Ultrasonics Sonochemistry 20 (2013) 906–913

Contents lists available at SciVerse ScienceDirect

Ultrasonics Sonochemistry

journal homepage: www.elsevier.com/locate/ultson

Production of cerium zinc molybdate nano pigment by innovative ultrasound assisted approach

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ARTICLE INFO

Article history:
Received 20 August 2012
Received in revised form 25 October 2012
Accepted 8 November 2012
Available online 24 November 2012

Keywords:
Cerium zinc molybdate
Acoustic cavitation (ultrasound)
Nucleation
Precipitation
Nanostructures

ABSTRACT

Ultrasound assisted synthesis of yellow rare earth cerium zinc molybdate anticorrosion nanopigment is presented. This new class of pigment is eco-friendly alternatives to lead, cadmium and chromium pigment as these pigments contains carcinogenic species like Cr^{6+} which is responsible for human disease. The synthesis of nanosized cerium zinc molybdate was carried out using cerium nitrate, sodium zinc molybdate as a precursor materials by conventional and ultrasound assisted chemical precipitation method without addition of emulsification agent. XRD, FTIR and elemental analysis confirm the formation of cerium zinc molybdate nanoparticles. The conductivity results indicate that conventional synthesis takes longer time, while in sonochemical technique (US), reaction completes within short period of time. Improved solute transfer rate, rapid nucleation, and formation of large number of nuclei are attributed to presence of cavitation. Saturation of the Ce^{3+} ions reaches earlier in case of sonochemical technique which restricts the growth of particles hence smaller size is obtained. The crystallite size of cerium zinc molybdate was found to be 27 nm from XRD analysis.

1. Introduction

Inorganic nanopigments are extensively used in a variety of applications such as paints, plastics, coatings, and glasses. The majority of inorganic pigments used in the anticorrosion application are derived from toxic metals such as cadmium, lead, chromium or cobalt [1]. Chromate surface treatments and chromate-containing epoxy primers are often used for corrosion control of aluminum alloy. It is also important to note that chromium provokes human disease and its replacement with other friendly protection methods is urgently required [2,3]. Therefore, it is necessary to explore environmental friendly materials which are low cost substitute for toxic pigments [4]. Rare earth pigments such as lanthanum oxide (La_2O_3), praseodymium dioxide (PrO_2) and cerium oxide gives red tinge to the smooth ceramic surface along with excellent heat and chemical-resistant properties and these represents potential new class of eco friendly inorganic pigments [5]. Cerium and molybdate has been used as a corrosion inhibitive components to a non-chromate protective solution useful for coating iron and iron alloys, particularly steel [6]. Cerium and molybdate pigments contains salts of rare earth elements like cerium and molybdate which acts as passivating agent without liberation of harmful species hence coating makes it more environmental friendly. Cerium molybdate is non-toxic pigment which shows excellent anticorrosion properties hence, it has been used along with number of coating binders for protection of engineering metal structures [7]. Sanyal [8] have used cerium molybdate as a core material in cerium molybdate containers loaded with 2-mercaptobenzo-thiazole. Liu et al. [9] have carried out the synthesis and evaluation of conversion coatings containing molybdate prepared by direct addition of sodium nitrate or sodium per sulfate as oxidizing agent into the coating formulation [9].

Further the photocatalytic activity of different morphology of molybdate based compound was also studied by the some of the researchers [10,11]. Dong et al. [10] have successfully synthesized cerium molybdate hierarchical architectures (such as the flower-like, micro sphere, and bundle like structure) via a facile route with the assistance of amino acid. An investigation of photocatalytic performances of cerium molybdate has been reported using different dyes, such as Cationic red X-GTL, Congo red, Methylene blue, Acid blue 80, and Methyl orange, as the model. The reported results show that cerium molybdate hierarchical architectures exhibit remarkably high efficiency to photo catalytic decomposition of organic compounds such as Congo red under visible light irradiation. Zhou et al. [11] have also successfully prepared visible-light-induced photocatalysts Bi_2MO_6 (M = W, Mo) nanocrystals via an ultrasonic-assisted method. It has been reported that the laminar structured Bi_2MO_6 nanoplates with size of 100 nm shows photocatalytic activities 4–6 times higher than that of the products prepared by traditional solid-state reaction with higher size. It has

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http://dx.doi.org/10.1016/j.ultsonch.2012.11.008

been reported that ultrasonic irradiation played an important role in the formation of the nanomaterials with a smaller crystal size and larger surface area, which is beneficial to their photocatalytic activities.

The sonochemical method has been proved to be a useful method to obtain nanosize pigment with narrow distribution [12,13]. The physical and chemical effects of ultrasound irradiation arise from acoustic cavitations, in other words, the formation, growth and implosive collapse of bubbles in a liquid medium, which results in an instantaneously high temperature and pressure pulse [14,15] and are useful for synthesis of smaller size nanoparticles. Cavitation can be useful for the formation of stable dispersion of the nanoparticles in the coatings. Ultrasonic irradiations are also prevents the agglomeration of the particles, which improves the dispersion ability of the coatings formulation. Ultrasound assisted precipitation method has been proved to be a useful to obtain novel nano sized oxides particles [16–18]. Extreme pressure (>500 atm) and temperature (>10000 K) with cooling rate of $>10^{10}$ K/s conditions caused due to ultrasonic irradiation leading to intense micromixing improves solute transfer and nucleation rate in aqueous suspension which lead to formation of nanometer size particles [16].

The aim of the present study to synthesize the anticorrosive cerium zinc molybdate using sonochemical and conventional method involving the reaction of zinc oxide, cerium nitrate, sodium molybdate and nitric acid. The effect of ultrasonic irradiation on the morphologies of the cerium zinc molybdate nanoparticles is also discussed. The effect of ultrasound on duration of reaction and final particles size distribution is discussed.

2. Materials and methods

2.1. Materials

Zinc oxide (Analytical Grade, 99%), sodium molybdate dihydrate (Analytical Grade, 99%) and nitric acid were procured from S.D. Fine chemicals Ltd., Mumbai and used without further purification for preparation of sodium zinc molybdate. Cerium nitrate hexahydrate (Analytical Grade, 99%) was purchased from Sigma–Aldrich Chemical Co., Mumbai used as received for the preparation of cerium zinc molybdate nanoparticles. Deionized water (DI water) with conductivity of <0.2 μS/cm has been used throughout the experimentation. All other chemicals were used without further purification.

2.2. Experimental set up

Experimental set up consist with ultrasound generator, heater and magnetic needle. Sonochemical synthesis was carried out in reactor 300 mL capacity fitted with ultrasound horn. The schematic of the set up is given in Fig. 1. The specification and details of the set up, processing parameters used during the experiments are as follows: ultrasonic processor: UP200S (Make Hielscher Ultrasonics GmbH Germany), working frequency: 24 kHz, nominal output power: 200 W, diameter of stainless steel tip of horn: 13 mm. Further the ultrasonic intensity was calculated by using the Eq. (1) reported below and it is 67.08 W/cm^2 in the case of ultrasound assisted synthesis of cerium zinc molybdate at 40 °C.

$$\text{Ultrasonic intensity} = \text{Power dissipated}/\text{Cross-sectional area of probe} \quad (1)$$

2.3. Synthesis of cerium zinc molybdate nanoparticles by conventional method

- *Synthesis of sodium zinc molybdate nanoparticles by conventional method:* Firstly, sodium zinc molybdate nanoparticles were synthesized by reacting zinc oxide aqueous solution (0.2 M) and sodium molybdate dihydrate aqueous solution (0.2 M) under constant agitation (800 rpm) and continuous heating at 80 ± 2 °C dilute aqueous solution of nitric acid (0.4 M) was prepared in 200 mL water and added dropwise during synthesis of sodium zinc molybdate. The dropwise addition was continued for 2 h 20 min under constant agitation. The reaction was allowed to proceed up to formation of white colloidal suspension. Finally, precipitate was filtered and washed 2–3 times with DI water. The obtained product was dried in an oven at 100 °C. Further, prepared sodium zinc molybdate was used for synthesis of cerium zinc molybdate.
- *Synthesis of cerium zinc molybdate nanoparticles by conventional method:* $Ce_2Zn_3(MoO_4)_6$ nanoparticles were synthesized by reacting aqueous solution of cerium nitrate hexahydrate (0.016 M) with 0.025 M solution of sodium zinc molybdate in 200 mL water under constant agitation (800 rpm) at 80 °C. The aqueous clear solutions turned yellowish white initially, but at the end of reaction (after 2 h 20 min) the reaction mass turns into light yellow colloidal suspension. The suspension was treated with hot DI water 2–3 times to dissolve the impurities such as $NaNO_3$. Separation of the final product (yellow precipitate) was carried out using centrifuge and then final product was dried in an oven at 80 °C.

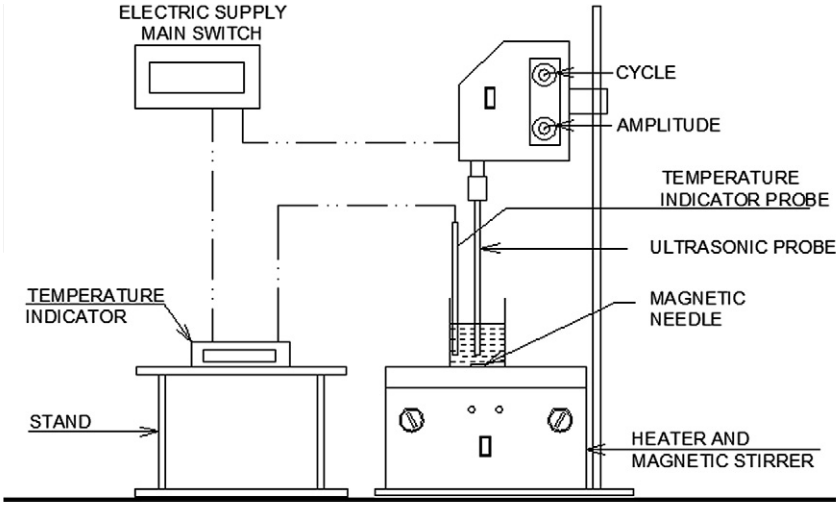

Fig. 1. Schematic presentation of sonochemical reactor (experimental setup).

Both conventional and ultrasound assisted synthesis of synthesis of sodium zinc molybdate nanoparticles as well as for cerium zinc molybdate were carried out by drowise addition of nitric acid solution. To control rate of reaction and hence restrict the growth of the particles, the dropwise addition was preferred. In overall during synthesis of sodium zinc molybdate nanoparticles by conventional method, the progress of the reaction was monitored by measuring the concentration of nitric acid which was used as a one of the reactant and added dropwise. It was found that after 2 h and 20 min, there was no consumption of nitric acid at 80 °C indicating the completion of the reaction and hence the time selected was 2 h and 20 min. Also if stoichiometric amount of nitric acid solution was added initially then precipitation of sodium zinc molybdate on the surface of zinc oxide particles and resulting into inferior quality sodium zinc molybdate [19]. This problem is resolved by dropwise addition of nitric acid during synthesis of sodium zinc molybdate. Further during synthesis of cerium zinc molybdate nanoparticles by conventional method at 80 °C sodium zinc molybdate and cerium nitrate was used as a precursors. It is observed that at the end of around 2 h and 20 min the suspension gets turned to light yellow color which an indication of formation of cerium zinc molybdate.

2.4. Synthesis ofcerium zinc molybdate nanoparticles by sonochemical method

- *Synthesis of sodium zinc molybdate nanoparticles by sonochemical technique:* Sodium zinc molybdate nanoparticles was synthesized by chemical reaction between zinc oxide and sodium molybdate dihydrate as per the procedure reported in Section 2.3 under ultrasonication at 40 ± 2 °C and also the ultrasound assisted synthesis was carried out at different temperature. A stoichiometric amount of nitric acid was (as reported in Section 2.3) added dropwise during this synthesis of sodium zinc molybdate with the aid of ultrasonic irradiation. Ultrasonic horn with 55% amplitude and 0.5 cycles (power discharge 0.5 s, pause 0.5 s) was used during sodium zinc molybdate synthesis. The reaction completes within 1 h, the aqueous clear solution converts into white colloidal suspension. Finally, obtained white precipitate was filtered, washed 2–3 times with DI water and dried in an oven at 100 °C. Further, prepared sodium zinc molybdate was used for synthesis of cerium zinc molybdate.
- *Synthesis of cerium zinc molybdate nanoparticles by sonochemical method*: Further, $Ce_2Zn_3(MoO_4)_6$ nanoparticles were synthesized by reacting sodium zinc molybdate with cerium nitrate hexahydrate aqueous solution, which was operated under ultrasonication. The reaction was allowed to proceed for 40 min under ultrasonication 40 ± 2 °C and also the ultrasound assisted synthesis was carried out at different temperature to study the effect of temperature on the particle size. Initially, the clear solution was turned yellowish white but as the reaction proceeds, it converts into light yellow colloidal suspension. The rest of the procedure was the same as described in Section 2.3.

2.5. Characterization

XRD diffraction patterns of sodium zinc molybdate and cerium zinc molybdate nanoparticles were recorded by using powder X-ray diffractometer (Philips PW, 1800). Transmission Electron Microscopy analysis (TEM) of the samples was carried out using a CM200, PHILIPS Microscopy (20–200 kV, Resolution 2.4 A° and magnification 1,000,000X). Elemental analysis of cerium zinc molybdate was carried out by using Atomic absorption spectroscopy (Perkin–Elmer, Model 31). UV absorbance of cerium zinc molybdate was measured using UV–vis spectrophotometer (SHIMADZU 160A model). FTIR analysis of samples were carried out (SHIMADZU 8400S) in the region of 4000–500 cm^{-1}. The particle size distribution measurements were carried out by Malvern Zetasizer Instrument (Malvern Instruments, Malvern, UK). Thermogravimetric (TG YRIS, Diamond) and differential thermal analysis (DTA) (TG/DTA, Perkin Elmer Technology, Waltham, USA) were operated with the calefactive velocity of 15 °C/min in nitrogen environment in the heating range from room temperature up to 700 °C, to follow the physicochemical changes of sample during calcinations. The ultrasound probe of 14 mm diameter was used for ultrasound generation. Experiments were carried out with and without ultrasound and the results were compared.

3. Results and discussion

The reaction mechanism for formation of cerium zinc molybdate nanoparticles is reported in reactions i, ii, iii. Due to ultrasonic irradiation and strong alkaline medium Na^+ ions gets released from sodium zinc molybdate nanoparticles during synthesis of cerium zinc molybdate. At the same time cerium nitrate gets dissociated in Ce^{3+} and NO_3- ions and free Na^+ ions gets combined with NO_3- ions to form water soluble $NaNO_3$ product. At the same time Ce^{3+} ions gets combined with Zn^{2+} and $(MoO_4)^{2-}$ ions to form cerium zinc molybdate nanoparticles. The rate of transfer of these ions gets significantly enhanced due to ultrasonic irradiation which results into reduction in reaction time significantly in case of sonochemical method compared to conventional mechanical mixing.

$$3Na_2Zn(MoO_4)_2 + H_2O \rightarrow 6Na^+ + 3Zn^{2+} + 6(MoO_4)^{2\,-} \tag{i}$$

$$2Ce(NO_3)_3 + H_2O \rightarrow 2Ce^{3+} + 6(NO_3)^- \tag{ii}$$

The overall reaction is given as follows:

$$6Na^+ + 3Zn^{2+} + 6(MoO_4)^{2-} + 2Ce^{3+} + 6(NO_3)^- \rightarrow Ce_2Zn_3(MoO_4)_6 + 6Na(NO_3)_3 \tag{iii}$$

The molecular structure of cerium zinc molybdate nanoparticles synthesized is presented in Fig. 2.

3.1. Investigation of reaction time, conductivity and molecular structure of cerium zinc molybdate nanoparticles

The growth of the primary particles is affected by residence time of particle in the reactor. Higher the time of reaction and growth period, the particle size will be larger. In conventional synthesis of $Ce_2Zn_3(MoO_4)_6$ nanoparticles, reaction was completed within 2 h and 20 min, while sonochemical reaction completed within 40 min. The residence time distribution (RTD) decides opportunities available for contact between nanoparticles. The more contact opportunities leads to collision and corresponding agglomeration/aggregation. Thus the profound RTD difference between ultrasonic processing and conventional method is one addi-

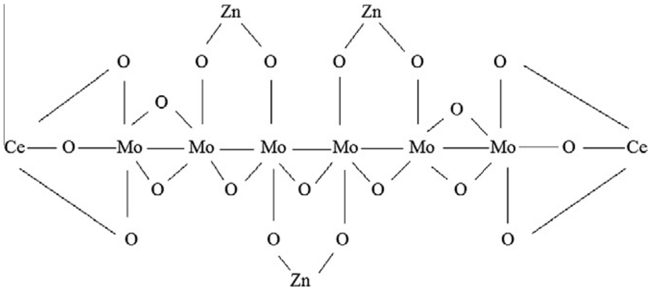

Fig. 2. Molecular structure of cerium zinc molybdate (cerium zinc molybdate).

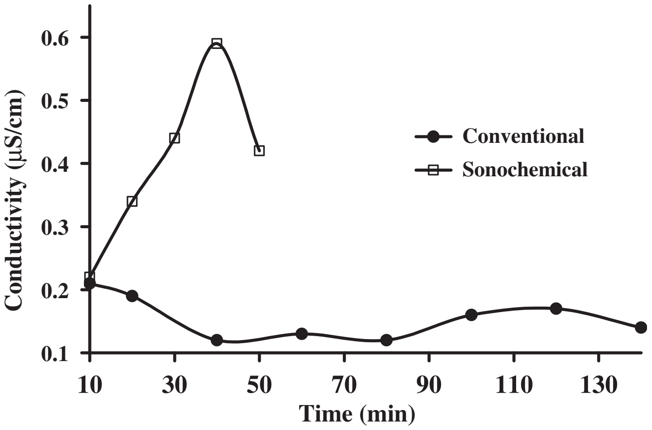

Fig. 3. Thermal conductivity of the conventionally (NUS) and sonochemically (US) synthesized $Ce_2Zn_3(MoO_4)_6$ nanoparticles at 80 °C.

tional reason for offer of finer particle size in ultrasound based synthesis. In addition, ultrasound offers intense micro mixing and faster nucleation rate. It is also found that sonochemical technique significantly affects the product yield of nanoparticle formation. The percentage yield was calculated after removal of unreacted components and water soluble by products from synthesized $Ce_2Zn_3(MoO_4)_6$ material. Also the percentage yield of the reaction was estimated on the basis of initial weight of the raw materials taken and final weight of product obtained after the complete drying. The highest percentage yield was observed during sonochemically synthesized cerium zinc molybdate nanoparticles (66.42 ± 1.5%) at the end of 40 min. While conventional synthesize procedure shown product yield near to 44.45 ± 1.5% at the end of 2 h 20 min. This reduction in reaction time and higher% yield is attributed to the rapid micro mixing there by fast mass transfer rate of solutes to form $Ce_2Zn_3(MoO_4)_6$ nanoparticles [16].

The evidence of higher yield, formation of large number of nuclei and reaching the super saturation of the reaction can be observed from the change in the conductivity against of time data as reported in Fig. 3. The observed conductivity during ultrasound assisted synthesis of cerium zinc molybdate increases initially due to release of Na^+ and MoO_4^- ions efficiently in a solution, while it is found decreased in conventional method due to less realease of these ions and resulting into decrease in the % yield in case of conventional method compared ultrasound assisted method.

3.2. Elemental and FTIR analysis of cerium zinc molybdate nanoparticles

The elemental analysis of product confirms the formation of cerium zinc molybdate by sonochemical precipitation method is reported in Table 1. It is found that the percentage of elements (Zn, Ce and Mo) presents in the sonochemically as well as conventionally synthesized cerium zinc molybdate compound is approximately similar to the theoretical values. Theoretical values of the elemental analysis are based on the molecular formula [20,21] reported in the reaction (iii) in the earlier section. The slight deviation in the experimental results compared to that of theoretical is due to the presence of small amount of impurities in the products.

Table 1
Elemental analysis for $Ce_2Zn_3(MoO_4)_6$ nanoparticles prepared by sonochemical method.

Sr. no.	Elements	Theoretical (%)	Experimental (%)	
			Conventional	Ultrasound
1.	Cerium	19.51	22.34	21.48
2.	Zinc	13.66	16.02	14.72
3.	Molybdenum	66.83	60.22	62.04

FTIR spectrum of cerium zinc molybdate prepared by sonochemical and conventional method is depicted in Fig. 4. In case of sonochemically synthesized cerium zinc molybdate nanoparticles, the prominent characteristic peak at 410, 727 and 833 cm^{-1} are attributed to molybdate ion and $Ce(OH)^{2+}$ [7,22]. Also the O–H stretching vibrations are depicted in region 2800–3300 cm^{-1}. The very weak characteristic peaks at 1633 and 3564 cm^{-1} is assigned to O–H stretching vibration of water molecules, due to presence of moisture in the sample. FT-IR spectra for the samples also show characteristic peaks at 1155 cm^{-1} corresponds to M–O–H bending mode and at 902 cm^{-1} corresponds to molybdate ion. Overlapping of the bands of molybdate ion and $Ce(OH)^{2+}$ in the regions of 400–800 cm^{-1} is observed which is shown in Fig. 4. Slight shift of characteristic peaks was observed in case conventionally synthesized cerium zinc molybdate nanoparticles compare to sonochemically synthesized cerium zinc molybdate nanoparticles. The shift in the characteristic peaks is attributed to the change in the phase of cerium zinc molybdate. In sonochemical synthesis of cerium zinc molybdate, cavitations generated by ultrasound can accelerate solid particles to high velocities leading to interparticle collisions and the energy generated during collision can induce the crystallization of the amorphous particles, which is responsible for the further crystallization process. However in case of conventional method of synthesis such type of intense energy is not available therefore formation of amorphous particles takes place which leads to shift in the characteristics peaks [11]. Also intense peaks were observed in FTIR spectrum of sonochemically prepared cerium zinc molybdate nanoparticles indicating strong bonding in the cerium, zinc and molybdate ions due to ultrasonic irradiation.

3.3. XRD analysis of cerium zinc molybdate nanoparticles

Fig. 5 depicts the XRD patterns of the cerium zinc molybdate nanoparticles prepared by sonochemical and conventional precipitation method. The diffraction peaks at 2θ value of 26.2, 34.3, 46.4, 47.6, 58.3 and 75.1° are corresponds to the planes (1 1 2), (2 0 0), (1 1 5), (2 0 4), (3 1 2) and (3 1 6) [4,9,20]. The diffraction peak at 26.2° represents the formation of cerium zinc molybdate nanoparticles, whereas peaks at 34.3 and 46.4° depict the formation of cerium molybdate nanoparticles [4]. The less intense peaks of cerium molybdate were observed in the case of sonochemically synthesized

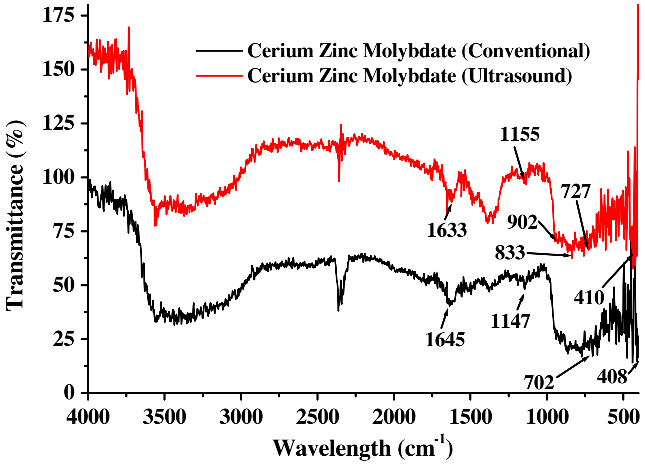

Fig. 4. FTIR pattern of the (A) conventionally (NUS) and (B) sonochemically (US) synthesized $Ce_2Zn_3(MoO_4)_6$ nanoparticles.

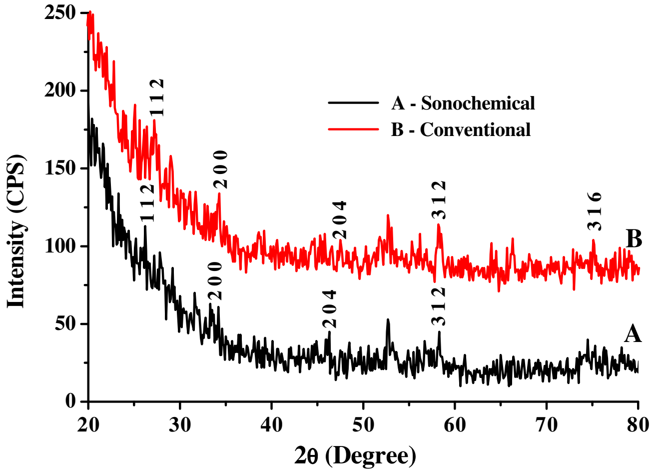

Fig. 5. XRD pattern of the (A) conventionally (NUS) and (B) sonochemically (US) synthesized $Ce_2Zn_3(MoO_4)_6$ nanoparticles.

cerium zinc molybdate nanoparticles compared to conventional method. Formation of cerium zinc molybdate was accomplished with the replacement of sodium from $Na_2Zn(MoO_4)_2$ by cerium ion which is generated through dissociation of $Ce(NO_3)_3$. Also during this chemical reaction molybdate ion can gets freed from $Na_2Zn(MoO_4)_2$ and combine with Ce to form cerium molybdate which is supported by XRD patterns. However this quantity is very small and is confirmed from elemental analysis. Further sonochemical synthesis of cerium zinc molybdate nanoparticles confirms the crystalline nature which is indicated by the intense peaks. It is also observed that there are many other peaks presents in the XRD pattern of conventionally synthesized cerium zinc molybdate nanoparticles. This might be due to the impurities such as cerium molybdate and traces of sodium nitrate present in the product.

The crystallite size of sonochemically synthesized cerium zinc molybdate nanoparticle is 27 nm at $2\theta = 26.2^\circ$ which was estimated by Debye Scherrer's formula, which has been reported below in Eq. (2)

$$X_d = \frac{k\lambda}{\beta\cos\theta} \qquad (2)$$

where $k = 0.9$, β = full-width at half-maximum height (FWHM) and θ is glancing angle of X rays with the sample holder. CuKα angel $\lambda = 1.5405$ Å radiation was used to obtain XRD patterns. Further due to uncalcined state of cerium zinc molybdate some peaks of ZnO and $NaNO_3$ is observed even after number of hot water washing cycles.

3.4. TEM and PSD analysis of cerium zinc molybdate nanoparticles

The TEM images of cerium zinc molybdate nanoparticles prepared by sonochemical and conventional method is depicted in Fig. 6. The TEM image of sonochemically prepared cerium zinc molybdate nanoparticles is reported in Fig. 6(A). It is found that the particle size of cerium zinc molybdate nanoparticles prepared by ultrasound assisted method is around 25 nm. The observed shape of the cerium zinc molybdate nanoparticles is distorted spherical. Further the particle size distribution shows narrow distribution without significant agglomeration. The particle size is controlled by smaller induction period and better control of the growth rate of crystal because of the presence of cavitation during chemical precipitation method [23]. Fig. 6(B) depicts the TEM image of conventionally prepared cerium zinc molybdate nanoparticles. The observed morphology depicts the formation of cerium zinc molybdate nanoparticles of size in the range 50–150 nm with broader size distribution. This is attributed to larger induction period for the nucleation of cerium zinc molybdate nanoparticles which leads to uncontrolled growth of cerium zinc molybdate nanoparticles in case of conventional method. Further agglomeration plays important role for increment in the size of cerium zinc molybdate nanoparticles in conventional method compared to ultrasound assisted method.

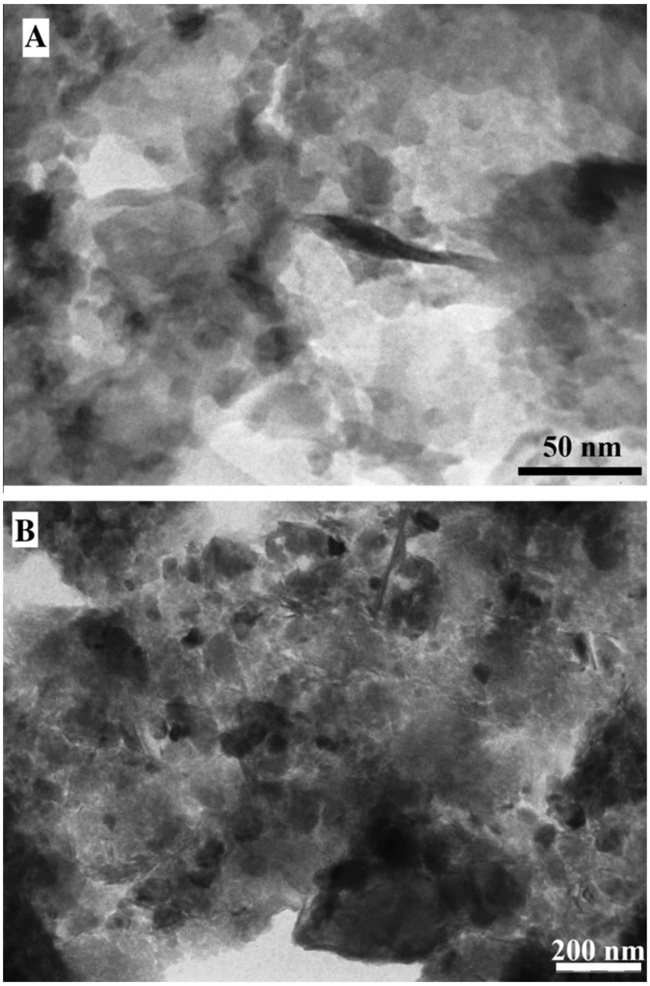

Fig. 6. TEM Images of (A) sonochemically (US) and (B) conventionally (NUS) synthesized $Ce_2Zn_3(MoO_4)_6$ nanoparticles.

The particle size distribution of sonochemically and conventionally synthesized cerium zinc molybdate nanoparticles is reported in Fig. 7. The range of the particle size of cerium zinc molybdate nanoparticles (Fig. 7A) found is 20–30 nm in case of sonochemical synthesis, whereas it is 100–200 nm in case of conventional method (Fig. 7B) and also the distribution showed only one narrow peak. The average particles size of cerium zinc molybdate particles observed is 26 nm in case of sonochemical method whereas it is 131 nm for conventional method. The particles were formed with a fairly narrow size distribution and uniform shape could be observed in both the cases. The significant reduction in the particle size of cerium zinc molybdate nanoparticles is attributed to the drastically enhanced micromixing, improved solute transfer rate, rapid nucleation, and formation of large number of nuclei due to physical effects of the ultrasonic irradiation. The probable justification for this reduction in the particle size is also the fast kinetics of the ultrasound assisted reaction, which does not, provides enough time for growth of particle leads to reduction in the particle size. Also particles size increases with reaction time. As more reaction time was required in the case of cerium zinc

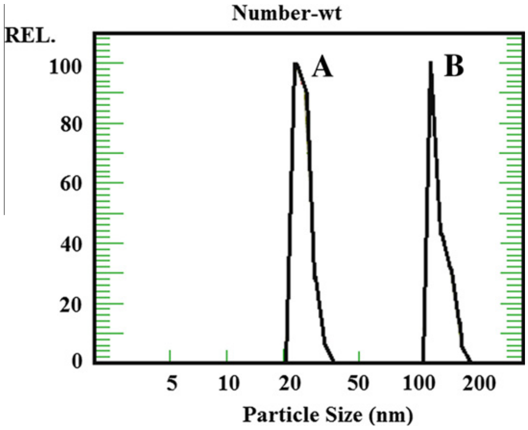

Fig. 7. Particle size distribution of cerium zinc molybdate nanoparticles prepared by (A) sonochemical method at 40 °C and (B) conventional method at 80 °C.

molybdate nanoparticles prepared by conventional method, the particle size observed is larger.

Further the effect of temperature on average particle size is depicted in Fig. 8. The largest average particle size (174.9 nm) is found in case ultrasound method at 80 °C temperature. The average particle size of cerium zinc molybdate nanoparticles is found to be decreased with decrease in the temperature of the reaction mixture in case of sonochemical method and it is found 26.3 nm at 40 °C. This is attributed to intense implosion of cavities generated by ultrasonic irradiation due to low vapor pressure at low temperature. With an increase in the temperature of the reaction medium the vapor pressure of the aqueous medium gets increases, which (vapor) fills the cavitating bubbles leads to less intense implosion of the cavities. Improper mixing, poorer solute transfer rate and nucleation because of less intense implosion of the cavities leads to formation of lesser number of nuclei which further results into larger particle size [16]. Further the particle size of cerium zinc molybdate nanoparticles is 131.4 nm in case of conventional method which significantly larger. Further the obtained particles size from particle size distribution is consistent with particle size obtained from TEM and XRD analysis.

3.5. Thermogravimetric and differential thermal analysis of cerium zinc molybdate nanoparticles

Thermogravimetric and differential thermal analysis was used to determine the decomposition and the transformation of cerium zinc molybdate crystal phase. TGA plot of the $Ce_2Zn_3(MoO_4)_6$ nanoparticles prepared by sonochemical method in Fig. 9 indicates the first weight loss (3.4%) in the range of 50–150 °C, which is attributed to desorption of free and physically adsorbed water on cerium zinc molybdate nanoparticles [20]. The second weight loss (5.56%) in the range of 150–325 °C is attributed to the removal of chemisorbed water; the monolayer of H_2O molecules that directly interact with the solid surface such as cerium cations and hydroxyls; and to the dehydroxylation (release of OH^- from the structure) [24]. The total weight loss up to 700 °C is observed to be 9.6%. The high energy generated due to cavitation phenomenon and micromixing caused by the same may increase the randomness of the Brownian motion of the cerium zinc molybdate molecules not allowing regular crystal formation which leads to a decrease in thermal stability of the cerium zinc molybdate nanoparticles which is confirmed by weight loss observed in TGA plot. Another possible reason behind the weight loss of cerium zinc molybdate nanoparticles prepared by sonochemical method may be that as the average particle sizes observed for the cerium zinc molybdate nanoparticles prepared by the sonochemical method is lower, it will conduct thermal radiation more efficiently and thus at a lower temperature it would feel a more significant effect of thermal convective currents leading to a possible phase transformation and thus weight loss can happen. However, it needs to carry out more work to conclude the above statement [16]. It is well known that the particle size affects on the weight loss of the material and is reported by Pinjari and Pandit [16] and Dang et al. [25]. The weight loss of the physically adsorbed water corresponds to the particle size that is the small particles obtain high specific surface area, resulting in more water molecules adsorbed. The particles size of cerium zinc molybdate nanoparticles prepared by ultrasound method is significantly less than that of conventional synthesis method and therefore it can be predicted that the weight loss in case of ultrasound method must be higher than conventional method.

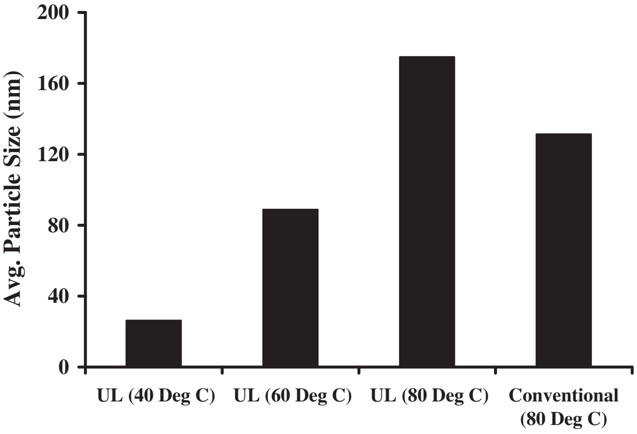

Fig. 8. Comparative study of average particle size of cerium zinc molybdate nanoparticles prepared by sonochemical method at different temperature and conventional method at 80 °C.

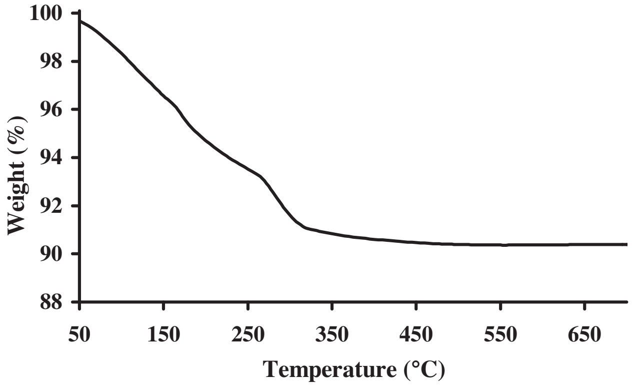

Fig. 9. TGA curve of $Ce_2Zn_3(MoO_4)_6$ nanoparticles synthesized by sonochemical in the temperature range 50–650 °C.

The DTA curve of cerium zinc molybdate nanoparticles depicted in Fig. 10, which shows three endothermic peaks at 180, 300 and 540 °C. The peak at 180 °C is attributed to desorption of free and physically adsorbed water on cerium zinc molybdate nanoparticles [20], which is line with the discussion made in TG analysis. The peak at 300 °C is due to the removal of chemisorbed water and to the dehydroxylation (release of OH^- from the structure) [24]. The endothermic peak at 540 °C is due to crystallization of amorphous cerium zinc molybdate into crystalline [20].

3.6. UV–vis analysis of cerium zinc molybdate nanoparticles

The method of preparation plays a significant role in controlling phases thereby the properties of the cerium zinc molybdate

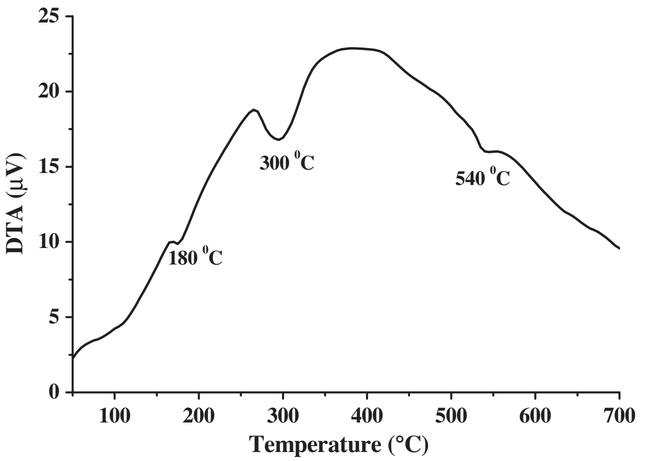

Fig. 10. DTA curve of $Ce_2Zn_3(MoO_4)_6$ nanoparticles synthesized by sonochemical in the temperature range 50–650 °C.

nanoparticles. Fig. 11 depicts the UV–visible spectra of sonochemically and conventionally prepared cerium zinc molybdate nanoparticles. As compared to the conventional method, significant increment in the absorption as had shown in case of ultrasound method for pure cerium zinc molybdate nanoparticles is observed. Ultrasonic irradiation plays a significant role in the structure of the nanomaterials and final photocatalytic activities. This extreme environment provides a favorable environment for the growth of nanocrystals. Cavitations and shockwaves created by ultrasound can accelerate solid particles to high velocities leading to interparticle collisions and inducing effective fusion at the point of collision. The energy generated during collision can induce the crystallization of the amorphous particles, responsible for the further crystallization process [26,27]. Therefore ultrasonic irradiations lead to the formation of product with higher surface area and smaller particle size. A similar result is reported by Zhou et al. [11] for the preparation of Bi_2MO_6 (M = W, Mo) photocatalysts via ultrasonic irradiations. In this study cerium zinc molybdate nanoparticles prepared by sonochemical method the higher absorbance i.e., photocatalytic activities compared to conventional method. It is attributed to the higher surface area (smaller size particle size in case of sonochemical method) of the cerium zinc molybdate nanoparticles since the absorbance i.e., photocatalytic reaction area is increased and the efficiency of the electron–hole separation is promoted [28].

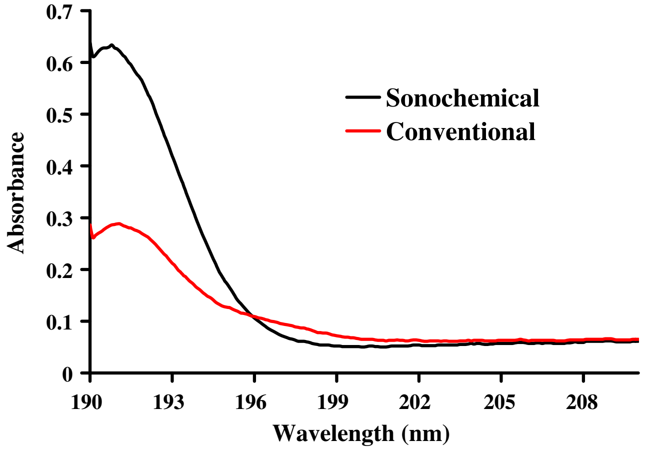

Fig. 11. UV–vis pattern of the (A) conventionally (NUS) and (B) sonochemically (US) synthesized $Ce_2Zn_3(MoO_4)_6$ nanoparticles.

3.7. Comparison of the energy efficiency

For the comparison of the energy required for these two synthesis methods (conventional (NUS) and sonochemical (US)) to obtain cerium zinc molybdate nanoparticles, a sample calculation of energy calculation for cerium zinc molybdate nanoparticles is reported in Appendix (A). It is already explained that reaction time to synthesize nanopigments were 40 min for sonochemical method and 2 h 20 min for conventional method. As compared to conventional method of synthesis of cerium zinc molybdate nanoparticles, use cavitation generated due to the ultrasonic irradiations improves the reaction and nucleation rate due to rapid micromixing. This signifies the sonochemical process with marginal reduction in the energy requirements for the synthesis of cerium zinc molybdate nanoparticles.

3.7.1. A.1. Energy delivered during sonication

- Energy delivered during sonication = energy required to synthesize cerium zinc molybdate.
- Electrical energy delivered during sonication using horn for 10 min (indicated by the power meter) = 5.34 kJ/min.
- Efficiency of horn taken for the calculation = 7.43% (estimated independently using calorimetric studies).
- Actual energy delivered by horn during sonication = energy delivered during sonication using horn × total reaction time × efficiency of horn = 5.34 × 40 × 7.43/100 = 15.87 kJ.
- Quantity of material processed = quantity of water + quantity of cerium nitrate + quantity of sodium zinc molybdate = 150 g + 10.9 g + 16.2 g = 177.1 g.
- Net energy delivered during sonication method = 15.87 kJ.
- Net energy supplied for processing of material using sonochemical method = actual energy delivered by horn during sonication/quantity of material processed = 15.87 (kJ)/177.1 (g) = 89.61×10^{-3} (kJ/g). (A).

3.7.2. A.2. Energy delivered during conventional method

- Voltage input in magnetic stirrer (Model RQ1210, Remi Metals Gujarat Limited, India) = 230 V.
- Current measured using digital multimeter (KUSAM-MECO Model 2718, Kusam Electrical Industries Ltd., Mumbai, India) = 37 mA = 37×10^{-3} A.
- Power input in overhead stirrer = voltage input × current measured = 230 (V) × 37×10^{-3} (A) = 8.51 W (J/s).
- Time required for completion of reaction = 2 h 20 min (8400 s).
- Net energy delivered during conventional method = power input in magnetic stirrer × time required for completion of reaction = 8.51 J/s × 8400 s = 71484 J = 71.484 kJ.
- Energy supplied in form of heat to maintain reaction temperature 80 °C $= mC_{p,\mathrm{mix}}(T_{\mathrm{process}} - T_{\mathrm{Ref}}) = 218 \times 3.238 \times (80\text{–}27.8)$ = 36.847 kJ.
- Quantity of material processed = quantity of water + quantity of cerium nitrate + quantity of sodium zinc molybdate = 200 g (60 ml) + 7.2 g + 10.8 g = 218 g.
- Net energy delivered during conventional method = 108.331 kJ.
- Net energy supplied for processing of material using conventional method = net energy delivered during conventional method/quantity of material processed = 108.331 (kJ)/218 (g) = 496.931×10^{-3} (kJ/g) (B).
- **Energy saved**

  Net energy saved = (net energy supplied for processing of material using conventional method (B)) − (net energy supplied for processing of material using sonochemical method (A) = $496.931 \times 10^{-3} - 89.61 \times 10^{-3} = 407.321 \times 10^{-3}$ (kJ/g).

4. Conclusion

The present study reports ultrasound assisted synthesis of cerium zinc molybdate anticorrosion nanopigment. The synthesis of nanosized cerium zinc molybdate was successfully carried out by an ultrasound assisted chemical precipitation method without addition of emulsification agent. The formation of cerium zinc molybdate compound is confirmed through XRD, FTIR and elemental analysis. The temperature (vapor pressure) and synthesis method has significant effect on the particles size of cerium zinc molybdate nanoparticle and is found to be 27 nm for ultrasound assisted synthesis at 40 °C. Also the conductivity results indicate that the reaction in the presence of ultrasonic irradiation is significant faster than in the case of conventional method. The drastic improvement in the reaction rate and thereby decrease in the particle size is attributed to improved solute transfer rate, rapid nucleation and formation of large number of nuclei in the presence of cavitation. The sonochemical synthesis technique is fast, simple, convenient, and time saving and can promise researchers a future large-scale synthesis for many applications in nanotechnology field.

Acknowledgements

B.A. Bhanvase is thankful to Vishwakarma Institute of Technology, Pune for providing the facility for this work. S.H. Sonawane acknowledges the support of Department of Science and Technology (DST), Government of India, for providing the Funds through Project Grant Reference No. SR/S3/CE/0060/2010.

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