Photocatalytic degradation of rhodamine B in water by visible light irradiated BMZ nanocomposite

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Abstract

The Bi_2MoZnO_7 nanocomposites have been successfully synthesized via co-precipitation and solid state method and followed by a low temperature calcinations treatment process. We find that such a Bi_2MoZnO_7 nanocomposite exihibits higher photoctatalytic activity and stability than Bi_2MoO_6, Bi_2O_3 and ZnO towards the aqueous phase degradation of Rhodamine B (RhB) under visible light (420 nm < λ). The presence of $Bi^{3+}/Mo^{6+}/Zn^{2+}$ ions in Bi_2MoZnO_7 and formation of defects in the lattice is believed to play an essential role in affecting the photoreactivity. The different types of active species scavengers are also play the photocatalytic process. The synthesized Bi_2MoZnO_7 nanocomposites were characterized by UV-Vis spectroscopy, X-ray diffraction (XRD), SEM, TEM, EDAX and IR techniques. The crystallite sizes, particle and grain sizes are 12±2, 5±1 and 100±5 nm, respectively. The rate of degradation of Rhodamine B by BMZ in aqueous phase is 7 times ($40.70\times10^{-3}min^{-1}$) faster in comparison to pure Bi_2O_3/ZnO. Copyright © 2017 VBRI Press.

Keywords: Nanocomposite (Bi_2MoZnO_7), Bi_2MoO_6, ZnO, photocatalytic degradation, rhodamine B, visible light.

Introduction

Dyes are one of the most notorious contaminants in aquatic environment because of their huge volume of production from industries, slow biodegradation, decoloration and toxicity **[1]**. Most of the azo dyes are extensively used in textile, paper, leather, gasoline, additives, foodstuffs and cosmetics industry **[2]**. So it is very much essential to develop methods that can lead to destruction of such hazardous compounds. Removal of coloured contaminates from industrial effluents has been a major concerned for waste water treatment. There are so many physical methods **[3]**, biological methods **[4-5]** and chemical methods **[6]** are most frequently employed for treatment of remove pollutants from dye industrial effluents. The presence of Rhodamine B, an organic dye in discharged dye effluents is most harmful for human beings **[7-9]**. The most effective photocatalytic degradation of many dyes was carried out by using nanocomposite semiconductor oxides. Nowadays, different kind of semiconductors has been studied as photocatalyst such as TiO_2, ZnO, CdS, WO_3, etc. Most of these semiconductor photocatalysts have band gap equivalent to or larger than 3.2 eV. Therefore, they promote photocatalysis by irradiated with UV radiation **[10-11]**. Surface area and surface defects play an important role in the photocatalytic activities of metal oxide nanocomposite. Nanocomposites are ideal candidates for application to photo catalytic degradation of dye since they offer a larger surface-to-volume ratio than nanoparticles. Photo-induced reaction takes place at the surface of the catalyst. A basic mechanism of photocatalytic reaction is on the generation of electron–hole pair and a photocatalyst is illuminated by the light stronger than its band gap energy. The electron migrates from valance band (VB) to conduction band (CB) and holes are formed in the valance band. These holes can generate hydroxyl radicals (·OH) which are highly oxidizing in nature. Probably hole can react with dye molecule and abstract electron from dye molecule and process of degradation start **[12-16]**. Recently, it has been demonstrated that the semi-conducting materials mediated photocatalytic oxidation reactions of organic compounds are very successful, conventional alternative methods for the removal of organic pollutants from water **[17-20]**. Among the various photo catalytic semiconducting metal oxide, Zinc oxide (ZnO) is considered to be a technologically prodigious

material having a wide spectrum of applications such as that of a semiconductor (*Eg*= 3.37 eV), magnetic material, electroluminescent material, UV-absorber, piezoelectric sensor and actuator, nanostructure varistor, field emission displaying material, thermoelectric material, gas sensor, constituent of cosmetics etc **[21-23]**. The uses of ZnO as a photocatalyst for photodegradation of environmental pollutants has also been extensively studied, because of its nontoxic nature, low cost, and high photochemical reactivity. Bismuth oxide (Bi_2O_3) has been investigated extensively due to its optical and electrical properties such as refractive index, large energy band gap, dielectric permittivity as well as remarkable photoluminescence and photoconductivity. At the same time molybdenum has also crucial role for his catalytic activity. Therefore, we are very much interested on nanocomposites due to different metal has different properties and gives promising result.

However, here we have been first time reported that the synthesis of Bi_2MoZnO_7 nanocomposites by co-precipition or solid state method. The main focus of this work is to investigate the photo catalytic degradation of Rhodamine B by the use of Bi_2MoZnO_7 nanocomposite under visible light. Among the two methods, solid state method is more effective for photocatalytic degradation of RhB. The molecular structure of Rh B and its Zwitterion form are shown in **Fig. 1** and **Fig. 2**.

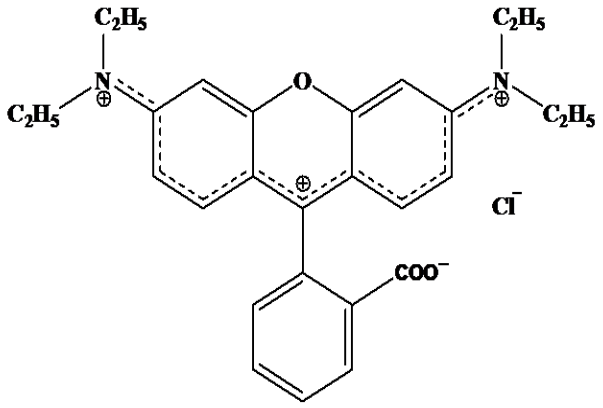

Fig. 1. Structure of Rhodamine B.

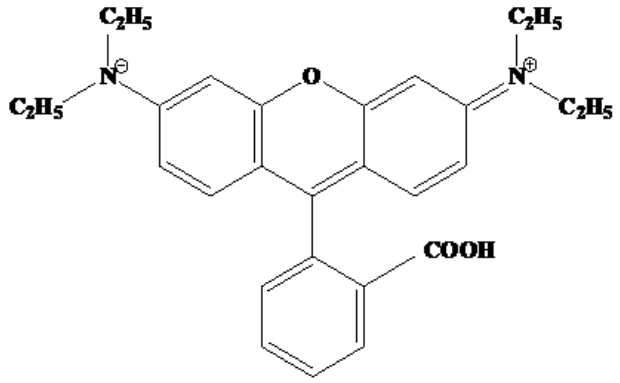

Fig. 2. Zwitterion Structure of Rhodamine B.

Experimental

Materials

$NaBiO_3$ (SDFCL, India), $(NH_4)_6Mo_7O_{24}.4H_2O$ (SDFCL, India), ZnO (Qualigens Fine Chemicals), dil. HCl (MERCK, India), Conc.NH_4OH (MERCK, India), Rhodamine-B (MERCK, India).

Synthesis of Bi_2MoZnO_7 nanocomposite by co-precipitation method

The nanocomposite of Bi_2MoZnO_7 was prepared by co-precipitation method. The total synthesis was carried out in following steps. In the first step, 1.003 g of $NaBiO_3$ was dissolved in 20 mL H_2O and proportionate amount of dil. HCl was added to prepare clear bismuth solution on heating at 100 ^oC and then added 20 mL EtOH with stirring condition. In the second step 0.1453 g of ZnO was dissolved in H_2O (5 mL) and dilute HCl to prepare Zn solution and dropwise added to Bi- solution. In the third step, 0.3215 g of $(NH_4)_6Mo_7O_{24}.4H_2O$ of aqueous solution was added and then stirred for an hour at room temperature. After that in stirring condition, conc. NH_4OH was added dropwise to the mixture to adjust the pH of 9.0, a light yellow precipitated was formed. The precipitated was filtered and washed with distilled water several times and dried in a vacuum oven at 100 ^oC for 2 h and finally obtained the fine powder of Bi_2MoZnO_7 nanocomposition. The schematic diagram is following in Flowchart 1 (supplementary file).

Synthesis of Bi_2MoZnO_7 nanocomposite by solid state method

The nanocomposite of Bi_2MoZnO_7 was also prepared by solid state method. 1.008 gm of $NaBiO_3$, 0.318 gm of $(NH_4)_4Mo_7O_{24}$.$4H_2O$ and 0.148 gm of ZnO was taken in the molar ratio 1:2:3 in a porcelain morter and added acetone drop wise with constant grinding for three hours. A golden yellow solid was obtained and dried it in hot air oven at 100 ^oC for half an hour.

Characterization of nanocomposite

The nanocomposite structure of the prepared photocatalysts was measured by X-ray diffractometer (XRD) at room temperature, using a XPERT-PRO PW3071 diffractometer with Cu Kα (λ=1.5418 Å) as target material using 40 kV accelerating voltage, 30 mA emission current. Absorbance of Rhodamine B was measured with the help of UV-VIS spectrophotometer PerkinElmer Lambda 35 (Singapore). The average grain sizes of nanocomposites and atomic level dispersion were measured by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) (JEOL JMS-5800). FT-IR spectra were recorded at room temperature using a Perkin-Elmer Paragon 1000 FT-IR spectrometer (JEOL JMS-5800). The fine structure of the prepared nanoparticles is analyzed by Transmission Electron Microscopy (TEM) (TM-300, Philips).

Photocatalytic experiments

The photocatalytic activity of the nanocomposite Bi_2MoZnO_7 is substantiated in the following procedure. The photocatalytic reaction was carried out under visible light irradiation. All the experiments were performed at room temperature. Reaction solutions were prepared by adding 0.156gm of photocatalyst nanopowder into 30 ml Rhodamine B (RhB) solution. In this solution, a small volume of the reactant liquid was siphoned out at regular time interval for analysis and the concentration of the dye was measured by absorption spectrometry using UV–vis spectrometer (PERKIN ELMER, LAMBDA 35) at its maximum absorption wavelength of 554nm. The percent of degradation (%) has been calculated as follows:

$$\% \text{ degradation} = (A_0 - A_t) \times 100 / A_0,$$

where, A_0 the initial absorbance and A_t is the absorbance of the sample irradiated at time, t minutes.

Results and discussion

XRD analysis of nanocomposites

The XRD technique was used to determine and confirm the nanocomposite structure of Bi_2MoZnO_7 (BMZ). XRD spectra of Bi_2MoZnO_7, Bi_2O_3 and Bi_2MoO_6 are shown in **Fig. 3(a)** in which most of the peaks can be observed at 2θ values of BMZ are align to Bi_2O_3 and Bi_2MoO_6 (vertical solid line) at 12.14º, 26.26º, 34.23º, 40.43º, 45.59º, 55.01º and 68.12º. The other major distinct peaks are at 18.26º, 22.02º, 32.04º and 41.12º may be ZnO. The peak of BMZ is slightly shifting from other compositions due to some oxide defects in the crystals. It clearly indicates that BMZ is a mixture of compositions of all the metal ions. The average crystallite sizes of BMZ, Bi_2O_3 and Bi_2MoO_6 at 46.59º and 34.23º are ~12.42, ~15.25 and 15.39nm (calculated from Scherer equation), respectively.

FT-IR spectra analysis of the BMZ nanocomposites

Fig. 3(b) represents the FT-IR spectra of the BMZ, Bi_2O_3 and Bi_2MoO_6 nanocomposites which are obtained after calcinations for 2 h. It shows that the nanocomposition of BMZ gives absorption peaks at 3121 cm^{-1} corresponds to the O–H bending mode of vibration is present on the surface due to moisture. The peak appeared at 1401cm^{-1} is due to the bending vibration of M–OH groups. The strong band at 837 cm^{-1} in the infrared spectrum of BMZ is probably arising from stretching modes of Zn–O bands. This spectrum also shows absorption peaks below 600 cm^{-1} which corresponds to the stretching frequency of Mo=O…Mo bond in BMZ.

SEM analysis of the BMZ nanocomposites

Scaning electron microscopy is widely used to study the morphological features and surface characteristics of adsorbent materials. **Fig. 4(a)** and **4(b)** indicate the **s**canning electron microscopy (SEM) at different magnification of Bi_2MoZnO_7 performed to gain information about the average grain sizes and surface morphology of nanocomposition. The SEM images of BMZ confirm that the polymers are flakes in shape and they are arranged in well-ordered manner and average grain sizes are ~ 100±5 nm.

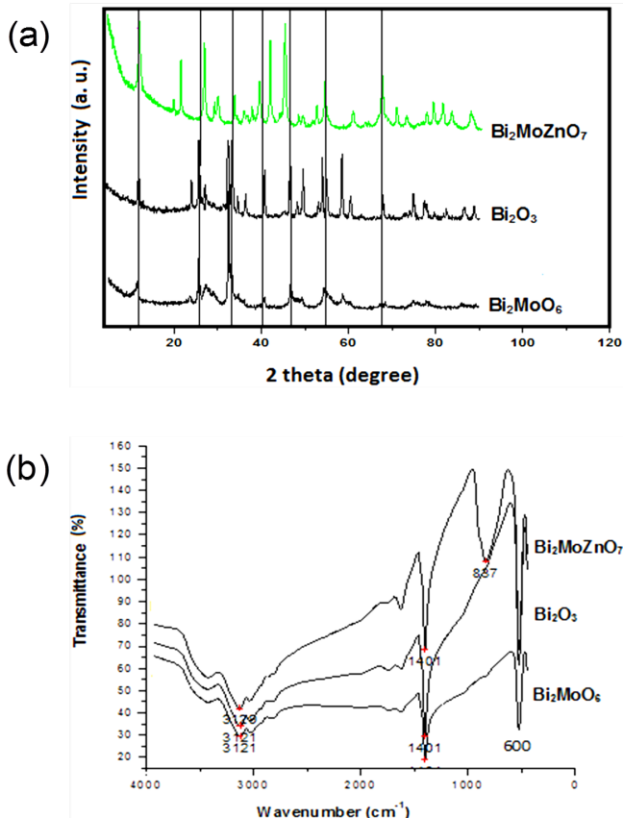

Fig. 3. (a) XRD Spectra of Bi_2MoZnO_7, Bi_2O_3 and Bi_2MoO_6 nanocomposite and (b) FT-IR spectra of BMZ, Bi2O3, and Bi_2MoO_6 nanocomposite.

Energy dispersive X-ray (EDX) spectra analysis of the BMZ nanocomposite

The elemental description of the BMZ was obtained from energy dispersive X-ray analysis. In **Fig. 5**, the peaks located between 2-4, 9-16 and 17-20, and 1-2, 8-9 keV are directly related to the characteristic of bismuth, molybdenum and zinc. Absorption peaks of Carbon, Copper and Zinc is also found and its weight% is high due to the composition is not purified or instrumental error. The weight and atomic % of metal ions are shown in table of Bi_2MoZnO_7.

TEM analysis of the BMZ nanocomposition

Transmission Electron Microscopy (TEM) is a vital characterization tool for directly imaging nanomaterials to obtain quantitative measures of particle size, size distribution and lattice fringes. The particle size and lattice fringes are measured from HRTEM (Model Philips TM-30, Philips Research Laboratories). The bright-field (BF) electron micrograph of the BMZ nanopowder is produced at 100 °C reflect a spherical particle, with average particle sizes of 5±1 nm (**Fig. 4(c)**) and the **Fig. 4(d)** represents the lattice fringes of BMZ

nanoparticles that obtained from HRTEM. The particles had been separated by well-defined boundaries, visible and uniformly distributed.

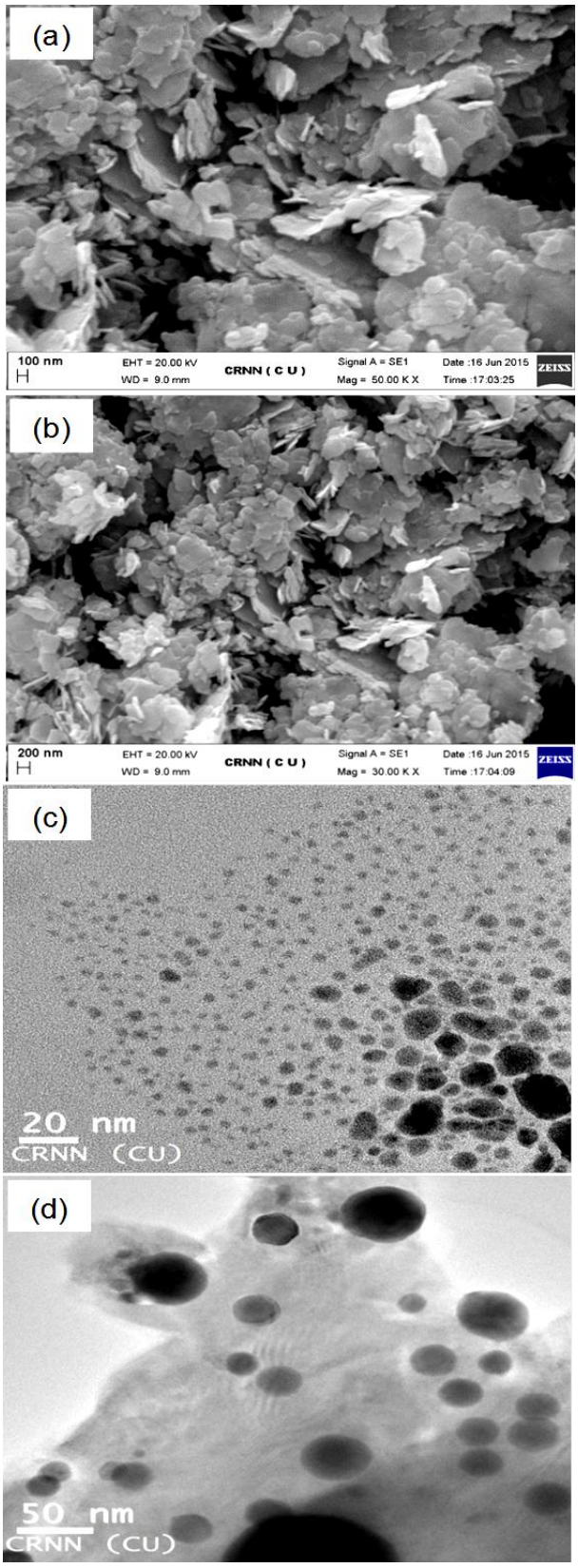

Fig. 4. (a) SEM images of BMZ at 20KV and 50KX magnification; (b) SEM images of BMZ at 20KV and 30KX magnification; (c) TEM image of nanocomposite BMZ; and (d) represent the HRTEM of BMZ.

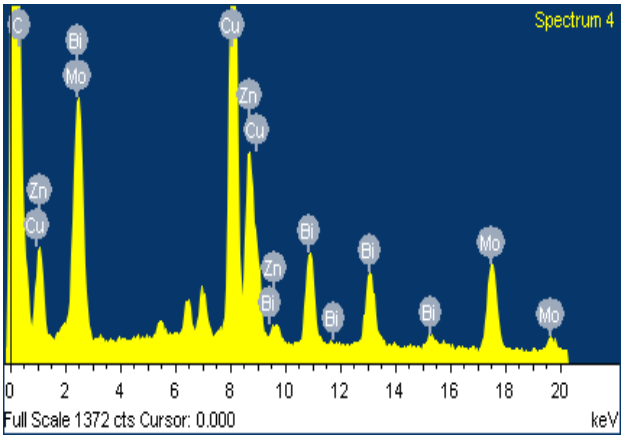

Fig. 5. EDX of BMZ nanocompositionand elemental analysis and determination of Weight% and Atomic% of Bi_2MoZnO_7 is shown in table.

Element	Weight (%)	Atomic (%)
C K	7.02	36.02
Cu k	34.56	33.50
Zn K	12.13	11.43
Mo K	15.56	9.99
Bi L	30.73	9.06
Totals	100.00	100.00

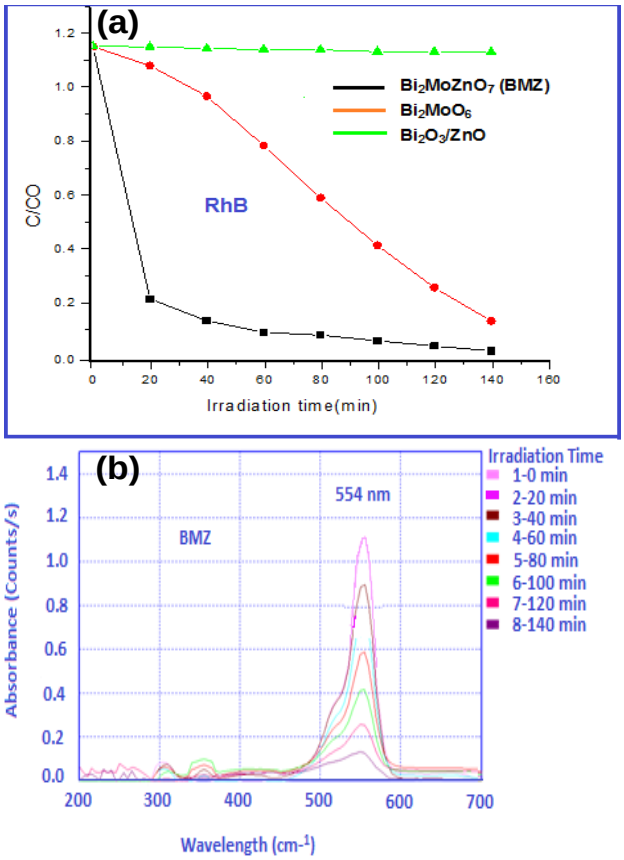

Fig. 6. (a) Degradation of RhB in presence of catalysts BMZ, Bi_2MoO_6 and Bi_2O_3/ZnO under UV light irradiation and (b) the changes in concentration of RhB in presence of BMZ nanocomposite at different irradiation time interval.

Photocatalytic activity of Bi_2MoZnO_7 Nanocomposite

The photocatalytic degradation of rhodamine B by Bi_2MoZnO_7 (BMZ) was investigated by using a standard UV-Vis spectrophotometer. To study of this reaction, the photocatalyst nanopowder BMZ (0.154 g), Bi_2MoO_6 and Bi_2O_3/ZnO were taken same amount of catalysts in 30 ml rhodamine B into separate beakers. Then a small volume of reactant liquid was siphoned out into a quartz cell and measures the UV-visible spectra in UV-visible spectrophotometer at constant time interval of 20 minutes. It was found that the initial absorption peak of Rh B appears at 554 nm with absorbance of 1.15 which is shown in **Fig. 6(a)**. After addition of the catalyst the pink color of Rh B fades away slowly with the progress of reaction. **Fig. 6(b)** represents the changes in concentration of RhB in presence of BMZ at different irradiation time interval. Among the all catalysts BMZ photocatalyst shows degradation rate 7 times (40.70×10^{-3} min^{-1}) faster compare the other compositions. The Bi_2O_3 or ZnO is almost ineffective for degradation of rhodamine B. The time taken for complete degradation of RhB on BMZ is 140 min shown in **Fig. 6(b)**.

We have study both the compositions of BMZ which are synthesized by co-precipitation and solid state method, the composition obtained by solid state method is slight better photoactive material compared with other method. The rate constant of RhB was measured after 50% decolorization (60 min) shown in **Table 1**. Reaction rate constants were measured after 60 and 140 minutes decolorization of RhB in presence of catalysts and visible light at room temperature.

Table 1. Resultant properties of BMZ, Bi_2MoO_6 and Bi_2O_3/ZnO nano-composites.

Acronym	Crystallites Size (nm)	Degradation rate constant of Rh B k ($x10^{-3}$ min^{-1})		Time required for complete degradation (min) of Rh
		60 (min)	140 (min)	
Bi_2MoZnO_7 (BMZ)	12.42	40.70	45.38	140
Bi_2MoO_6	15.39	6.04	14.54	180
Bi_2O_3/ZnO	15.25	1.51	1.44	No change

Conclusion

In summary, we report the facile and green method to synthesize highly stable dispersions of nanocomposite B_2MoZnO_7 by co-precipitation and solid state method. The various characteristics of the synthesized nanocomposites are analyzed by UV-vis., XRD, EDX and SEM, TEM and IR analyses. The nanocomposite structures were confirmed by XRD. The catalytic activity is investigated by studying the degradation of RhB by BMZ. It shows that the catalytic degradation of RhB with synthesized nanocomposites is much faster in contrast to pure Bi_2MoO_6 and Bi_2O_3/ZnO. The degradation of RhB was found 90% in 150 min by BMZ (co-precipition method) and it was 98% in 140 min (solid state method). Since solid state method is relatively simple, fast and environment friendly, this can be scaled up for the bulk production of nanocomposites.

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Author's contributions

Conceived the plan: Tanmay K Ghorai; Performed the expeirments: Suranjan Sikdar; Data analysis: S. Sikdar, & T K Ghorai; Wrote the paper: Tanmay K Ghorai, S. Sikdar, (T K Ghorai are the initials of authors); Materials Characterization (TEM, SEM & XRD); Sutanuka Pattanayek. Authors have no competing financial interests.

Supporting information

Supporting informations are available from VBRI Press.

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