

Accepted Manuscript

10.1039/D0NJ01272F.

View Article Online View Journal

A journal for new directions in chemistry

This article can be cited before page numbers have been issued, to do this please use: E. ERUSAPPAN, S.

Thiripuranthagan, D. Mani, S. Kumaravel and T. Vembuli, New J. Chem., 2020, DOI:

<text><text><text><text><image><image><image><image><image>

This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/njc

Photocatalytic performance of visible active boron nitride supported ZnFe₂O₄ (ZnFe₂O₄/BN) nanocomposites for the removal of aqueous organic pollutants

Elangovan Erusappan ^a, Sivakumar Thiripuranthagan ^{a*}, Mani Durai ^b, Sakthivel Kumaravel ^a and Thanigaivel Vembuli ^a

^aCatalysis Laboratory, Department of Applied Science and Technology, A.C. Tech, Anna University, Chennai, Tamilnadu, India

^bCentre for Nanoscience and Technology, A.C. Tech, Anna University, Chennai, Tamilnadu, India *Corresponding author Email: <u>tssivakumar@yahoo.com</u>

Graphical Abstract



New Journal of Chemistry Accepted Manuscrip

Highlights

- ✓ ZnFe₂O₄/BN nanocomposites were synthesized by solvothermal method.
- ✓ The HR-TEM and FE-SEM/EDX images revealed uniform dispersion of ZnFe₂O₄ nanospheres on the surface of BN nanosheet.
- ✓ Photoluminescence studies showed lower electron-hole pair recombination.
- ✓ ZnFe₂O₄/9.3% BN nanocomposite catalyst showed outstanding photocatalytic activity compared to bare and nanocomposite catalysts.
- \checkmark COD and TOC studies confirm the formation of non-toxic fragments.

Abstract

Visible active novel ZnFe₂O₄/BN heterostructured nanocomposites with different wt % of BN nanosheets were prepared by solvothermal method. Their structural, morphological and optical properties were studied by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Energy-Dispersive X-ray spectroscopy (EDX), Fourier-Transform Infrared (FT-IR), UV-Visible spectrophotometer, Photo Luminescence (PL) and X-ray Photoelectron Spectroscopy (XPS). The photocatalytic performance of ZnFe₂O₄/BN hybrid nanocomposite was evaluated towards oxidative degradation of organic pollutants such as Congo Red (CR) and Tetracycline (TC) under visible light irradiation. The porous BN nanosheets act as catalytic support and enhance the photoactivity of ZnFe₂O₄ in the nanocomposite. The results also indicated that the presence of BN nanosheets lowers the recombination rate and shows significantly improved separation of the photo-induced electron-hole pairs in ZnFe₂O₄/BN when compared to bare ZnFe₂O₄. Among the different ZnFe₂O₄/BN nanocomposites, 9.3 wt % of BN loaded ZnFe₂O₄ hybrid was found to show the most efficient photocatalytic activity towards the degradation of Congo red and Tetracycline under visible light irradiation. The apparent rate constant values of ZnFe₂O₄/9.3% BN were found to be three and five times higher than bare ZnFe₂O₄ in the degradation of CR and TC respectively.

Keywords: ZnFe₂O₄/BN, nanocomposites, photocatalysts, Congo Red (CR) and Tetracycline (TC)

4

5 6

7 8

9 10

38 39

40 41

42

43 44

45 46

47

48 49

50 51

52 53

54

1. Introduction

Over the past few years research has been focused on photodegradation of organic pollutants present in wastewater using Advanced Oxidation Processes (AOPs) involving semiconductor photocatalysts such as TiO₂, ZnO, Fe₂O₃, etc.,¹⁻¹⁰ These semiconductors have several advantageous characteristics which include low cost, abundant and non-toxicity. However, some of their inherent properties limit their widespread practical applications.¹¹⁻¹⁵ Hence it is imperative to address the limitations of semiconductor based photocatalyst. While the wide bandgap semiconductors require light of intense energy (which is economically not attractive), the narrow band gap semiconductors show quick recombination of e⁻/h⁺. When both these limitations are addressed, there comes an issue of separation of catalyst and the cost. Hence the new heterostructured catalyst should meet the requirements of visible activity, low or zero recombination of electrons, ease of recovery and should be cheap. Designing & developing low cost, visible light-driven catalyst is the need of the hour. ZnFe₂O₄ with its spinel structure is a narrow band gap semiconductor (1.9 eV). Owing to the attractive features of $ZnFe_2O_4$ such as low cost, high photochemical stability, optimal band gap to be driven by visible radiation, unique electrical & optical properties and more importantly its magnetically separable nature, it has been extensively used as photocatalyst & water-splitting catalyst.¹⁶⁻²² Its magnetically separable nature makes it as a recyclable, cost-effective catalyst. In spite of all the above, ZnFe₂O₄ still does not satisfy the requirements for practical applications due to its limited adsorption property, poor dispersion in aqueous solution & fast recombination.²³⁻²⁸ In order to address the limitations of ZnFe₂O₄ it is proposed to develop a 2D heterostructured ZnFe₂O₄ hybrid with graphene-like boron nitride (BN).²⁹⁻³³

Boron nitride is another fascinating 2D material like graphene as thin layer of BN exhibits many wonderful thermal, electrical, magnetic & metallic properties. BN also called as white graphene and non-carbon graphene is a wide band gap material (5.2-5.5ev) ^{34,35} with high surface area (3300 m²/g⁻¹) ³⁶ and high thermal conductivity (600W m⁻¹ K⁻¹) and hence has great potential for various applications in the areas of adsorption,^{37,38} catalysis^{39,40} and energy storage devices.^{41,42} As BN is a very good electron transporter-like graphene, its presence along with a photocatalyst will aid electron transport to the surface whereby the transient species are generated for the degradation of organic pollutants. Hence BN has been coupled with several photocatalysts BiOBr/BN,⁴³ Fe₂O₃/BN, ⁴⁴ AgBr/BN,⁴⁵ TiO₂/BNNT,⁴⁶ BN/AgPO₄,⁴⁷ ZnO/BN,⁴⁸ TiO₂/h-BN,⁴⁹ g-

 C_3N_4 /h-BN,⁵⁰ etc either to improve the visible activity or to prevent recombination or for both. However, to the best of our knowledge, only little and scarce attempts have been made with the heterostructured ZnFe₂O₄ hybrids.

Herein, we report the construction of heterostructure comprising of a spinel semiconductor oxide (ZnFe₂O₄) and BN support (ZnFe₂O₄/x% BN where x: 6.4, 9.3 and 12.1%). The synthesized nanocomposites were characterized by various physicochemical & instrumental techniques and finally subjected towards the photodegradation of congo red & tetracycline under visible irradiation. ZnFe₂O₄/BN heterostructures show enhanced absorption in the visible region when compared to the bare spinel oxide nanospheres. The kinetics studies reveal that the degradation followed pseudo-first-order kinetics and based on the results a possible mechanism was also proposed.

2. Experimental

2.1 Materials

Boric acid (98 % purity), urea (\geq 99 % purity), NH₄HCO₃ (\geq 99.7 % purity), zinc acetate dihydrate (\geq 99 % purity) were obtained from Sisco Research Laboratory Chemicals, India. Ferric nitrate monohydrate (99.99 % purity) and ethylene glycol were purchased from Sigma Aldrich, India. Congo Red (98 % purity) dye and Tetracycline were purchased from Colourise Industries, India.

2.2 Synthesis of Boron nitride (BN)

BN was synthesized by using boric acid and urea as reported elsewhere.⁵¹ In a typical synthesis, boric acid and urea in the ratio of 1:24 were taken dissolved in water and heated at 65 °C overnight. The dried white solid obtained was then heated at 900 °C for 6 hr in N₂ atmosphere in the tubular furnace to get white BN powder.

2.3 Synthesis of ZnFe₂O₄/BN

The synthesized BN (50 mg) was dispersed in 30ml ethanol and sonicated for 30 min (A) then, 3 mmol of Zn (CH₃COO)₂.2H₂O and 6 mmol Fe (NO₃)₃.9H₂O were dissolved in 120ml of ethylene glycol (B). The two solutions A and B were mixed together and 90 mmol NH₄HCO₃ was added to the reaction mixture at room temperature. The whole reaction mixture was stirred vigorously for 30 min. The solution was then transferred into Teflon-lined stainless-steel autoclave and subjected to solvothermal treatment at 180 °C for 24 hr. The obtained precipitate was filtered,

4 5

6

7 8

9 10

Chnobadisiduqua

42

43 44

45 46

47 48

49

50 51

52 53

54 55

washed with ethanol followed by deionized water for several times and dried at 60 °C. Further, the powder was finally calcined at 450 °C for 10 hr to obtain ZnFe₂O₄/BN 6.4 Wt % nanocomposite. In the same way, ZnFe₂O₄/BN 9.3 Wt % and ZnFe₂O₄/BN 12.1 Wt % nanocomposites were also prepared by taking 75 and 100 mg of BN respectively. The bare ZnFe₂O₄ was also synthesized by the above procedure but without adding BN.

2.4 Characterization

Powder X-Ray diffraction (XRD) patterns of the solid products were analyzed using the Power X-ray diffractometer (Rigaku, Miniflex) with graphite-monochromatized Cu K α radiation at 30KV and 15mA. UV-vis diffuse reflectance spectra of the obtained samples were analyzed on a UV-vis spectrophotometer (JASCO V-750, Jasco, Japan) with BaSO₄ as reference. Nitrogen adsorption-desorption isotherms were obtained at -196 °C using a (BEL SORP-mini, Beljan). Prior to the adsorption measurement, the sample (ca.0.1g) was evacuated at 150 °C for 12 hr. FT-IR spectra were recorded using Thermo Scientific NICOLET 4700 with resolution 4 cm⁻¹ at room temperature after pelletizing the sample with KBr salt. Photoluminescence spectra were recorded by using Micro-PL analyzer using 320 nm excitation wavelength (MORIBA LabRam HR). The specific surface area, pore size distribution and pore volume distribution were obtained from N₂ adsorption-desorption isotherms of the samples using a volumetric sorption analyzer (Micromeritics ASAP 2020, Norcross, GA, USA). The morphology was observed using a Hitachi S-8000 Scanning Electron Microscope (FE-SEM) coupled with energy-dispersive X-ray (EDX) analyzer. Transmission Electron Microscopy (TEM) images were taken using Hitachi H9500 TEM at an acceleration voltage of 300 kV.

2.5 Evaluation of Photocatalytic activity

The photocatalytic activities of the synthesized ZnFe₂O₄/BN nanocomposite catalysts were evaluated towards the degradation of CR dye and TC antibiotic under visible light irradiation. The initial concentration of 10 ppm of dye, antibiotic was taken for the present study. A 500 W tungsten lamp was used as the visible light source which was located inside a quartz cell with a circulating water bath. 50 mg of catalyst was dispersed in 100 ml of dye/antibiotic and kept in the dark for 30 min to reach adsorption-desorption equilibrium between catalyst and pollutants. Then the suspension was exposed under visible light irradiation. During the reaction, 3 ml of the solution was withdrawn at definite time intervals, centrifuged and analyzed by UV-vis spectrophotometer

(Hitachi U 2000). The % degradation of CR dye and TC antibiotic was determined by using the following equation:⁵²

$$D \% = C_0 - C_t / C_0 \times 100 \tag{1}$$

 C_0 = initial concentration and C_t =concentration at time T

In order to check whether the decolorization was followed by degradation or not, Chemical Oxygen Demand (COD) and total organic carbon (TOC) analysis were also made by using Shimadzu TOC-L analyzer. The degradation percentage of dyes was calculated following the procedure as report by as and other ^{53,54}

3. Results and Discussion

3.1 XRD analysis

The XRD patterns of bare BN, ZnFe₂O₄, and ZnFe₂O₄/BN nanocomposites were recorded and shown in Fig 1. The characteristic diffraction peaks at $2\theta = 18.25^{\circ}$, 30.06° , 35.15° , 42.9° , 53.2° , 56.8° , 62.3° , 70.50° , 73.5° , 78.7° , 86.4° , 89.13° correspond to (111), (220), (311), (400), (422), (511), (440), (620), (533), (444), (642) and (731) planes of ZnFe₂O₄, respectively (JCPDS card no.22-1012).^{55,56}



Figure 1 XRD patterns of (A) bare BN, (B) bare ZnFe₂O₄ and ZnFe₂O₄/x% BN composite catalysts (x = 6.4, 9.3 and 12.1%)

The wide-angle diffraction peaks at 2 θ value 26.2° and 42.3° are assigned to (002) and (100) planes of hexagonal BN (JCPDS 85-1068).⁵⁷ However, there was no typical pattern of BN

observed in the composites which may be due to the low BN content in the samples.⁵⁸ The absence of any other peak confirms the high purity of the composite. The average crystalline size of prepared materials was determined by using the following formula

$$D = K\lambda/\beta \cos\theta$$

$D=K\lambda/\beta\cos\theta$			(2)			
Where D is the average	crystalline size, K	is constant (0.8	89), $λ$ -is the wav	elength of the	Cu ka	
radiation (λ=0.15418 nr	n), β-is full width a	at half maximu	m and θ-is the d	iffraction ang	le. The	
average grain sizes of th	e ZnFe ₂ O ₄ /x% BN (x = 6.4, 9.3 and	12.1%) composi	tes are given in	n Table	
1.			_	-		
Table 1 Physicoc	hemical characteri	stics of the syr	thesized catalys	ts.	0	
Catalysts	Crystalline size ^a	Band gan ^b	Surface area ^c	Pore size ^c	Pore volume ^c	
Catalysis	(nm)		(m^2/a)	(nm)	(cm^3/a)	
7nEq.O	(1111)	(ev)	(117g)	21.04	(cm /g)	
$ZnFe_2O_4$	19	1.//	<u> </u>	51.04	0.25	
$ZnFe_2O_4/6.4\%$ BN	53	1.68	32	32.17	0.25	
ZnFe ₂ O ₄ /9.3% BN	57	1.75	34	35.65	0.30	
ZnFe ₂ O ₄ /12.1% BN	72	1.70	35	35.18	0.30	
^a By XRD					2	
^b By UV DRS						
^c By BET						
					U	
3.2 FT-IR Spectra					Ō	
FT-IR analysis was	carried out to find ou	it the surface fu	inctional groups a	and chemical b	onding	
present in the catalysts.	Figure 2 shows the	FT-IR spectra	of bare and com	posite catalys	ts. The	
bands at 3424 cm^{-1} an	d 1620 cm ⁻¹ are as	ssociated with	O-H stretching	and O-H-O b	bending	
vibrations of the surface	adsorbed water mo	lecules. ⁵⁹ The d	characteristic stre	tching vibratio	on band	
observed between 400-	500 cm^{-1} in bare Zn	Fe ₂ O ₄ is attribu	ited to the Fe-O s	tretching vibr	ation. ⁶⁰	
The FTIR spectrum of F	N shows two main	characteristic o	hearntion hands	at 1378 cm ⁻¹ a	and 805	
am ⁻¹ corresponding to	the R N stratabi	ng and D N I	R out of plana	handing with	rations Z	

Physicochemical characteristics of the synthesized catalysts. Table 1

^c By BET

3.2 FT-IR Spectra

FT-IR analysis was carried out to find out the surface functional groups and chemical bonding present in the catalysts. Figure 2 shows the FT-IR spectra of bare and composite catalysts. The bands at 3424 cm⁻¹ and 1620 cm⁻¹ are associated with O-H stretching and O-H-O bending vibrations of the surface adsorbed water molecules.⁵⁹ The characteristic stretching vibration band observed between 400- 500 cm⁻¹ in bare ZnFe₂O₄ is attributed to the Fe-O stretching vibration.⁶⁰ The FTIR spectrum of BN shows two main characteristic absorption bands at 1378 cm⁻¹ and 805 cm⁻¹ corresponding to the B-N stretching and B-N-B out of plane bending vibrations respectively.61,62



Figure 2 FT-IR spectra of bare BN, ZnFe₂O₄ and ZnFe₂O₄/x% BN composite catalysts (x = 6.4, 9.3 and 12.1%)

3.3 BET Surface area

The N₂ adsorption-desorption isotherms were constructed and their corresponding Barrett-Joyner-Halenda (BJH) pore size distribution curves were plotted for bare $ZnFe_2O_4$ and $ZnFe_2O_4$ / BN (6.4%, 9.3% and 12.1%) nanocomposites to get an insight into their porous nature (Fig.3a). Type IV N₂ adsorption-desorption isotherms with hysteresis loop obtained clearly indicates the porous nature of $ZnFe_2O_4/BN$ (6.4%, 9.3% and 12.1%) nanocomposites and the considerable hysteresis loop at high relative pressure (P/P⁰) range of 0.60–1.00 confirms that the BN and porous $ZnFe_2O_4$ nanospheres coexist in the synthesized samples.⁶³



Figure 3(a) N2 adsorption-desorption isotherms and (b) pore size distribution (PSD)plots of bare ZnFe2O4 and ZnFe2O4/x% BN composite catalysts (x = 6.4, 9.3and 12.1%)

The Brunauer-Emmett-Teller (BET) specific surface area values of the catalysts were calculated to be 33, 32, 34 and 35 m² g⁻¹ for bare $ZnFe_2O_4$ and $ZnFe_2O_4/BN$ (6.4%, 9.3% and 12.1%) nanocomposites catalyst respectively. The bare BN also showed a very low surface area of 52 m²/g (Measured by Single point method) due to the high calcinations temperature (900 Deg) employed in the synthesis. Their corresponding BJH pore size distributions were found in the range of 8-28 nm (Table 1) (Fig. 3b). This wider pore size distributions can be attributed to the irregular shapes and sizes of the pores derived from the accumulation of nanospheres.

3.4 XPS analysis

To investigate the valence and chemical state of the elements present in $ZnFe_2O_4/9.3\%$ BN catalyst XPS analysis was performed. Fig 4a. demonstrates the survey spectra of the $ZnFe_2O_4/9.3\%$ BN nanocomposite. Fig.4 (b-f) shows high-resolution core-level spectra of Zn, Fe, O, B, and N present in the composite. The high resolution spectra of Zn and Fe [Fig.4 (b & c)] show characteristic Zn 2p $_{3/2}$, Zn 2p $_{1/2}$ and Fe 2p $_{3/2}$, Fe 2p $_{1/2}$ peaks of Zn²⁺ and Fe $^{3+}$ ions with the binding energies of 1022 eV, 1045 eV (for Zn²⁺) and 710.6 eV, 724 eV (for Fe³⁺).^{64,65} The additional peaks observed around 720.5 eV and 731.5 eV corresponding to Fe 2p $_{3/2}$ and Fe 2p $_{1/2}$ s are satellite peaks.⁶⁶ The peak at 530.1 eV is attributed to O 1s (Fig 4 (d)). The peaks of B 1s and N 1s appeared at the binding energies of 198.8 eV and 398.8 eV ^{67,68} as shown in Fig. 4 (e & f) respectively.

New Journal of Chemistry Accepted Manuscript

These observations are in agreement with the previous reports and hence this study confirmed that BN has been successfully attached with ZnFe₂O₄.⁶⁹



Figure 4XPS (a) Full survey spectrum and (b-f) core level spectra of ZnFe2O4/9.3% BN
catalyst

3.5 Morphological study

FE-SEM was used to know the surface morphology and to determine the particle size and shape of bare $ZnFe_2O_4$, BN and $ZnFe_2O_4/BN$ composites (Fig. 5). In the formation of $ZnFe_2O_4$ nanospheres, the replacement of Fe^{3+} ion with Zn^{2+} at the tetrahedral site takes place as Zn^{2+} always prefers the tetrahedral sites. The ion exchange by Kirkendall effect was also reported between Zn^{2+} ion and Fe^{2+} ion Fe_3O_4 .⁷⁰ Herein the synthesized bare $ZnFe_2O_4$ hollow spheres show the crystal diameter of 170 nm (Fig 5c) whereas the same $ZnFeO_4$ in the composites have the particle size less than 80 nm (Fig 5f)



Figure 5 FE-SEM images of (a-c) ZnFe₂O₄ (d) BN (e & f) ZnFe₂O₄/9.3% BN composite catalysts

The EDAX mapping further confirms the intact nature of the composites and the presence of all the elements such as B, N, O, Zn, & Fe. (Fig. 6).



Figure 6 EDAX mapping of ZnFe₂O₄/9.3% BN composite catalyst

The TEM and HRTEM images were also recorded to get detailed morphology of $ZnFe_2O_4/9.3\%$ BN composite catalyst and they are shown in Fig. (7 a-c). It further confirms the nano hollow spherical morphology of $ZnFe_2O_4$ with average particle diameter in the range between 10 to 20 nm dispersed in BN 2D sheet. However few particles with diameter around 60 to 70 nm were also seen in the TEM image.



Figure 7 (a-c) HR-TEM (d) SAED pattern of the most active ZnFe₂O₄/9.3% BN composite catalyst

3.6 DRS UV-vis spectra

Fig. 8a shows the UV-Vis diffuse reflectance spectra of bare $ZnFe_2O_4$ and $ZnFe_2O_4/BN$ (x = 6.4, 9.3 and 12.1%) nanocomposites. These absorption spectra were used to investigate the effect of BN modification on the electronic structure of $ZnFe_2O_4$. All the catalysts exhibit the absorption edges in the visible region. BN modified $ZnFe_2O_4$ nanocomposites show a steep edge in the visible region can be attributed to intrinsic band transition.^{71,72} All are visible active as they absorb > 700 nm.⁷³ Incorporation of BN in $ZnFe_2O_4$ has marginal effect on the bang gap value. The presence of BN prevents recombination as it is a good electron transporter.



Figure 8(A) UV-vis Diffuse reflectance spectra and (B) Band gap calculations of bareZnFe2O4, and ZnFe2O4/x% BN composite catalyst (x=6.4, 9.3 and 12.1%)

Fig. 8b shows the band gap energy of prepared materials calculated by plotting $(\alpha h\nu)^2$ Vs photon energy (TAUC plot).^{74,75} The calculated band gap values of ZnFe₂O₄, ZnFe₂O₄/6.4% BN, ZnFe₂O₄/9.3% BN and ZnFe₂O₄/12.1% BN were found to be 1.77 eV, 1.68 eV, 1.75 eV and 1.70 eV respectively.

3.7 PL spectra

The rate of recombination of electrons and holes in a semiconductor can be studied by the PL emission spectra. Generally, the lower PL intensity indicates the lower recombination of the photogenerated carriers and higher photocatalytic activity.⁷⁶ Fig. 9 shows the PL spectra of bare ZnFe₂O₄ and ZnFe₂O₄/BN composite catalysts. The bare ZnFe₂O₄ shows a high-intensity emission peak around 360 nm and the intensity of this emission peak decreased significantly for composites and among the composites ZnFe₂O₄/9.3% BN showed the peak with the lowest intensity indicating lowest recombination of photo-generated carriers. The result clearly indicated that the introduction of boron nitride improves the separation efficiency of photo-generated electron-hole pairs and its presence is expected to enhance the photocatalytic activity.



Figure 9 Photoluminescence spectra of bare ZnFe₂O₄ and ZnFe₂O₄/x% BN composite catalysts (x = 6.4, 9.3 and 12.1%)

3.8 Electrochemical impedance spectra

The charge transfer resistance and recombination properties of the prepared composites were evaluated by using electrochemical impedance spectroscopy (EIS). The EIS spectra were recorded in the range of 1-100 MHz at an amplitude of 10 mV. Fig 10 shows the Nyquist plots of ZnFe₂O₄, ZnFe₂O₄/6.4% BN, ZnFe₂O₄/9.3% BN and ZnFe₂O₄/12.1% BN. In general, lower the radius of the arc, lower is the electron transfer resistance.^{77,78} Among all the prepared catalysts, ZnFe₂O₄/9.3% BN composite catalysts showed the arc with a smaller radius than bare ZnFe₂O₄ and ZnFe₂O₄/9.3% BN composite catalysts. This reveals that the electron transfer resistance is the lowest in ZnFe₂O₄/9.3% BN composite catalyst. Thus, EIS studies indicate efficient charge separation and better electron transport character due to the incorporation of 9.3% BN over ZnFe₂O₄ catalysts.



Figure 10 Impedance spectra of bare $ZnFe_2O_4$ and $ZnFe_2O_4/x$ % BN composite catalysts (x = 6.4, 9.3 and 12.1%).

3.9 TG and DTA

Thermal stability of the most active catalyst ZnFe₂O₄/9.3% BN was determined by TG and DTA measurements in nitrogen atmosphere from ambient temperature to 1000 °C at a heating rate of 10 °C min and the thermograms are shown in Fig.11. The result clearly indicates that the composite catalysts are highly stable and about 3% wt loss was observed in the entire temperature range due to moisture and residual organic species that may be present.⁷⁹ The first weight loss that occurs below 110 °C is due to loss the of physically adsorbed water on the surface of the catalyst and it is about. 1.5%. Another 1% second mass loss that occurs between 110°C and 520 °C may be due to the combustion of residual organic group if any present.





4. Photocatalytic activity

The photocatalytic activities of the as-prepared bare ZnFe₂O₄ and ZnFe₂O₄/BN nanocomposites were evaluated towards the degradation of Congo red (CR) and Tetracycline (TC) under visible light irradiation. Before illumination, the adsorption experiments were first conducted in the dark for 30 min and after the adsorption-desorption equilibrium the catalysts were evaluated for their photocatalytic activities towards the decolorisation of CR and TC and the results are shown in Fig 12.



Figure 12 Photodegradation of (a) CR and (b) TC by the as-synthesized catalysts

Fig. 12 clearly indicates that the photolysis experiment (without the catalyst) resulted in insignificant degradation of CR and TC. Bare ZnFe₂O₄ catalyst showed better degradation than obtained in the photolysis experiment but showed less degradation when compared to composite catalysts. The catalytic activities of the composite catalysts were found to be significantly high due to the presence of 2D material (BN sheet). Among the composite catalysts, ZnFe₂O₄/9.3% BN showed the highest photocatalytic activity in the degradation of Congo red (92%) and Tetracycline (80%) after irradiation for 240 and 180 min respectively.

The rates of photocatalytic reaction in the degradation of dye and antibiotic catalyzed by both bare and composite catalyst were calculated by modified Langmuir-Hinshelhood expression:¹¹

$$k_{app.} t = -\ln \left(C_t / C_0 \right) \tag{3}$$

Where, k_{app} -apparent reaction rate constant, C_0 - initial concentration of organic dye, C_t - concentration of dye at the reaction time. The kinetic plots are shown in Fig.13.



Figure 13 Kinetic plots in the photodegradation of (a) CR and (b) TC by the as-synthesized catalysts

The straight lines in the figure indicate that the degradation followed pseudo-first-order reaction. From the slopes, the rate constant (min⁻¹) and $t_{1/2}$ values were determined for each catalyst and given in Table 2. Among them, the rate constant values of ZnFe₂O₄/9.3% BN were found to be 0.00982, 0.01019 min⁻¹ in the photodegradation of dye (CR) and antibiotics (TC) respectively. The highest rate constant of ZnFe₂O₄/9.3% BN may be attributed to the significant synergistic effect between ZnFe₂O₄ and Boron Nitride sheets.

Catalysts	Congo Red			Tetracycline			
-	K _{app} (min ⁻¹)	t _{1/2} (min)	R ²	Kapp (min ⁻¹)	t _{1/2} (min)	R ²	
Blank	0.00042	1650	0.99064	0.00035	1980	0.97394	
ZnFe ₂ O ₄	0.00304	227.96	0.99695	0.00282	245.13	0.98764	
ZnFe ₂ O ₄ /6.4% BN	0.00692	100.14	0.95107	0.00469	147.76	0.93696	
ZnFe ₂ O ₄ /9.3% BN	0.00982	70.57	0.96695	0.01019	68.02	0.98327	
ZnFe ₂ O ₄ /12.1% BN	0.00840	82.51	0.94555	0.00767	90.35	0.96966	

Table 2Kinetic parameters and \mathbb{R}^2 values obtained in the degradation of CR and TC.

The UV-Visible absorption evolution spectra of CR and TC obtained over $ZnFe_2O_4/9.3\%$ BN composite catalyst at different time intervals are shown in Fig. 14. It shows that the absorbance of Congo red and Tetracycline decreased gradually at their irrespective λ max values 497 & 363 nm respectively with increase in the reaction time over $ZnFe_2O_4/9.3\%$ BN composite under visible light irradiation. Almost complete degradation of dye and significant degradation in the case of antibiotics were observed.



Figure 14 Absorption evolution spectra of (a) CR and (b) TC over ZnFe₂O₄/9.3% BN catalyst under visible light irradiation at different intervals of time.

To analyze the % photo mineralization in the photocatalytic degradation process, the total organic carbon (TOC) and Chemical Oxygen Demand (COD) analysis were carried out for the samples catalyzed by the active composite catalyst i.e ZnFe₂O₄/9.3 % BN under optimized reaction conditions. The samples were collected at different time intervals such as 30,120 and 240 min for CR and 30,120 and 180 min for TC were analyzed for their TOC content and COD made and the corresponding percentage mineralization values are given in Table.3. The TOC and COD values were found to be lower than the % decolorisation. The result suggested that the dye and antibiotic molecules are not completely degraded into minerals such as CO₂, H₂O during the photocatalytic reaction and the product mixture may contain petite amounts of various organic salts such as formates, acetates, etc.,^{80,81}

Zhrez04/9.5 % biv catalyst at unierent time intervals.								
	Congo red			Tetracycline				
Reaction time (min)	30	120	240	30	120	180		
% degradation by visible spectrophotometry	22	75	93	34	76	80		
% mineralization by TOC	14	66	81	22	69	72		
% mineralization by COD	11	61	72	14	51	64		

Table 3% Degradation and % Mineralization of Congo red and Tetracycline overZnFe2O4/9.3% BN catalyst at different time intervals.

The economic feasibility and photostability of the catalyst were analyzed by recyclability studies. After the first run, ZnFe₂O₄/9.3% BN composite catalyst was filtered, washed with deionized water and ethanol and dried for 60 °C and reused for another four successive photocatalytic results. The activities obtained after each run are shown in Fig 15. It can be observed that there was almost no activity loss even after four repeated runs.



Figure 15 Photo-stability of ZnFe₂O₄/9.3% BN composite catalyst in the degradation of (a) CR and (b) TC.

The spent ZnFe₂O₄/9.3% BN photocatalyst were further characterized by XRD and FESEM. There was no observable change in the morphology of the FESEM image as shown (Fig. 16). This further confirms the high stability and durability of the photocatalyst.



Figure 16 (a) XRD patterns and (b) HR-SEM image of used ZnFe₂O₄/9.3% BN composite catalyst

4.1 Trapping experiments

In order to determine the main active species responsible for the degradation of CR dye the radical trapping experiments were conducted over $ZnFe_2O_4$ / BN composite catalyst. Three different quenchers viz., tert-butanol, ammonium oxalate (AO) and *p*-benzoquinone were used as the hydroxyl radical (•OH), hole (h⁺) and superoxide radical anion (O₂•-) scavengers, respectively.⁸² Fig.17 shows the degradation of CR dye over $ZnFe_2O_4/9.3\%$ BN composite with different scavengers.



Figure 17 Effect of quenchers in the photocatalytic degradation of CR over ZnFe₂O₄/9.3% BN composite catalyst under visible light irradiation

The results indicate that all the above active transient species (OH[•], h⁺, O₂^{•-}) are responsible for the oxidation of CR dye but to different extents. Among them, *p*-benzoquinone reduced the activity from 80% to 66% which clearly proves that superoxide radical anion (O₂^{•-}) is the most active oxidizing species in the CR decolorisation. The addition of ammonium oxalate also reduces the degradation percentage from 80 to 55 of CR which indicates that the hole (h⁺) is the second dominant oxidizing species in this photocatalytic degradation process. The addition of tert-butanol to the reaction system has very less influence on CR degradation which indicates that hydroxyl radicals play a minor role in this photocatalytic system.

4.2 Photocatalytic mechanism

On the basis of the above experimental results, a possible visible light photocatalytic mechanism of CR degradation by $ZnFe_2O_4/BN$ composites is proposed (Fig. (14)). Upon the irradiation of $ZnFe_2O_4/BN$ composite, photo-induced electrons and holes are generated. The photoinduced electrons are then excited from the valence band (VB) to the conduction band (CB)

New Journal of Chemistry Accepted Manuscript

of ZnFe₂O₄ whereby the electron are then transferred to the surface of BN sheets,⁸³ leaving the holes to the VB of ZnFe₂O₄. The high surface area of BN coupled with its excellent transportation property made it easier to transfer the photoinduced electrons to the adsorbed oxygen and produce superoxide radical anion (O₂^{•-}), which oxidizes the harmful organics. As observed in the above experiment, hydroxyl radicals do not play a major role in this photocatalytic system because the VB of ZnFe₂O₄ is negative than the standard redox potential of $E^0 = (-OH/•OH)$ (1.99 eV vs NHE), ^{84,85} suggesting that the generated holes in ZnFe₂O₄ cannot directly oxidize H₂O to the hydroxyl radicals (•OH).



Figure 18 A possible degradation mechanism of ZnFe₂O₄/BN nanocomposite in the photocatalytic reaction.

5 Conclusion

Bare ZnFe₂O₄ nanospheres and ZnFe₂O₄/BN heterostructured nanocomposites with different BN nanosheets amounts were synthesized successfully by solvothermal method. The successful incorporation of BN with ZnFe₂O₄ was confirmed by XRD, FTIR as well XPS and

4

5 6

7 8

9 10

> 38 39

> 40 41

42

43 44

45 46

47

48 49

50 51

52 53

EDAX mapping. Photoluminescence spectra confirm that the presence of nanosheets decreases the recombination of e^{-}/h^{+} pairs due to its excellent transport property and hence effectively increases photocatalytic activity under the visible light when compared to bare ZnFe₂O₄ nanospheres. The enhanced photocatalytic activity is due to higher charge separation efficiency of photogenerated electron-hole pair by the introduction of graphene-like BN nanosheets. ZnFe₂O₄/BN heterostructured nanocomposites could serve as better photocatalyst to remove the organic pollutants present in the wastewater and other ecosystems.

Conflicts of interest

There are no conflicts to declare.

Acknowledgment

The third author is grateful for CSIR through SRF (Award letter No. 09/468/0516/2018 EMR-I, 13/04/2018) and the last author thank DST-TPD (Ref. No. DST/TDT/TDP-06/2017) for financial support.

Reference

- M. R. Hoffmann, S.T. Martin, W. Choi and D. W. Bahnemann, *Chem. Rev.*, 1995, 95, 69-96.
- M. Sathish, B. Viswanathan, R. P. Viswanath and C. S. Gopinath, *Chem. Mater.*, 2005, 17, 6349-6353.
- A. Du, Y. H. Ng, N. J. Bell, Z. Zhu, R. Amal and S. C. Smith, *J. Phys. Chem. Lett.*, 2011, 2, 894-899.
- R. Ramakrishnan, S. Kalaivani, J. Amala Infant Joice and T. Sivakumar, *Appl. Surf. Sci.*, 2012, 258, 2515-2521.
- K. Saito, M. Kozeni, M. Sohmiya, K. Komaguchi, M. Ogawa, Y. Sugahara and Y. Ide, *Phys. Chem. Chem. Phys.*, 2016, 18, 30920-30925.
- X. Wang, J. Liu, S. Leong, X. Lin, J. Wei, B. Kong, Y. Xu, Z. X. Low, J. Yao and H. Wang, ACS appl. Mater. Inter., 2016, 8, 9080-9087
- 7. K. Thamariselvi and T. Sivakumar Appl. Catal., B, 2017, 207, 218-232.

- B. Zhang, W. Fu, X. Meng, A. Ruan, P. Su and H. Yang, *Ceram. Int.*, 2017, 43, 5934-5940.
- 9. A. Brindha and T. Sivakumar, J. Photochem. Photobiology A Chem., 2017, 340, 146-156.
- 10. D. Mani, N. Tsunoji, Y. Yumauchi, M. Arivanandhan, R. Jayavel and Y. Ide, J. Mater. Chem. A, 2018, 6, 5166-5171.
- W. J. Ong, L. L. Tan, S. P. Chai, S. T. Yong and A. R. Mohamed, *Nanoscale*, 2014, 6, 1946-2008.
- 12. A. Brindha, K. Kathiravan and T. Sivakumar, J. Ind. Eng. Chem., 2016, 36, 184-193.
- 13. F. J. Zhang, X. Li, X. Y. Sun, C. Kong, W. J. Xie, Z. Li and J. Liu, *Appl. Surf. Sci.*, 2019, 487, 734-742.
- 14. I. J. J. Amala and T. Sivakumar, RSC Adv., 2015, 5, 9792-9805.

4

5 6

7 8

9 10

MdZ2:25:E0202/E1

²Chnobadsil

ii ຊີອິດ 37

> 38 39

> 40 41

> 42

43 44

45 46

47 48

49

50 51

52 53

54 55

- 15. F. J. Zhang, S. F. Zhu, F. Z. Xie, J. Zhang and Z. D. Meng, *Sep. Purif. Technol.*, 2013, **113**, 1-8.
- 16. D. Peng, S. Beysen, Q. Li, J. Jian, Y. Sun and J. Jiwuer, Particuology., 2009, 7, 35-38.
- 17. T. Wang, L. Zhang, H. Wang, W. Yang, Y. Fu, W. Zhou, W. Yu, K. Xiang, Z. Su, S. Dai and L. Chai, ACS Appl. Mater. Interfaces., 2013, 5, 12449-12459.
- j. Liu, G. Liu, C. Yuan, L. Chen, X. Tian and M. Fang, New. J. Chem., 2018, 42, 3736-3747.
- **19.** C. T. Lie, P. C. Kuo, W. C. Hsu, I. J. Chang and J. W. Chen, *J. Magn. Magn. Mater.*, 2002, **239**, 160-163.
- R. Sahoo, S. Santra, C. Ray, A. Pal, Y. Negishi, S. K. Ray and T. Pal, *New. J. Chem.*, 2016, 40, 1861-1871.
- Z. Mousavi, F. Soofivand, M. Esmaeili-Zare, M. Salavati-Niasari and S. Bagheri, *Sci. Rep.*, 2016, 6, 20071.
- 22. J. Liu, Y. Bin and M. Matsuo, J. Phys. Chem. C., 2011, 116, 134-143.
- 23. A. A. Tahir and K. U. Wijayantha, J. Photochem. Photobiol., A, 2010, 216, 119-125.
- 24. Y. Xu, S. Wu, X. Li, Y. Huang, Z. Wang, Y. Han, J. Wu, H. Meng and X. Zhang, New. J. Chem., 2017, 41, 15433-15438.
- 25. M. Li, Y. Wang, P. Tang, N. Xie, Y. Zhao, X. Liu, G. Hu, J. Xie, Y. Zhao, J. Tang and T. Zhang, *Chem. Mater.*, 2017, 29, 2769-2776.
- 26. B. Bian, Q. Liu and S. Yu, New. J. Chem., 2018, 42, 18189-18200.

4 5

6

7 8

9 10

²Chnobadsil

iiq 37 37

> 38 39

> 40 41

> 42

43 44

45 46

47 48

49

50 51

52 53

- 27. P. Zhang, I. Lo, D. O'Connor, S. Pehkonen, H. Cheng and D. Hou, J. Colloid Interface Sci., 2017, 508, 39-48.
 - 28. X. S. Nguyen, G. Zhang and X. Yang, ACS Appl. Mater. Interfaces., 2017, 9, 8900-8909.
 - 29. H. Xu, Z. Wu, M. Ding and X. Gao, Mater. Des., 2017, 114, 129-138.
 - 30. X. Lv, J. Wang, Z. Yan, D. Jiang and J. Liu, J. Mol. Catal. A: Chem., 2016, 418, 146-153.
 - 31. C. Tang, Y. Bando, T. Sato and K. Kurashima, Chem. Commun., 2002, 12, 1290-1291.
 - **32.** M. Yankowitz, K. Watanabe, T. Taniguchi, P. San-Jose and B. J. LeRoy, *Nat. Commun,* 2016, **7**, 1-8.
 - 33. C. Huang, C. Li and G. Shi, Energy Environ. Sci., 2012, 5, 8848-8868
 - 34. Z. Zhang, E. S. Penev and B. I. Yakobson, Chem. Soc. Rev., 2017, 46, 6746-6763.
 - 35. P. Wu, S. Yang, W. Zhu, H. Li, Y. Chao, H. Zhu, H. Li and S. Dai, *Small*, 2017, 13, 1701857.
 - 36. G. Xie, K. Zhang, B. Guo, Q. Liu, L. Fang and J. R. Gong, Adv. Mater., 2013, 25, 3820-3839.
 - 37. J. Wang, J. Hao, D. Liu, S. Qin, C. Chen, C. Yang, Y. Liu, T. Yang, Y. Fan, Y. Chen and W. Lei, *Nanoscale*, 2017, 9, 9787-9791.
 - 38. D. Liu, W. Lei, S. Qin and Y. Chen, Sci. Rep., 2014, 4, 4453
 - **39.** K. Zhang, Y. Feng, F. Wang, Z. Yang and J. Wang, *J. Mater. Chem. C.*, 2017, **5**, 11992-12022
 - 40. L. Wang, P. Hu, Y. Long, Z. Liu and X. He, J. Mater. Chem. C, 2017, 5, 22855-22876.
 - **41.** S. R. Naqvi, G. S. Rao, W. Luo, R. Ahuja and T. Hussain, *ChemPhysChem.*, 2017, **18**, 513-518.
 - 42. J. Zhu, H. Wang, J. Liu, L. Ouyang and M. Zhu, J. Nanotechnol., 2017, 28, 115604.
 - 43. J. Di, J. Xia, M. Ji, B. Wang, S. Yin, Q. Zhang, Z. Chen and H. Li, *Appl. Catal.*, B., 2016, 183, 254-262.
 - 44. H. S. Lim, J. W. Oh, S. Y. Kim, M. J. Yoo, S. D. Park and W. S. Lee, *Chem. Mater.*, 2013, 25, 3315-3319.
 - **45.** J. Zhu, Z. Da, H. Xu, J. Yan, H. Ji, H. Shu and H. Li, *Appl. Surf. Sci.*, 2014, **313**, 1-9.
 - 46. M. Nasr, R. Viter, C. Eid, R. Habchi, P. Miele and M. Bechelany, *New J. Chem.*, 2017, 41, 81-89.

4 5

6

7 8

9 10

²Chnobadsil

ii ຊີອິດ 37

> 38 39

> 40 41 42

> 43 44

> 45 46

47 48

49

50 51

52 53

54 55

- **47.** Y. Song, H. Xu, C. Wang, J. Chen, J.Yan, Y. Xu, Y. Li, C. Liu, H. Li and Y. Lei, *RSC Adv.*, 2014, **4**, 56853-56862.
- 48. J. Feng, Y. Wang, L. Zou, B. Li, X. He, Y. Ren, Y. Lv and Z. Fan, J. Colloid Interface Sci., 2015, 438, 318-322.
- **49.** Q. Weng, X. Wang, X. Wang, Y. Bando and D. Golberg, *Chem. Soc. Rev.*, 2016, **45**, 3989-4012.
- Z. He, C. Kim, L. Lin, T. H. Jeon, S. Lin, X. Wang and W. Choi, *Nano Energy*, 2017, 42, 58-68.
- A. Nag, K. Raidongia, K. P. Hembram, R. Datta, U. V. Waghmare and C. N. R. Rao, ACS Nano, 2010, 4, 1539-1544.
- **52.** E. Elangovan, T. Sivakumar, A. Brindha, K. Thamaraiselvi, K. Sakthivel, K. Kathiravan and S. Aishwarya, J. Nanosci, 2019, **19**, 4429-4437.
- D. A. Aljuboury, P. Palaniandy, H. B. Abdul Aziz, s. Feroz and S. S. Abu Amr, Water. Sci. Technol., 2016, 74, 1312-1325.
- **54.** S. Thamaraiselvi, T. Sivakumar, P. Sahaya Murphin Kumar, K. Sakthivel, K. Kathiravan and D. Arulselvan, *J. Photochem. Photobiol. A.*, 2018, **356**, 425-439.
- 55. W. Song, J. Xie, S. Liu, G. Cao, T. Zhu and X. Zhao, New .J. Chem., 2012, 36, 2236-2241.
- 56. C. Xiong and W. Tu, Eur. J. Inorg. Chem., 2014, 3010-3015.
- 57. J. Di, J.X. Xia, M.X. Ji, B. Wang, S. Yin, Q. Zhang, Z.G. Chen, H.M. Li, ACS Appl. Mater. Interfaces., 2015, 7, 20111–20123.
- 58. J. Di, J.X. Xia, M.X. Ji, H.P. Li, H. Xu, H.M. Li, R. Chen, Nanoscale., 2015, 7, 11433– 11443
- **59.** G. Li, B. Shen, Y. Li, B. Zhao, F. Wang, C. He, Y. Wang, and M. Zhang, *J. Hazard. Mater.*, 2015, **298**, 162-169.
- Zhang, Ping, Irene Lo, David O'Connor, Simo Pehkonen, Hefa Cheng, and Deyi Hou. J. Colloid. Interf. Sci., 2017, 508, 39-48.
- 61. Z. Zhao, Z. Yang, Y. Wen and Y. Wang, J. Am. Ceram. Soc., 2011, 94, 4496-4501.
- R. C. Zhang, D. Sun, A. Lu, S. Askari, M. Macias-Montero, P. Joseph, D. Dixon, K. Ostrikov, P. Maguire and D. Mariotti, ACS Appl. Mater. Interfaces., 2016, 8, 13567-13572.
- 63. H. Lv, L. Ma, P. Zeng, D. Ke and T. Peng, J. Mater. Chem., 2010, 20, 3665-3672.

New Journal of Chemistry Accepted Manuscript

- 64. M. Wang, Z. Ai and L. Zhang, J. Phys. Chem. C., 2008, 112, 13163-13170.
- 65. Y. Sharma, N. Sharma, G. S. Rao and B. V. R. Chowdari, *Electrochim. Acta.*, 2008, 53, 2380-2385.
- 66. L. Li, H. Bi, S. Gai, F. He, P. Gao, Y. Dai, X. Zhang, D. Yang, M. Zhang and P. Yang, *Scientific reports.*, 2017, **7**, 43116.
- 67. F. Li, X. Liu, Q. Yang, J. Liu, D. G. Evans and X. Duan, *Mater. Res. Bull.*, 2005, 40, 1244-1255.
- 68. Z. Zhao, Z. Yang, Y. Wen and Y. Wang, J. Am. Ceram. Soc., 2011, 94, 4496-4501.
- 69. L. Ci, L. Song, C. Jin, D. Jariwala, D. Wu, Y. Li, A. Srivastava, Z. F. Wang, K. Storr, L. Balicas and F. Liu, Nat. *Mater.*, 2010, **9**, 430.
- 70. W. Li, Q. Wang, L. Huang, Y. Li, Y. Xu, Y. Song, Q. Zhang, H. Xu and H. Li, RSC Adv., 2015, 5, 88832-88840.
- 71. S. H. Xu, W. F. Shangguan, J. Yuan, J. W. Shi and M. X. Chen, Mater. Sci. Eng. B., 2007, **137**, 108–111.
- 72. P. M. Botta, E. F. Aglietti and J. M. PortoL_opez, Mater. Res. Bull., 2006, 41, 714-723
- 73. J. Han, K. Liu, R. Chang, L. Zhao and X. Yan, Angew. Chem., 2019, 131, 2022-2026.
- 74. S. K. Khore, S. R. Kadam, S. D. Naik, B. B. Kale and R. S. Sonawane, New. J. Chem., 2018, 42, 10958-10968.
- **75.** K. Maruthathurai, T. Sivakumar, S. Aishwarya, R. Sudhakar, V. Thanigaivel, K. Sakthivel, and E. Elangovan, *Mater. Res. Bull.*, 2020, 110782.
- 76. H. Lv, L. Ma, P. Zeng, D. Ke and T. Peng, J. Mater. Chem., 2010, 20, 3665-3672.
- 77. J. Li, H. Yuan and Z. Zhu, Applied Surface Science, 2016, 385, 34-4
- 78. J. Liqiang, Q. Yichun, W. Baiqi, L. Shudan, J. Baojiang, Y. Libin, F. Wei, F Honggang and S. Jiazhong, *Sol. Energy Mater. Sol. Cells.*, 2006, **90**, 1773-1787.
- 79. T. B. Nguyen and R. A. Doong, *RSC Adv.*, 2017, 7, 50006-50016.
- 80. J. Li, H. Yuan and Z. Zhu, Appl. Surf. Sci., 2016, 385, 34-4.
- 81. L. Yin, Z. Wang, L. Lu, X. Wan and H. Shi, New Journal of Chemistry, 2015, 39, 4891-4900.
- A. Brindha, T. Sivakumar, R. Sudhakar, E. Elangovan and K. Kathiravan, *Ecotox. Environ. Safe.*, 2018, **151**, 118-126.

- 83. H. Zhu, M. Fang, Z. Huang, Y. G. Liu, K. Chen, C. Tang and X. Wu, RSC adv., 2016, 6, 56069-56076.
- 84. B. Krishnakumar, T. Imae, J. Miras and J. Esquena, Sep. Purif. Technol., 2014, 132, 281-288.
- 85. J. Su, Q. Shang, T. Guo, S. Yang, X. Wang, Q. Ma, H. Guan, F. Xu and S. C. Tsang, *Mater. Chem. Phys.*, 2018, **219**, 22-29.

New Journal of Chemistry Accepted Manuscript