alkaline earth tungstates. Like many other

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ABX₄ type compounds, BaWO₄ crystallizes at ambient conditions in the tetragonal scheelite-type structure (space group [SG]: *I41/a*, No. 88, *Z* = 4) [6]. BaWO₄ is extensively investigated because of its good electrical conductivity, magnetic and photoluminescence properties [7]. As one of the most reactive alkaline earth tungstates, BaWO₄ based materials play an important role in wide variety of technological applications as light emitting diodes [8], humidity sensors [9], optic filters [10], scintillator detectors [11], photocatalysts [12], microwave dielectrics [13], phosphors [14] and solid state lasers [15]. Recently, many studies have been reported on the preparation and characterization of metal tungstates using various preparation methods such as Czochralski process [16], precipitation method [17], hydrothermal synthesis [18], solid-state reaction [19], pulsed laser deposition method [20], electrochemical process [21], molten salt synthesis [22], polymeric precursor method [23], solvothermal synthesis [24], sonochemical route [25] and DNA-templated synthesis [26].

It was found that, Rhodamine B is a most important basic dye of the xanthene class. It is highly water soluble and is widely used as a colorant in textile industry, food stuffs and is a well-known water tracer fluorescent. It is harmful to human beings and animals, and causes irritation of the skin, eyes and respiratory tract. The carcinogenicity, reproductive and developmental toxicity, neurotoxicity and chronic toxicity of Rhodamine B toward humans and animals have been experimentally proven. Also, it was found that Rhodamine B cannot be effectively removed by biological treatment processes due to the slow kinetics reaction [27].

The first part of this research work has been focused on the synthesis of BaWO₄ nanoparticles by simple soft chemical route and systematic characterization of these materials in order to explore their structural, microstructural, elemental, chemical and surface properties. The second part has been dealt with the study of photocatalytic properties of BaWO₄ to degrade organic dye (Rhodamine B) present in water under UV-light irradiation. The obtained results are discussed and presented in this research article.

Experimental

Materials

The analytical grade chemicals such as Barium Nitrate (99.8 % purity, Merck, India), Sodium Tungstate (99.0 % purity, Merck, India), Rhodamine B (>95.0 % purity, Sigma-Aldrich, India) and Ethanol (99.0 % purity, Merck, India) were used in this study. These materials were used as

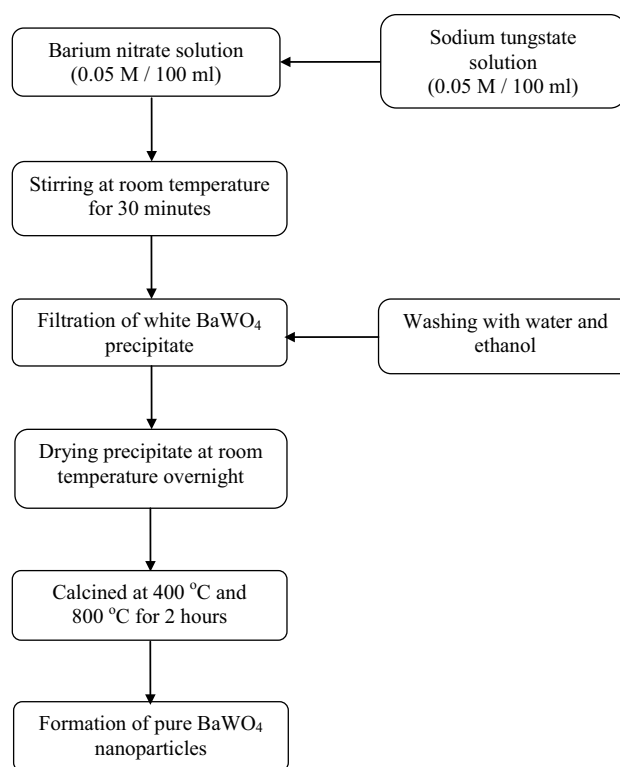
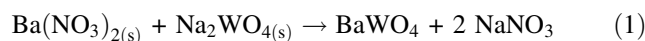


Fig. 1 Flow chart to prepare BaWO₄ nanoparticles by simple soft chemical route

received without any further purification. All reactions were carried out with deionized water.

Preparation of BaWO₄ nanoparticles

The BaWO₄ nanoparticles were by simple soft chemical route as follows: Barium nitrate (Ba(NO₃)₂) and sodium tungstate (Na₂WO₄·2H₂O) aqueous solutions were prepared with desired molar ratio. They were mixed together and stirred well for about 30 min in a magnetic stirring apparatus at room temperature. The obtained precipitate was filtered and washed thoroughly with (1:9) ethanol/distilled water mixture several times to remove the by-products. Finally, the precipitate was dried at room temperature overnight. The dried particles were calcined at 400 °C and 800 °C for 2 h each to check the phase purity of BaWO₄. The flow chart to synthesize BaWO₄ nanoparticles is indicated in Fig. 1. The main reaction which is taking place during the synthesis of BaWO₄ nanoparticles is mentioned below:



Characterization

The crystallographic properties of BaWO₄ were examined by X-ray diffraction (Shimadzu XRD6000) using Cu K α



Fig. 2 Pyrex photo reactor equipped with the UV light

($\lambda = 0.154059$ nm) radiation with a nickel filter and a power of $40 \text{ kV} \times 30 \text{ mA}$. The intensity data were collected at 25°C over a 2θ range of $10\text{--}90^\circ$ with a scan rate of $10^\circ \text{ min}^{-1}$. The FTIR spectra of the BaWO_4 were examined by Fourier transform infrared spectrometer (Shimadzu spectrophotometer) using KBr pellet technique in the range from $2,000$ to 400 cm^{-1} (spectral resolution was 4 cm^{-1} and number of scans was 20). The morphology, particle size and elemental compositions of the prepared material were studied by scanning electron microscope (SEM JEOL JSM-6610) equipped with an energy dispersive X-ray (EDAX) spectrophotometer and operated at 20 kV . Absorbance spectra of the catalyst were obtained by UV–Visible spectrophotometer (Shimadzu 1800). The samples were loaded into a quartz experimental set-up and the spectrum was recorded in the range $200\text{--}600 \text{ nm}$ using absorbance method. The photoluminescence spectral analysis was examined by spectrofluorometer (JASCO) at room temperature.

Photocatalytic experiments

The photocatalytic activity of BaWO_4 nanoparticles was investigated in an aqueous solution of Rhodamine B as per the following procedure: The typical catalytic reactions were carried out at room temperature with 50 mL of an aqueous dye solution of Rhodamine B (0.2 g/L) taken in a simple Pyrex photoreactor equipped with the 6 W-UV light emitting source as indicated in the Fig. 2. To the above dye solution, 5 mg of BaWO_4 nanoparticles (as prepared sample, calcined at 400 and 800°C) were added individually and the mixture was allowed to react for about 30 min until they reach the level of equilibrium. After the given time interval, 2 mL of the solution was withdrawn from the Pyrex photoreactor and the UV–visible absorption spectrum was taken at 554 nm as indicated in the literature

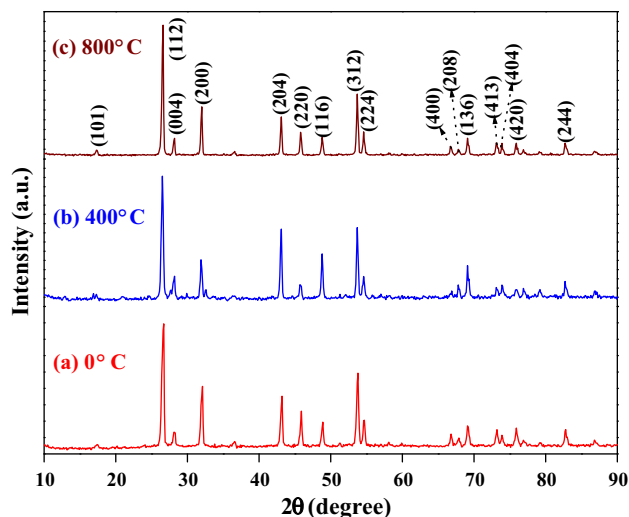


Fig. 3 XRD pattern of BaWO_4 nanoparticles (a) 0°C (as prepared), (b) calcined at 400°C and (c) calcined 800°C

[28]. The percentage of degradation of dye [29] was calculated with the following formula:

$$\% \text{ of degradation of dye} = (C_0 - C_t / C_0) \times 100 \quad (2)$$

where, C_0 is the initial absorbance of the dye solution and C_t is the absorbance at time interval, respectively.

Results and discussion

Characterization of BaWO_4 nanoparticles

X-ray diffraction

Figure 3 shows the typical XRD patterns obtained on the BaWO_4 nanoparticles (as prepared, calcined at 400 and 800°C). The XRD spectra of all the three samples were found to be uniform. The peak positions of each sample exhibit the tetragonal type structure of BaWO_4 in comparison with the reported JCPDS card No. 85-0588. Further, no other impurity peak was observed in the XRD pattern. The crystalline sizes of all the samples were calculated using Scherrer [30] formula (which is mentioned below),

$$D = 0.9\lambda / \beta \cos\theta \quad (3)$$

where, ' λ ' is the wavelength of X-ray radiation, ' β ' is the full width at half maximum (FWHM) of the peaks at the diffracting angle θ . The calculated crystalline sizes of each sample are presented in Table 1.

The theoretical [31] density (D_x) values were calculated using the formula (4),

$$D_x = (Z \times M) / (N \times a^2 \times c) \text{ g cm}^{-3} \quad (4)$$

Table 1 The crystallographic parameters of the BaWO₄ nanoparticles

Sample	Crystal structure	Unit cell lattice parameter 'a and c' (Å)	Unit cell volume (Å) ³	Theoretical density (g/cc)	Crystallite size (nm)
BaWO ₄ (JCPDS No. 85-0588)	Tetragonal body centered	a = 5.613 c = 12.720	400.81	6.383	–
As prepared sample	Tetragonal body centered	a = 5.590 c = 12.637	394.88	6.477	4.2592
Calcined at 400 °C	Tetragonal body centered	a = 5.594 c = 12.657	396.07	6.459	4.922
Calcined at 800 °C	Tetragonal body centered	a = 5.598 c = 12.687	397.58	6.434	5.1881

where, 'Z' is the number of chemical species in the unit cell, 'M' is the molecular mass of the sample (g/mol), 'N' is the Avogadro's number (6.022×10^{23}) and 'a' and 'c' are the lattice constants (cm). The crystallographic parameters obtained on BaWO₄ nanoparticles are indicated in Table 1.

Fourier transform infrared spectroscopy

Figure 4 shows the FTIR transmittance spectra obtained on BaWO₄ nanoparticles (as prepared, calcined at 400 and 800 °C) and shows intense peaks at 1,525, 1,560, 1,590, 824, 822, 629, 628, 627, 517, 474 and 438 cm⁻¹. It is noted that the vibrations at 1,525–1,590 cm⁻¹ are related to a COO stretching mode for a bidentate complex [32]. In addition, the spectrum displays a very broad absorption band from 1,000 to 400 cm⁻¹. This band is attributed to the M–O bonds, of a solid oxide network [32]. For T_d symmetry, the vibrations for the [WO₄]²⁻ tetrahedral units [33] can be calculated as per the Eq. (5).

$$T_d = A_1(\nu_1) + E(\nu_2) + F_2(\nu_3) + F_2(\nu_4) \quad (5)$$

In Eq. 9, all four vibrational modes are Raman active but only the F₂(ν₃) and F₂(ν₄) modes are IR active [34]. Therefore, a strong W–O stretching in [WO₄]²⁻ tetrahedrons was detected at 822–824 cm⁻¹. Also, a weak W–O bending was found in the range 438–629 cm⁻¹ [35]. The obtained results are in accordance with the reported data.

Scanning electron microscopy

Figure 5 shows the SEM images of BaWO₄ nanoparticles (as prepared, calcined at 400 and 800 °C), which can also allow the estimation of the average particle size distribution of samples by counting approximately 200 particles using image tool software. The SEM results demonstrated the morphology of BaWO₄ nanoparticles and this was strongly dependent on size of particles. Figure 5a shows

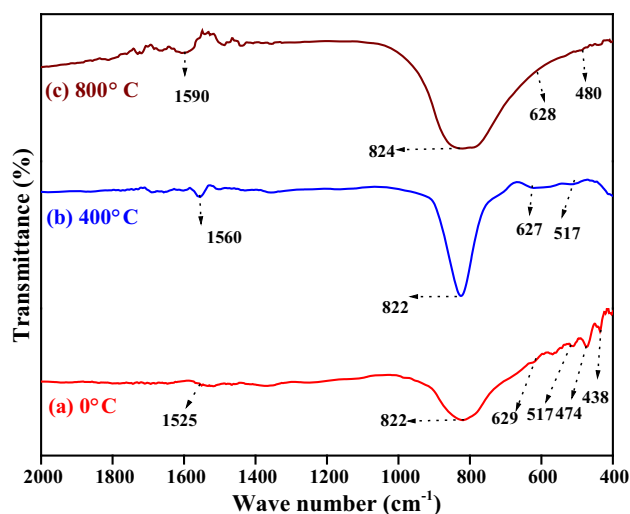


Fig. 4 FTIR transmittance spectrum of BaWO₄ nanoparticles (a) 0° C (as prepared), (b) calined at 400 °C and (c) calcined at 800 °C

the SEM photograph of as-prepared BaWO₄ nanoparticles, which have granular-like grains with sizes 700–800 nm. Figure 5b shows the SEM photograph of calcined (at 400° C) BaWO₄ nanoparticles, which contain particles with grain sizes between ~750 and 850 nm range. Figure 5c shows the SEM photograph of calcined (at 800° C) BaWO₄ nanoparticles with grain sizes between ~800 and 900 nm range. All the SEM photographs show the presence of particles with less than 500 nm also in the samples. Considerably big particles present in the sample may be due to the agglomeration of particles at high temperature treatment [36].

EDAX analysis

Figure 6 shows the EDAX spectrum of BaWO₄ nanoparticles. The presence of elements such as Ba, W and O in the

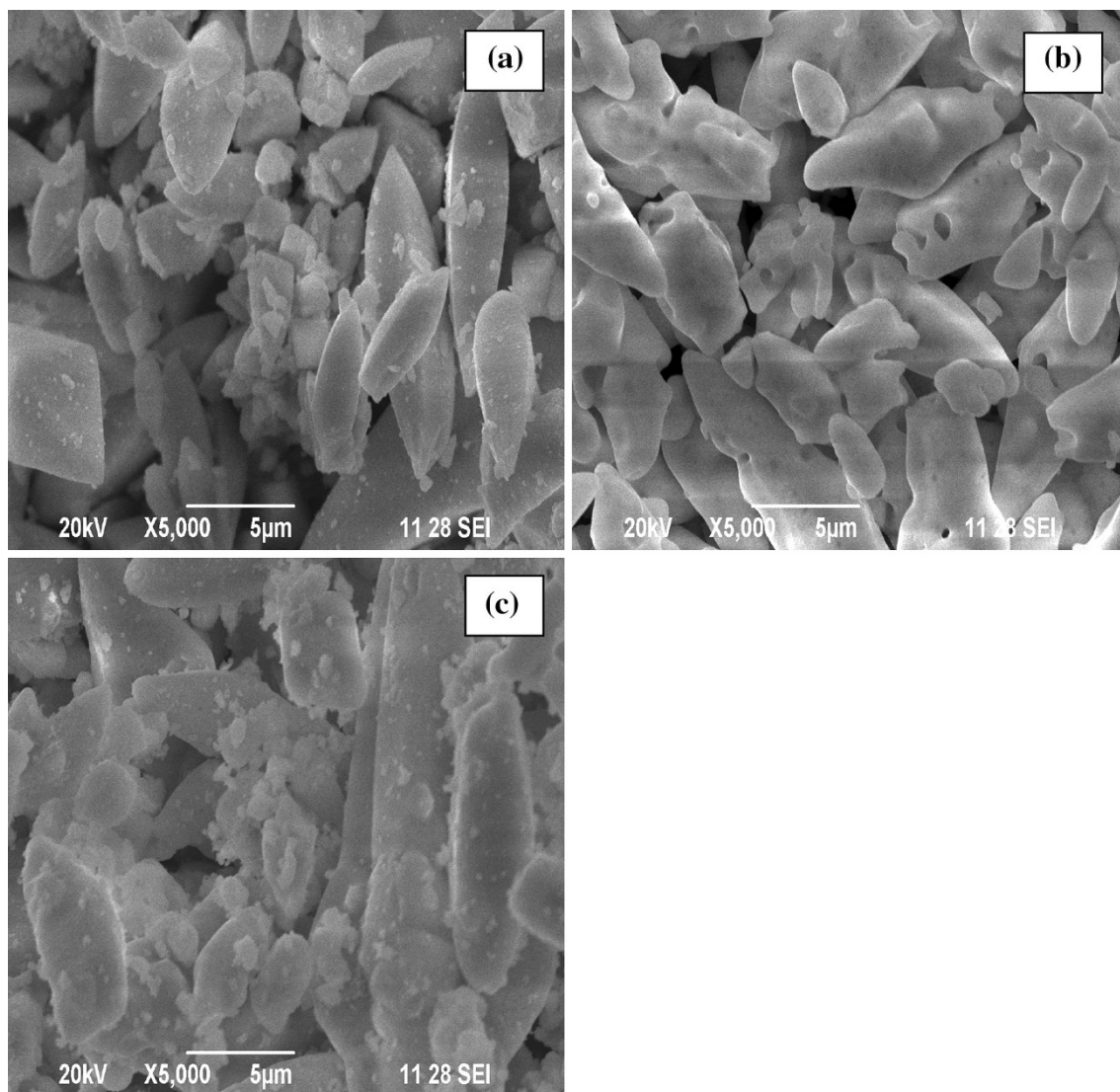


Fig. 5 SEM images of BaWO₄ nanoparticles (a) 0 °C (as prepared), (b) calcined at 400 °C and (c) calcined at 800 °C

samples is confirmed by EDAX analysis. The atomic percentages of each element are given in Table 2. These results show the appropriate quantities of Ba, W and O present in the samples.

Optical properties

Figure 7 shows the optical absorption spectrum obtained on BaWO₄ nanoparticles (as prepared, calcined at 400 and 800 °C). It was reported that absorption is a powerful, non-destructive technique to explore the optical properties of semiconducting nanoparticles [37]. The optical absorbance spectra for BaWO₄ nanoparticles (as prepared, calcined at 400 and 800 °C) appeared in the ultraviolet region: 274, 272 and 271 nm (Fig. 7a, b, c). In order to calculate the direct band gap of the nanoparticles, Tauc [38] relationship is used in this research study as indicated in Eq. (6),

$$\alpha hv = A(hv - E_g)^{1/2} \quad (6)$$

where, ' α ' is the absorption coefficient, ' A ' is a constant and $n = 1/2$ for direct band gap semiconductor. An extrapolation of the linear region of a plot of $(\alpha hv)^2$ vs. hv gives the value of the optical band gap (E_g) as shown in the inset of Fig. 8. The measured band gap was found to be 5.77, 5.82 and 5.88 eV for BaWO₄ nanoparticles, which is almost similar to the reported value of 5.78 eV [32].

Photoluminescence properties

Figure 9 shows the PL spectrum of BaWO₄ nanoparticles (as prepared, calcined at 400 and 800 °C). The photoluminescence (PL) spectra for BaWO₄ nanoparticles were studied at room temperature with the excitation wavelength of 350 nm. The excitation wavelength was fixed based on

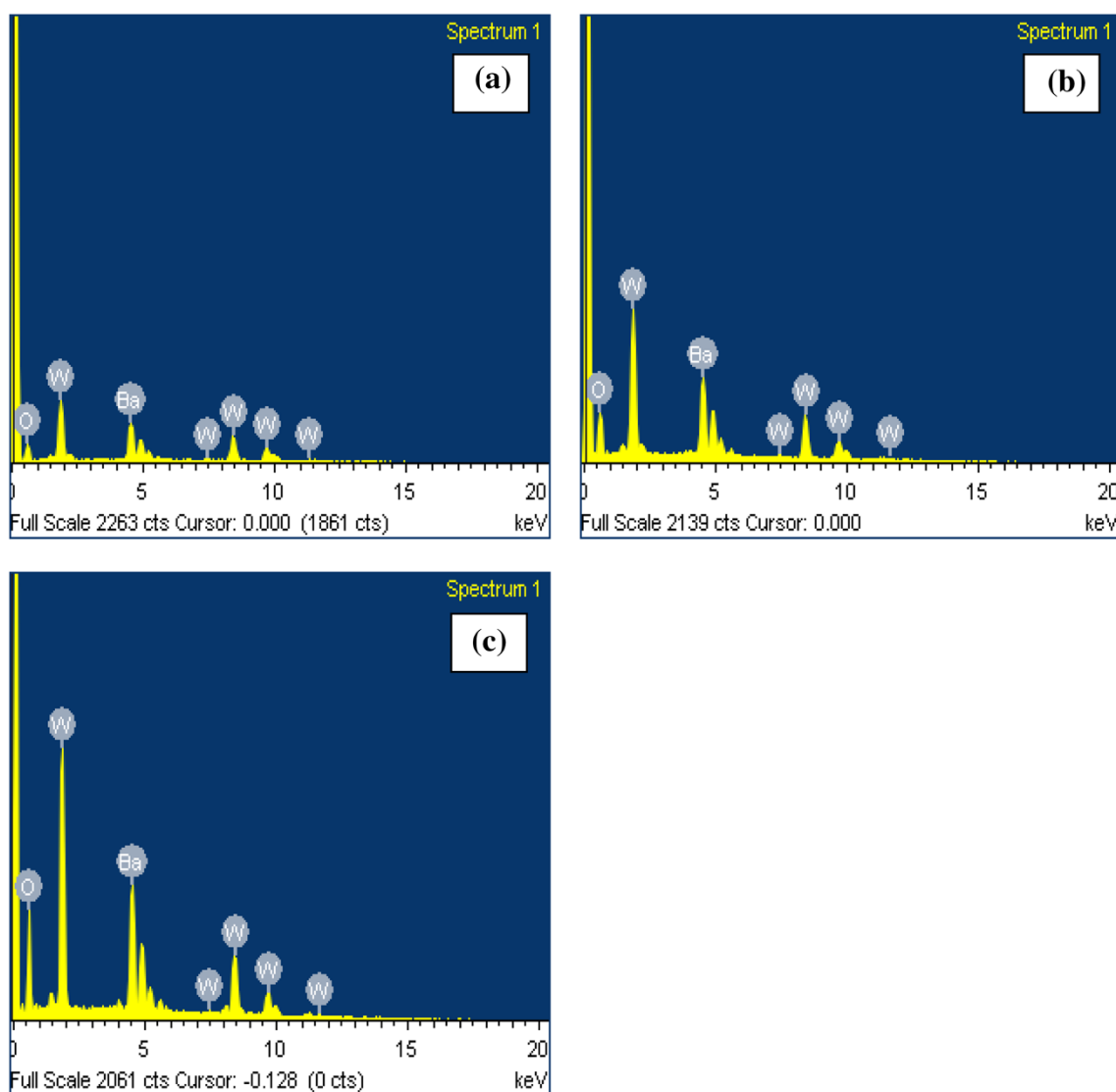


Fig. 6 EDAX spectrum of BaWO₄ nanoparticles (a) 0 °C (as prepared), (b) calcined at 400 °C and (c) calcined at 800 °C

Table 2 The atomic weight percentage elemental composition of BaWO₄ nanoparticles by EDAX analysis

Sample	Percentage of chemical composition		
	Ba	W	O
As prepared	20.22	15.16	64.62
Calcined at 400 °C	17.28	14.95	67.77
Calcined at 800 °C	16	14.67	69.34

the result obtained from the UV studies. From the data, it was found that a strong broad PL emission peak appeared at 545, 544 and 544 nm for the samples. From the reported data, the appearance of strong PL emission peak in the above range is attributable to the emission band at visible region of green emission [17] as found in the literature.

Also, the presence of broad peak is corresponding to the multilevel or multi-photon processes [39, 40]. As per the reported literature, the metal tungstates can exhibit blue PL spectra due to the charge transfer transition of the tetrahedral [WO₄]²⁻ group [41]. The emission peaks of BaWO₄ nanoparticles may be responsible for blue shift in the PL spectra which may be due to the quantum size effect of the nanoparticles [42, 43].

Photocatalytic properties

Figure 10 shows the absorption spectrum of Rhodamine B in presence of BaWO₄ nanoparticles (as prepared, calcined at 400 and 800 °C). The catalytic activity of BaWO₄ nanoparticles was investigated for the degradation of Rhodamine B present in water at room temperature using

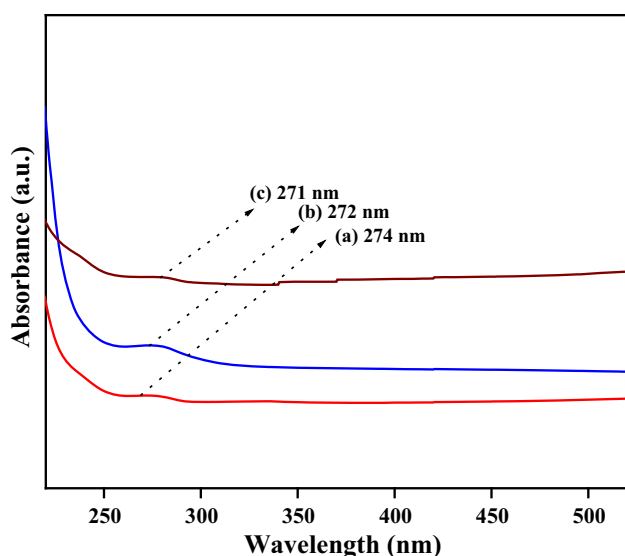


Fig. 7 Absorption spectrum of BaWO₄ nanoparticles (a) 0 °C (as prepared), (b) calcined at 400 °C and (c) calcined at 800 °C

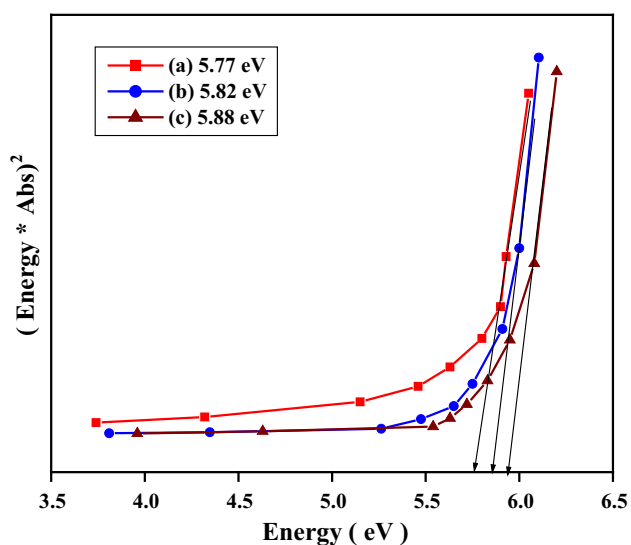


Fig. 8 Band gap spectrum of BaWO₄ nanoparticles (a) 0 °C (as prepared), (b) calcined at 400 °C and (c) calcined at 800 °C

UV–visible spectroscopy. The chemical structure of Rhodamine B is shown in Fig. 11. The absorption wavelength was maintained at 554 nm throughout the study and the percentage of degradation of Rhodamine B was carefully monitored at various time intervals such as 0, 30, 60, 90, 120, 150 and 180 min, respectively. From Fig. 10, it was found that the sample without any catalyst degraded 37 % of Rhodamine B present in water sample. However, the presence of catalysts (as prepared, calcined at 400 °C and calcined at 800 °C) degraded the Rhodamine B successfully (~95, 90 and 88 %, respectively) after three hours of

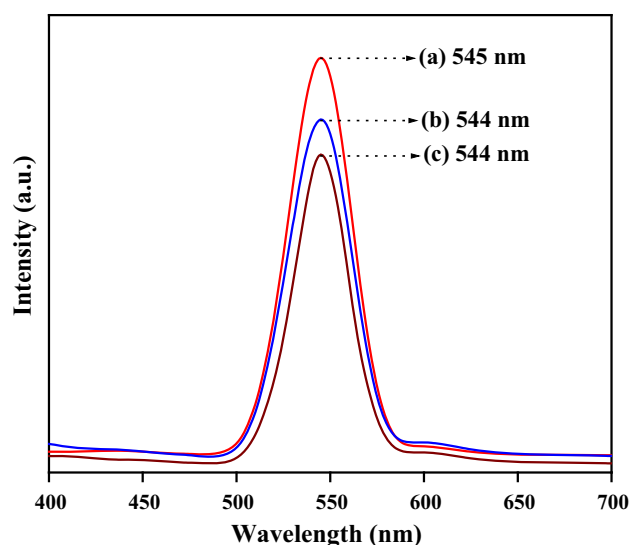


Fig. 9 PL spectrum of BaWO₄ nanoparticles (a) 0 °C (as prepared), (b) calcined at 400 °C and (c) calcined at 800 °C

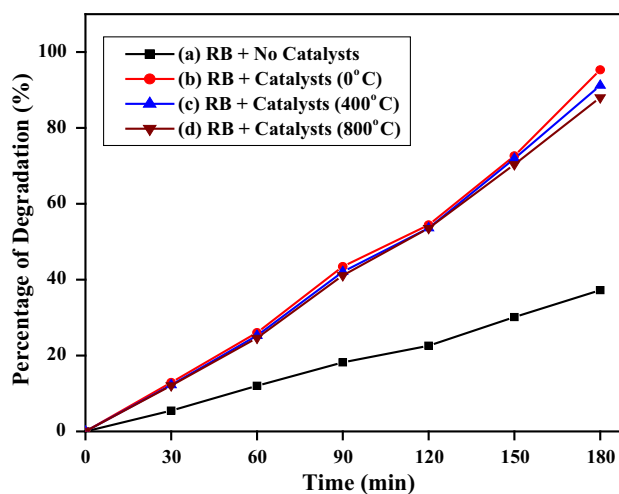


Fig. 10 Degradation spectrum of Rhodamine B in the presence of BaWO₄ nanoparticles

exposure in presence of UV light at 554 nm. This result demonstrates that as-prepared BaWO₄ sample is more efficient to degrade Rhodamine B in presence of UV light.

A plot drawn between $\ln(C/C_0)$ versus Time is presented in Fig. 12 and it resembles the first-order kinetics curve as reported in the literature [44]. The degradation reactions of all BaWO₄ nanoparticles with Rhodamine B dye exhibited pseudo first-order kinetics model with respect to the degradation time as indicated in the linear Eq. (7).

$$\ln(C/C_0) = -kt \quad (7)$$

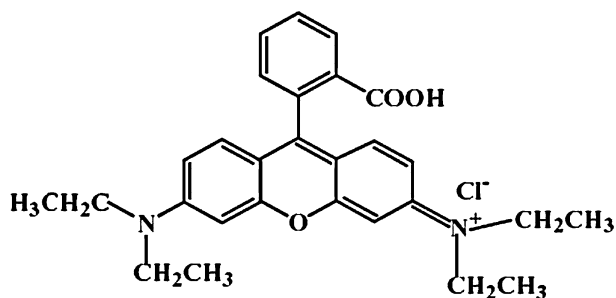


Fig. 11 Structure of Rhodamine B dye

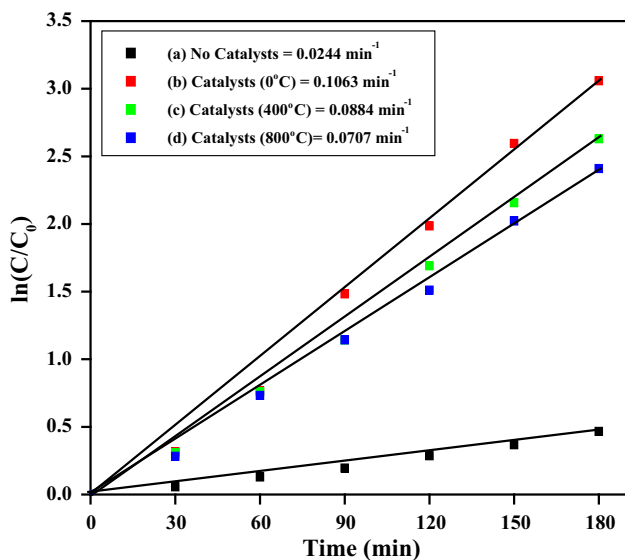
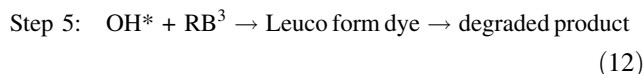
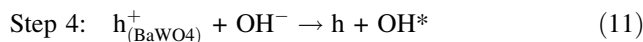
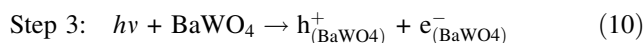
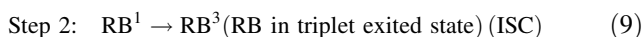
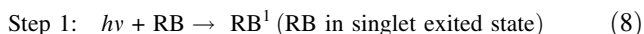


Fig. 12 First order kinetic plot of Rhodamine B dye using BaWO₄ nanoparticles

where, ' C_0 ' is the initial concentration of dye and ' C ' is the concentration at time ' t ', ' k ' is the reaction constant of the first-order reaction. The slope of the linear line gives the first-order rate constant. The rate constant values were found to be 0.0244 min^{-1} (absence of catalysts), 0.10629 min^{-1} (as prepared sample BaWO₄), 0.0884 min^{-1} (sample heat-treated at $400 \text{ }^\circ\text{C}$) and 0.0707 min^{-1} (sample heat-treated at $800 \text{ }^\circ\text{C}$). From the result, it was found that that the catalytic activity of as-prepared BaWO₄ nanoparticles is greater than that of samples heat treated at 400 and $800 \text{ }^\circ\text{C}$, respectively.

The photocatalytic mechanism suggested for the degradation of Rhodamine B dye present in water sample with BaWO₄ nanoparticles in presence of UV light is indicated below [28, 45]:



From the mechanism, it was found that reactions can be split into fragments.

In the first step, the Rhodamine B dye can absorb photons from light source and may be excited to singlet state. By losing some energy through inter-system crossing, the Rhodamine B dye can be converted into triplet state. On the other hand, BaWO₄ absorbs photon, and one electron from its conduction band is transferred to valence band, generating a hole. This hole may be responsible for bleaching of Rhodamine B dye. This hole may abstract an electron from OH⁻ ion and free radical OH* is generated. This free radical abstracts an electron from conjugated and weaker site of the Rhodamine B dye. As a result Rhodamine B dye is broken down into fragments. Scavenger study has proved the participation of free radical in the reaction. Finally, various degraded products such as NO₂, CO₂, H₂O, etc. may take place in the process.

Conclusion

The BaWO₄ nanoparticles were prepared by the simple, low-temperature route; furthermore, they were characterized by the XRD, FTIR, SEM, EDAX and UV-visible spectroscopy techniques. The XRD patterns show that the prepared samples are of tetragonal-type structure. No impurity phase has been observed in XRD. FTIR spectra confirmed the presence of M–O bond in the product. The SEM studies confirmed the presence of granular-like grains in the samples. The EDAX data confirmed the presence of corresponding elements in the samples. The band gap data obtained on the sample based on absorbance spectra studies are similar to the reported data. It was found that among the samples studied, the as-prepared BaWO₄ is more effective in degrading the Rhodamine B dye present in the water sample in presence of UV light at the wave length of 554 nm at normal room temperature. Hence, BaWO₄ nanoparticles are suggested as a potential candidate to remove organic pollutants present in water by simple photocatalysis at room temperature.

Author contribution ASN has guided MMJS to carry out this research study. MMJS has carried out the experiments and he has written the raw manuscript. ASN has edited and refined the manuscript towards publication. Both authors have read and approved the final manuscript.



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Conflict of interest The authors declare that they have no conflict of interest.

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