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# Metal peroxides as potential photocatalysts for environmental remediation†

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Inorganic oxide materials such as TiO<sub>2</sub> and ZnO have been extensively studied for environmental remediation, that operates through photo generated Reactive Oxygen Species (ROS) such as H<sub>2</sub>O<sub>2</sub>, ·OH and O<sub>2</sub><sup>·-</sup> to decontaminate waste water. However, inorganic solid oxidants such as metal peroxides capable of generating ROS in aqueous solutions have not been studied for environmental remediation. Towards this objective, we have synthesized peroxides of Zn, Mg, and Ba and characterized these by powder X-ray diffraction, Transmission Electron Microscopy, UV-visible spectroscopy, and X-ray photoelectron spectroscopy. The photocatalytic activity of these wide band gap semiconductors has also been investigated. The novelty of the work is in the use of these peroxides as chemical sources of ROS in aqueous suspensions in addition to their photochemical generation. Hence, these peroxides, in particular Ba, exhibit high photocatalytic activity, better than the well-known ZnO. The mechanisms of ROS generation and subsequent dye degradation are elucidated. ROS has been estimated and is correlated to the photocatalytic activity. This work reports for the first time BaO<sub>2</sub> as potential photocatalyst.

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## 1. Introduction

Since the breakthrough discovery of sunlight driven water splitting on the TiO<sub>2</sub> surface by Fujishima and Honda in 1972, inorganic materials belonging to the class of semiconducting oxides have been extensively investigated as photocatalysts for environmental remediation.<sup>1–5</sup> Oxides such as ZnO and TiO<sub>2</sub> have been studied for dye degradation in wastewater treatment through an advanced oxidation process.<sup>6,7</sup> It is an efficient process as this involves Reactive Oxygen Species (ROS) such as O<sub>2</sub><sup>·-</sup>, ·OH radical, H<sub>2</sub>O<sub>2</sub>. These ROS are powerful oxidizing agents that can oxidize dyes and other organic contaminants. ROS are produced at the surface of a semiconductor through the well-established photo excitation across its band gap.<sup>8–10</sup> Among the various ROS, the most stable H<sub>2</sub>O<sub>2</sub> can serve as the reservoir of active ROS. Under UV irradiation, H<sub>2</sub>O<sub>2</sub> can undergo photolysis to form ·OH. In a photocatalytic process, H<sub>2</sub>O<sub>2</sub> accepts electrons from the conduction band, facilitating charge separation and forms reactive hydroxyl radicals ·OH that are most powerful oxidizing agents.<sup>11,12</sup>

The addition of small amounts of H<sub>2</sub>O<sub>2</sub> into the system is known to enhance the photocatalytic process.<sup>13,14</sup> If H<sub>2</sub>O<sub>2</sub> can be

generated by the photocatalyst itself then, it would be advantageous. In this connection, inorganic solid oxidants such as metal peroxides are important as these could function as both semiconductor photocatalysts as well H<sub>2</sub>O<sub>2</sub> sources. Accordingly, inorganic peroxides, MO<sub>2</sub> (M = Zn, Mg, Ba) can chemically generate H<sub>2</sub>O<sub>2</sub> in aqueous suspension as per the equation, in equilibrium.



It is a surface reaction that generates H<sub>2</sub>O<sub>2</sub> and MO in ppm levels. The released H<sub>2</sub>O<sub>2</sub> under UV light generates ·OH radicals which are powerful oxidizing agents that can oxidize contaminants. Inorganic solid oxidants like CaO<sub>2</sub>, MgO<sub>2</sub> and ZnO<sub>2</sub> are useful in different fields<sup>15–17</sup> including cancer treatment. There is only one study each on the peroxides of Mg & Zn for dye degradation.<sup>18,19</sup> These deal with the photochemical generation of H<sub>2</sub>O<sub>2</sub> and not on the chemical generation of H<sub>2</sub>O<sub>2</sub> by these peroxides. In this work, we present our study on dye degradation [Rhodamine (RhB), Methylene Blue (MB)] by the peroxides of Zn, Mg and Ba under UV light and it proves that these are potential photocatalysts due to chemical and photochemical generation of ROS.

## 2. Experimental

### 2.1 Materials

For preparation of metal peroxides, the precursors such as Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O (AR grade 99.99%), Mg(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O (AR grade 99.99%), Ba(CH<sub>3</sub>COO)<sub>2</sub> (AR grade) and KOH are

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procured from SD Fine chemicals using without any further purification. Hydrogen peroxide (30%  $\text{H}_2\text{O}_2$ ) obtained from Merck was used as a peroxide source and for photocatalytic studies, Rhodamine B and Methylene Blue were purchased from SRL Chemicals.

## 2.2 Synthesis of metal peroxides

Metal peroxides were synthesized *via* a simple precipitation method with the following procedure. 25 ml of 2 M KOH was added into 25 ml of 1 M metal acetate,  $\text{M}(\text{CH}_3\text{COO})_2$  ( $\text{M} = \text{Zn}, \text{Mg}, \text{Ba}$ ) solution under stirring. Then, hydrogen peroxide (30% w/v) was added under stirring. Precipitates were formed, filtered and washed with ethanol and deionized water, and finally dried at 60 °C for 3 h.

## 2.3 ROS estimation

**2.3.1 Estimation of  $\text{H}_2\text{O}_2$ .**  $\text{H}_2\text{O}_2$  generated was estimated by  $\text{KMnO}_4$  redox titrations. A known quantity of metal peroxide was suspended in 50 ml of water. Then, appropriate amounts of  $\text{KMnO}_4$  and  $\text{H}_2\text{SO}_4$  were added. It was kept under constant stirring under ambient condition. At regular intervals, 5 ml aliquots were withdrawn, filtered through membrane filter.  $\text{H}_2\text{O}_2$  was estimated by a standard back titration.

**2.3.2 Estimation of  $\cdot\text{OH}$  radicals by pCBA.** The amount of  $\cdot\text{OH}$  radicals released in the aqueous suspensions of metal peroxides under UV light was measured by degradation of *p*-

chlorobenzoic acid (pCBA).<sup>20</sup> To 50 ml of 10 ppm pCBA, 25 mg of metal peroxide was added. The suspension was irradiated under UV light and at regular intervals of 30 min, 1 ml of suspension was taken and centrifuged, the supernatant was examined by HPLC-UV for pCBA. Agilent 1100 series instrument (EVO C18 column) was employed, in an isocratic mode with solvent composition 40% water and 60% MeOH and flow rate of  $0.5 \text{ ml min}^{-1}$ . The production of  $\cdot\text{OH}$  is directly proportional to degradation of pCBA and concentration of  $\cdot\text{OH}$  can be obtained by the following equation

$$-d[\text{pCBA}]/dt = K_{\text{OH}} \text{pCBA}[\cdot\text{OH}] \quad (2)$$

where,  $K_{\text{OH}} \text{pCBA}$  is the rate constant of pCBA and  $[\cdot\text{OH}]$  is the steady state concentration of  $\cdot\text{OH}$  radicals.

**2.3.3 Estimation of superoxide ( $\text{O}_2^-$ ).** Superoxide radicals generated in metal peroxide suspensions were estimated by Nitro Blue Tetrazolium (NBT).<sup>21</sup> NBT absorbs maximum at 259 nm but on reaction with superoxide radicals, it is degraded to mono formazon and difarmazon. The release of superoxide radicals was followed by monitoring the degradation of NBT employing UV-Visible Spectroscopy.

## 2.4 Photocatalytic degradation of dye

20 mg of metal peroxides was suspended in the dye (50 ml, 10 ppm) and stirred for 30 min in dark to achieve adsorption and desorption equilibrium. 2 ml of aliquots from suspension were

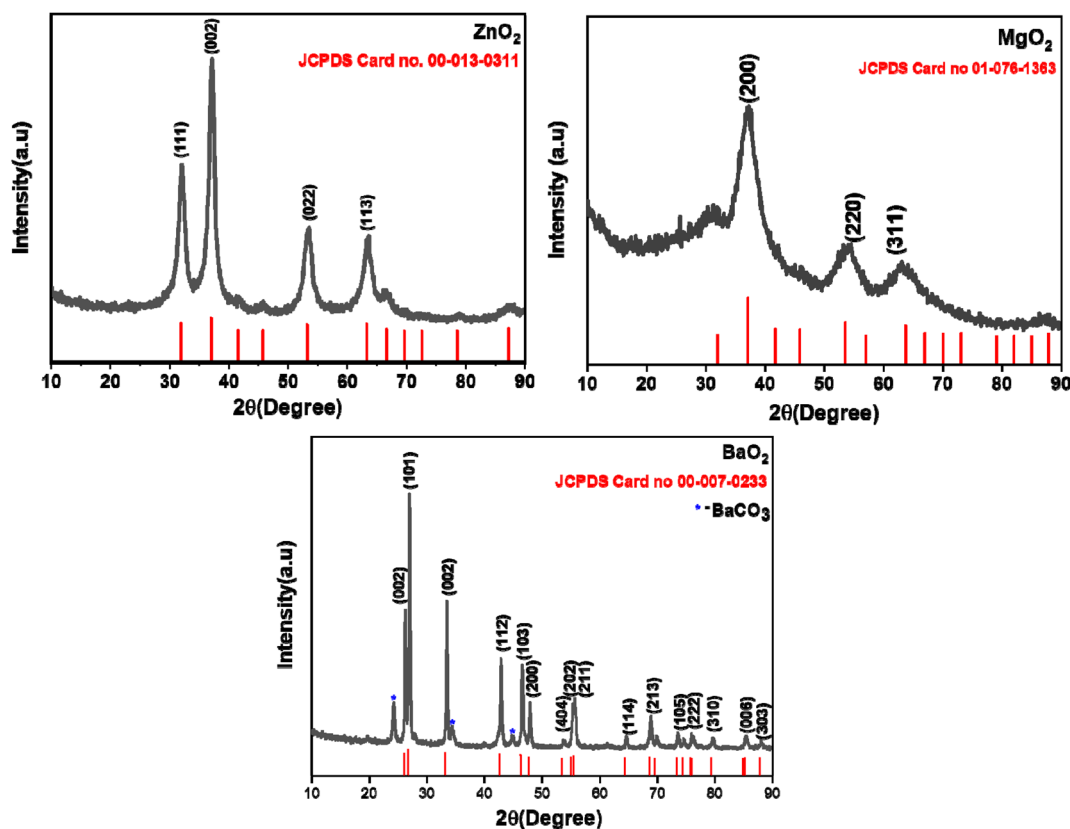


Fig. 1 Powder X-ray diffraction patterns of  $\text{ZnO}_2$ ,  $\text{MgO}_2$  and  $\text{BaO}_2$ .



drawn at regular intervals, centrifuged at 4000 rpm. Rhodamine B degradation was followed by UV-visible spectroscopy through monitoring the absorption maximum of the dye with time. Photocatalysis was carried out under UV irradiation using Hg lamp ( $17 \text{ mW cm}^{-2}$ ) as UV source. Dye solution without catalyst was used as control to negate the effect of light on dye. The degradation rate is calculated using the formula,

$$\% \text{ degradation} = (C_0 - C)/C_0 \times 100 \quad (3)$$

where  $C_0$ ,  $C_t$  is the concentration at  $t_0$  & at time 't' respectively.

### 2.5 TOC (total organic content)

To study the extent of mineralization, TOC of RhB (10 ppm) before and after UV irradiation were analyzed using Aurora TOC analyzer (O.I analytics) through converting carbon (from sample) *via* acidification and oxidation to  $\text{CO}_2$ , the TOC was measured using an infra-red detector.

### 2.6 Characterization

Phase formation was analyzed by Bruker D8 Advance powder X-Ray Diffractometer (Bruker AXS GmbH, Karlsruhe, Germany) with  $\text{CuK}_\alpha$  source. The crystallite size was calculated using Scherrer formula. Transmission Electron Microscopy (FEI-

Tecni G2 20 S-TWIN) was used for studying morphology and particle size. UV-Visible Diffuse Reflectance spectra were measured using Jasco V 570 UV-Vis spectrophotometer. X-Ray photoelectron spectra were recorded using K-Alpha instrument (XPS K-Alpha surface analysis, Thermo fisher scientific, UK).

## 3. Results and discussion

### 3.1 Material characterization

XRD patterns (Fig. 1) confirm that the products of  $\text{ZnO}_2$ ,  $\text{MgO}_2$  and  $\text{BaO}_2$  are single phasic, nano crystalline ( $\text{BaO}_2$  contains  $\text{BaCO}_3$  impurity, around 5%) by referring to the JCPDS database.  $\text{ZnO}_2$  (JCPDS: 00-013-0311) and  $\text{MgO}_2$  (JCPDS: 01-076-1363) have cubic structure with lattice parameters 4.785 Å and 4.820 Å respectively.  $\text{BaO}_2$  (JCPDS: 00-007-0233) crystallizes in tetragonal system with  $a = 3.810$  Å and  $c = 6.840$  Å. Average crystallite sizes as calculated by Scherrer formula for  $\text{ZnO}_2$ ,  $\text{MgO}_2$  and  $\text{BaO}_2$  are 5 nm, 2 nm and 30 nm respectively.

TEM images (Fig. 2) confirm that the particles of  $\text{ZnO}_2$  and  $\text{MgO}_2$  are mostly spherical with sizes in the range of 3–5 nm.  $\text{BaO}_2$  shows flower like morphology. The optical band gap is measured from absorption spectrum using Tauc plot (Fig. 3) obtained from UV-Vis-DRS data

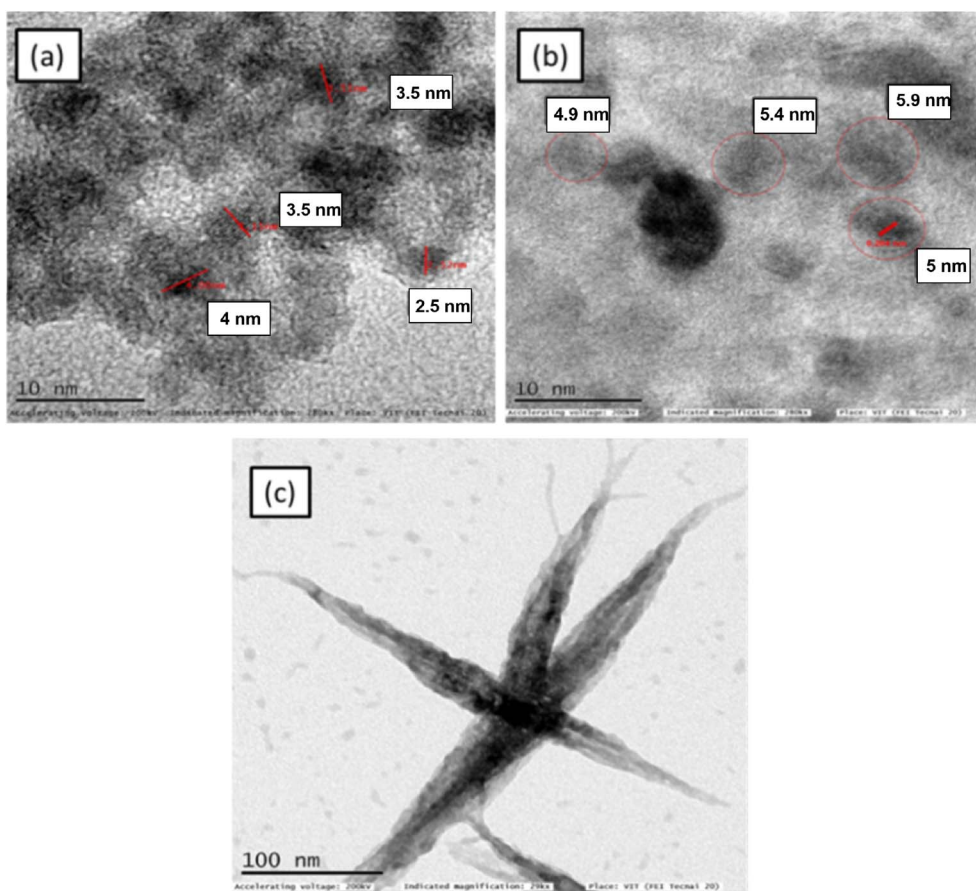


Fig. 2 TEM images of (a)  $\text{ZnO}_2$  (b)  $\text{MgO}_2$  (c)  $\text{BaO}_2$ .



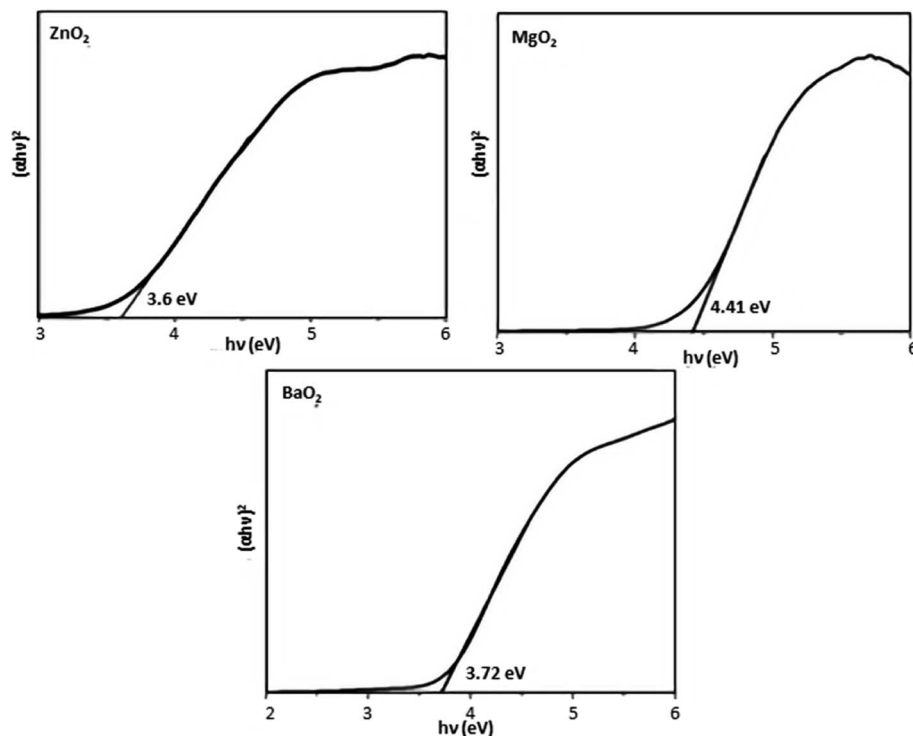


Fig. 3 Tauc's plots of metal peroxides.

$$(\alpha hv)^n = A(hv - E_g) \quad (4)$$

where,  $hv$  is the discrete photon energy,  $\alpha$  denotes absorption coefficient,  $A$  is constant,  $E_g$  is the band gap and exponent  $n$  depends on type of transition. The measured band gaps of  $ZnO_2$ ,  $MgO_2$  and  $BaO_2$  are 3.6, 4.41 and 3.72 eV respectively (Fig. 3).

To ascertain esp the presence of peroxide species, we have recorded XPS spectra. Fig. 4a–f shows XPS of synthesized metal peroxides. XPS spectra (a) of Zn shows a peak at 1021 eV ( $2p_{3/2}$ ) and 1044 eV ( $2p_{1/2}$ ) confirming valence of Zn in  $2^+$ . O 1s spectra (b) of  $ZnO_2$  exhibits three peaks, the peak at higher binding energy 532.5 eV corresponds to  $O_2^{2-}$  species and 531.2 eV corresponds to hydroxyl species which are associated with oxygen vacancy.<sup>22</sup> Peak at lower binding energy 528.4 eV corresponds to loosely bound oxygen species.<sup>23,24</sup> The binding energy of Mg (c) 1s is 1034 eV confirming  $Mg^{2+}$  state in  $MgO_2$ . O 1s (d) of  $MgO_2$  shows a peak at 532.5 eV confirming peroxides species. The high-resolution Ba 3d (e) spectra, which comprise two dominant peaks 779.5 eV and 794.9 eV correspond to the binding energy of Ba  $3d_{5/2}$  and Ba  $3d_{3/2}$ , respectively. The energy states of Ba,  $3d_{5/2}$  and  $3d_{3/2}$  confirm the presence of barium in its bivalent state ( $Ba^{2+}$ ). The XPS data for the O 1s state in  $BaO_2$  reveals a peak at 532.7 eV O 1s confirming the peroxide group.

### 3.2 Estimation of ROS from metal peroxides

It is important to estimate the ROS released to understand the photocatalytic activity. Fig. 5a shows  $H_2O_2$  release with time in aqueous suspensions.  $BaO_2$  produces relatively higher

concentrations of  $H_2O_2$  (35 ppm) followed by  $MgO_2$  and  $ZnO_2$ . The concentration of  $\cdot OH$  radicals produced by metal peroxides under UV light were analyzed by pCBA degradation. Table S1† shows % degradation of pCBA by metal peroxides with time under UV light. Fig. 5b shows the release of  $\cdot OH$  radicals from aqueous suspensions under UV light and its concentration increases with time.  $BaO_2$  releases the highest amount of  $\cdot OH$  radicals. These peroxides release  $H_2O_2$  in aqueous suspension in ppm levels and is a surface reaction as depicted in eqn (1).

$H_2O_2$  formed in ppm level [saturation level] is sufficient to degrade dyes present in ppm levels in the waste water. More importantly, the products formed MO (ref. 25–27) in ppm levels are also UV active photocatalysts. It is to be noted that  $H_2O_2$  formed undergoes photochemical reactions with UV light generating  $\cdot OH$  radicals. The photocatalytic activity is correlated to the amount of ROS released during the process. The higher the amount, the higher is the activity.

To ascertain the presence of  $O_2^-$ , NBT degradation study is carried out. Fig. 6 shows kinetics of degradation of NBT by metal peroxides under UV irradiation. Significant degradation of NBT with time is observed indicating the release of  $O_2^-$ .

### 3.3 Photocatalytic degradation of dyes under UV irradiation

Rhodamine B dye degradation is illustrated under UV irradiation to demonstrate the photocatalytic activity. Fig. 7 shows degradation of RhB (20 ppm) as followed by the absorption maximum at 554 nm with time. It confirms the degradation of RhB as indicated by the decrease of intensities of absorption maximum with time. Table 1 lists the % degradation and time



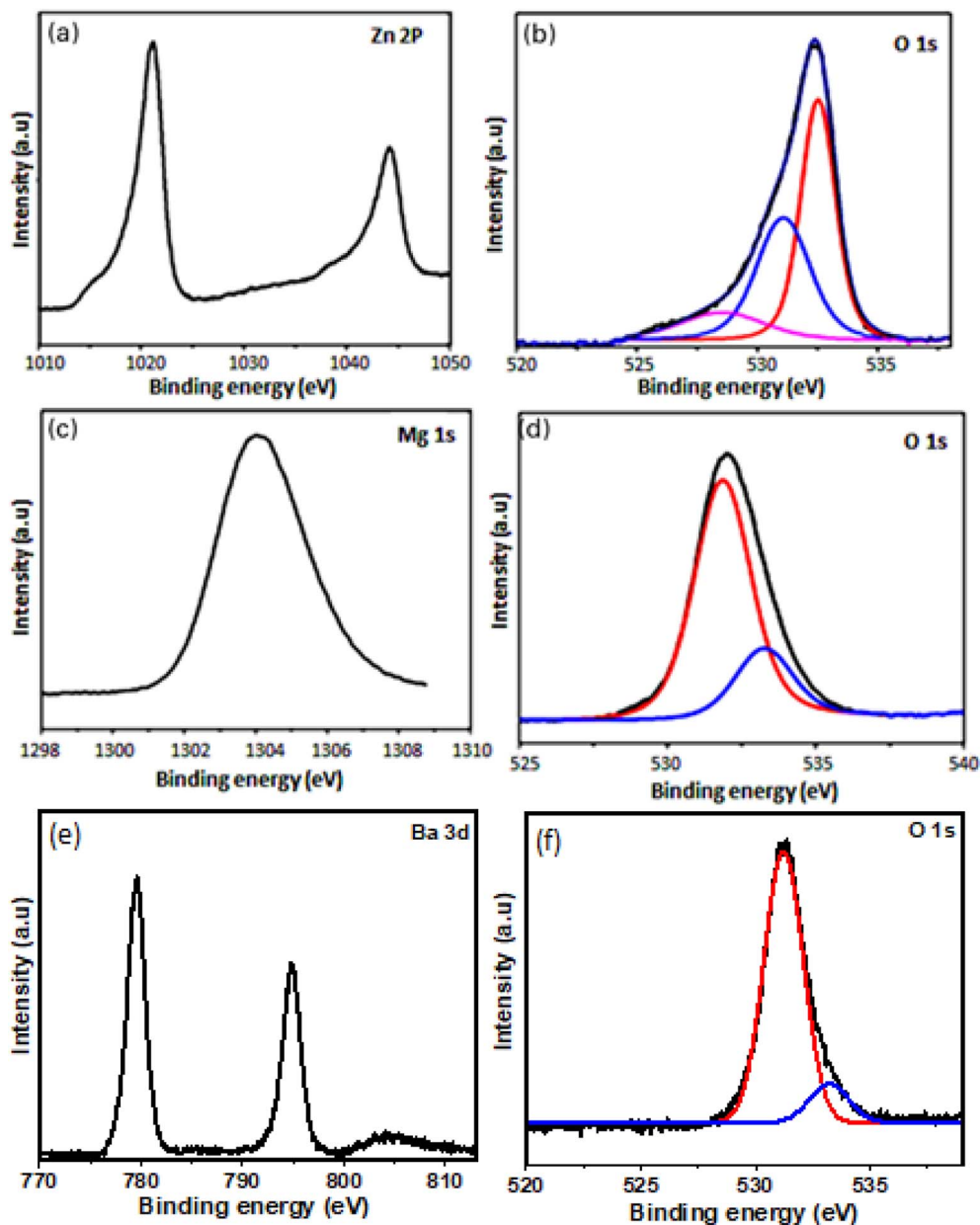


Fig. 4 X-ray photoelectron spectra of (a) Zn 2p (b) O 1s of ZnO<sub>2</sub> (c) Mg 2p (d) O 1s of MgO<sub>2</sub> (e) Ba 3d (f) O 1s of BaO<sub>2</sub>.

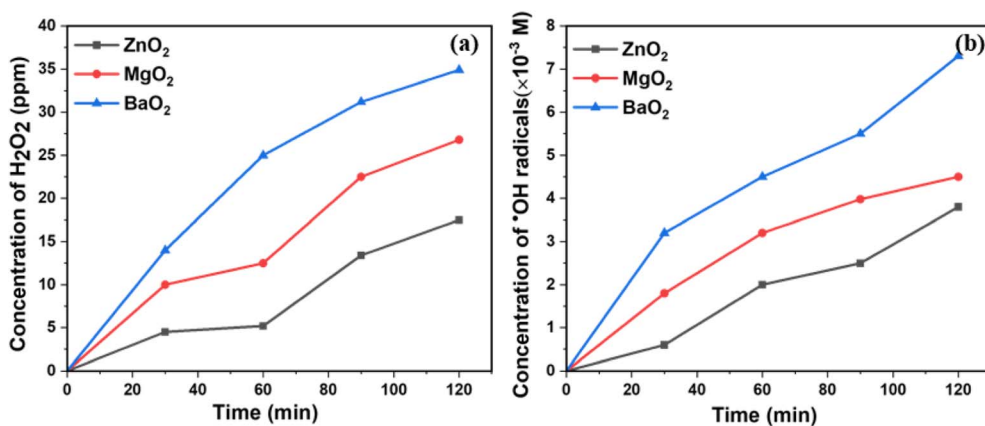


Fig. 5 (a) H<sub>2</sub>O<sub>2</sub> produced (b) ·OH radicals produced by metal peroxides under UV light.



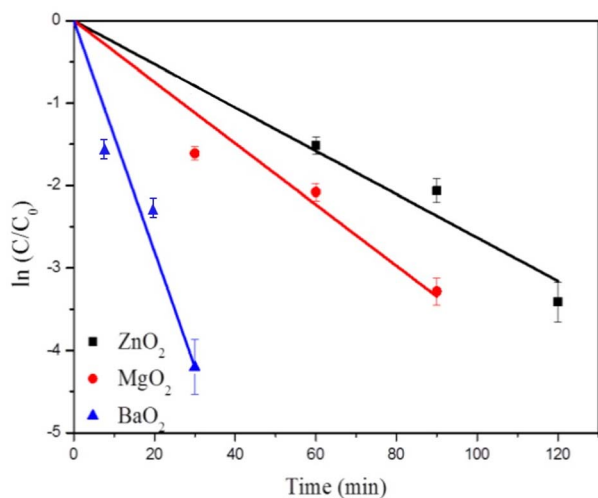


Fig. 6 Degradation of NBT.

duration along with rates of degradation. All the three catalysts degrade more than 95% within 120 minutes. Most of the dye is degraded within the first 30 minutes over the surfaces of the catalysts. BaO<sub>2</sub> exhibits highest photocatalytic activity close to 100% degradation within 30 min, followed by MgO<sub>2</sub> and ZnO<sub>2</sub>. The kinetics of dye degradation is shown in Fig. 8 and it follows

first order kinetics in agreement with Langmuir–Hinshelwood mechanism. Accordingly, a plot of  $\ln(C/C_0)$  versus time is a straight line and the slope is equal to the rate constant,  $C$  concentration at time  $t$ , whereas  $C_0$  is the initial concentration. BaO<sub>2</sub> shows the highest rate of degradation  $13.4 \times 10^{-2} \text{ min}^{-1}$  (Fig. 8).

ZnO<sub>2</sub>, MgO<sub>2</sub> and BaO<sub>2</sub> have been studied against MB too and Table 1 depicts the results (Fig. S1†). Ba peroxide shows maximum activity with highest rate of degradation. It can be attributed to the highest amount of H<sub>2</sub>O<sub>2</sub> released from BaO<sub>2</sub> and hence more amount of ROS. FT-IR data of the ZnO<sub>2</sub> before and after the reaction confirm that no dye adsorption occurs in the photocatalytic process (Fig. S2†).

These peroxides having band gaps in the range 3.6 to 4.4 eV are expected to be active in narrow range of the solar spectrum but interestingly these generate H<sub>2</sub>O<sub>2</sub> in aqueous suspensions which on excitation with UV light can produce most reactive ·OH radicals. It can degrade the dyes or organic contaminants as per mechanisms below. Due to the chemical generation of H<sub>2</sub>O<sub>2</sub>, all the three peroxides exhibit significant dye degradation under UV light.

#### 3.4 Mechanism of dye degradation under UV light

Metal peroxides when suspended in water release H<sub>2</sub>O<sub>2</sub> as shown in eqn (1). Harbour *et al.* observed that H<sub>2</sub>O<sub>2</sub> under UV

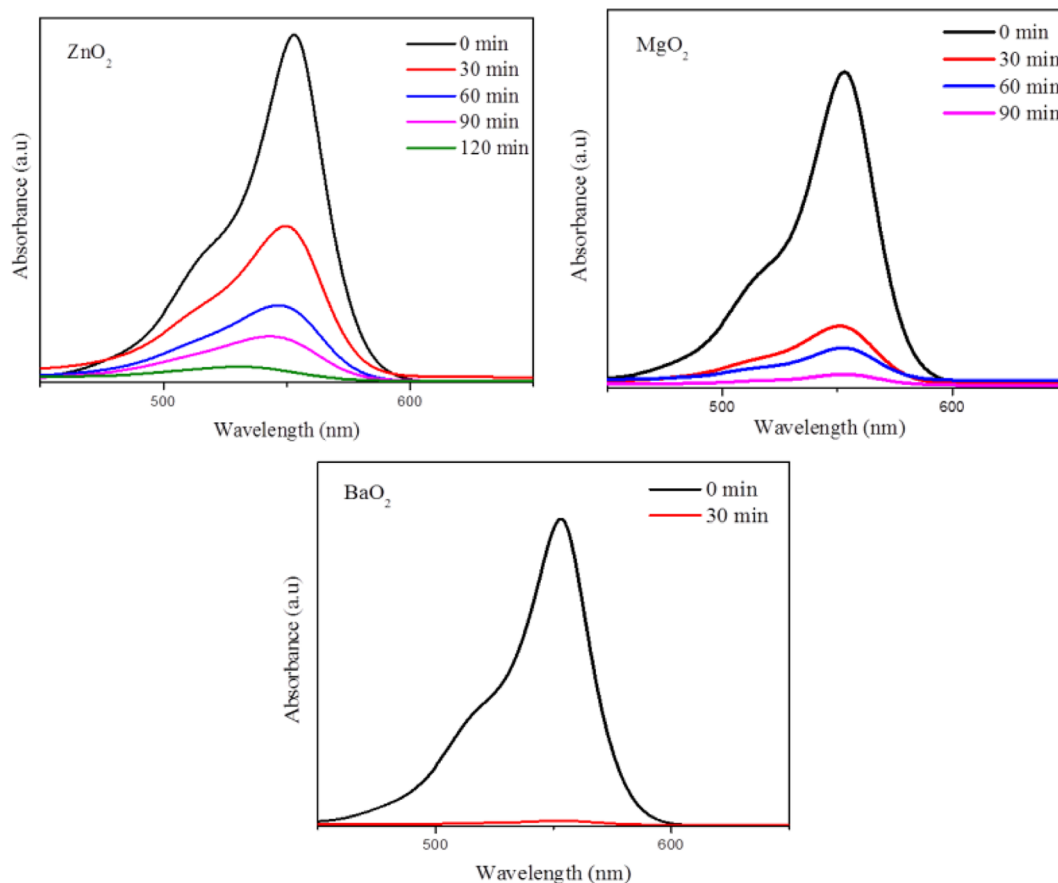


Fig. 7 Dye (RhB) degradation with time as followed by UV-visible spectroscopy.

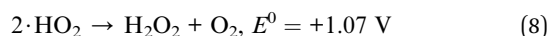
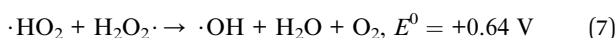
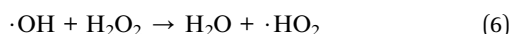
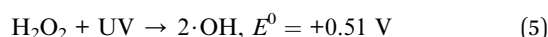


Table 1 % Of degradation and rate of degradation of dyes by metal peroxides under UV irradiation

| Composition      | Dye (10 ppm) | % Degradation/min | Rate of degradation ( $\text{min}^{-1}$ ) $\times 10^{-2}$ |
|------------------|--------------|-------------------|--|
| ZnO <sub>2</sub> | RhB          | 95.5/120          | 2.6  |
| MgO <sub>2</sub> | RhB          | 96/90             | 3.7  |
| BaO <sub>2</sub> | RhB          | 98.8/30           | 14   |
| ZnO <sub>2</sub> | MB           | 99/120            | 3  |
| MgO <sub>2</sub> | MB           | 99/60             | 4.7  |
| BaO <sub>2</sub> | MB           | 99/30             | 13.4   |

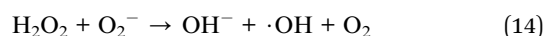
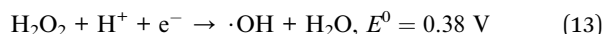
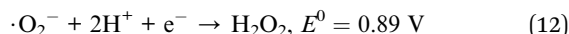
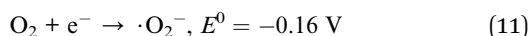
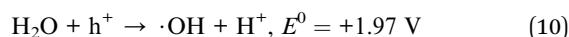
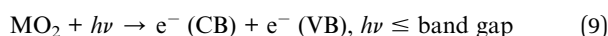
light produces  $\cdot\text{OH}$  and  $\cdot\text{HO}_2$  confirmed through Electron Paramagnetic Resonance (EPR) spectroscopy using spin trap experiments.<sup>28</sup>  $\text{H}_2\text{O}_2$  released undergoes hemolytic fission to form ROS under UV light as shown below<sup>29</sup>

## Mechanism I



$\text{H}_2\text{O}_2$  released chemically is expected to promote the photocatalytic activity through eqn (5)–(8) under UV light. The redox potential of UV photolysis of  $\text{H}_2\text{O}_2$  is +0.51 V which is less than valence band energy level ( $E_{\text{VB}}$ ) of the synthesized metal peroxides (Fig. S3†) suggesting that this reaction is thermodynamically favorable. The redox potential of production of  $\cdot\text{OH}$  and  $\text{H}_2\text{O}_2$  from  $\cdot\text{HO}_2$  are +0.64 and +1.07 V respectively and these are lower than  $E_{\text{VB}}$  of synthesized metal peroxides. Hence, these reactions are also thermodynamically favorable by synthesized metal peroxides.<sup>30</sup> In addition to photolysis of  $\text{H}_2\text{O}_2$ , ROS will be released through the absorption of UV light by wide band gap semiconductors ( $\text{MgO}_2$ ,  $\text{BaO}_2$  and  $\text{ZnO}_2$ ) resulting electron–hole pairs causing redox reaction as shown in eqn (9)–(14).

## Mechanism II



The production of ROS by metal peroxides under UV irradiation could be correlated to the electronic structure of metal peroxides and redox potentials of ROS generation reactions.<sup>31</sup> Fig. S3 and Table S2† show the  $E_{\text{VB}}$ , conduction band energy level  $E_{\text{CB}}$  of metal peroxides.  $E_{\text{H}}$  for  $\cdot\text{OH}$  production by oxidation

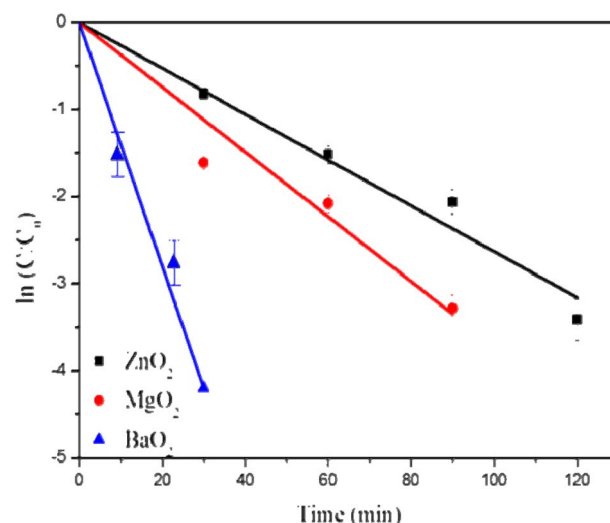


Fig. 8 Rates of degradation of RhB by metal peroxides under UV light.

of water is 1.97 V (ref. 32) which is equal and less than  $E_{\text{VB}}$  of metal peroxides suggesting that  $h^+$  of synthesized metal peroxides can oxidize water to produce  $\text{OH}\cdot$  radical. Reducing power of photo excited  $e^-$  contribute for the production of  $\cdot\text{O}_2^-$ .  $E_{\text{CB}}$  of synthesized metal peroxides as shown in Table S2†

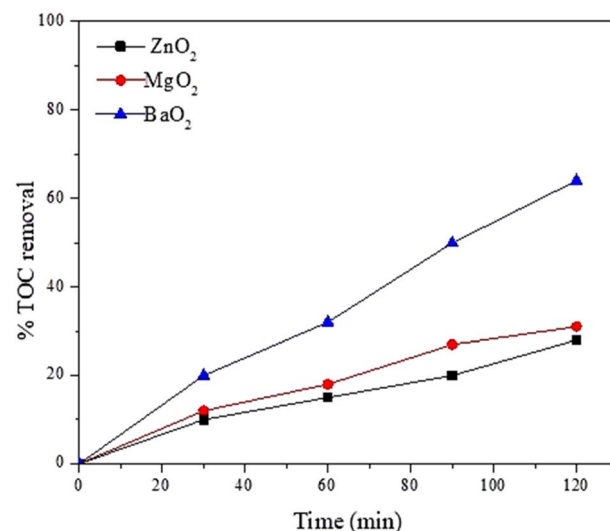


Fig. 9 TOC removal.



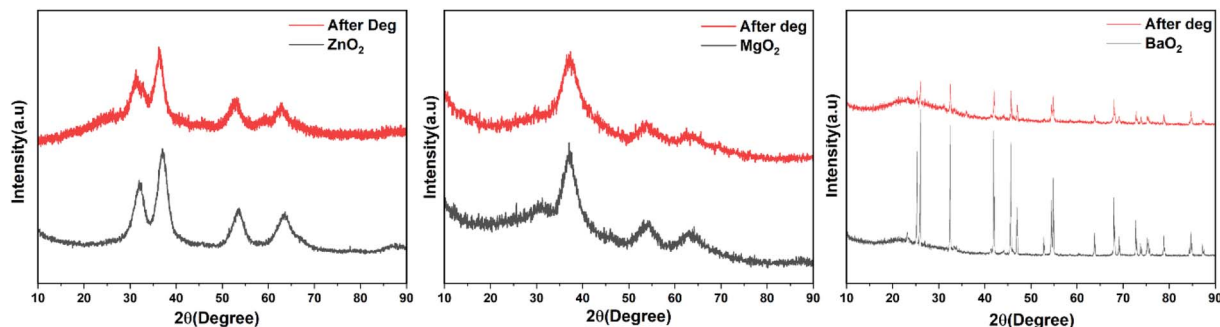


Fig. 10 XRD patterns of metal peroxides after 3 cycles of photocatalytic degradation of dyes under UV light.

proves that synthesized metal peroxides can donate  $e^-$  to  $O_2$  to form  $\cdot O_2^-$ .<sup>32</sup> Valence band XPS and DRS suggest that these metal peroxides in aqueous suspensions could generate large amounts of ROS and hence could function as better photocatalysts comparing other wide band gap semiconductors ( $TiO_2$ ,  $ZnO$ )<sup>33,34</sup> esp. in terms of rates of degradation. Mechanism I is expected to be more dominant than mechanism II in these catalysts.

In order to understand degradation of the dye by the catalysts, TOC (Total Organic Content) of reaction mixture drawn at different intervals was analyzed. However, in the case of metal peroxides ( $ZnO_2$ ,  $MgO_2$  &  $BaO_2$ ), residual TOC removal percentages 70%, 30% and 28% respectively are observed after 2 h irradiation. Fig. 9 reveals an exponential decrease.  $BaO_2$  shows the highest TOC removal.

### 3.5 Reusability of metal peroxides for dye degradation

To understand the stability and reusability of metal peroxides for dye degradation under UV light, catalyst after dye degradation was centrifuged, washed with water and dried in oven at 60 °C and the dried powder was used for degradation of dye. This cycle is repeated 3 times and at the end of 3<sup>rd</sup> cycle, XRD of the products after reaction was recorded. Fig. 10 shows that the metal peroxides are stable and reusable. Fig. S4† shows % degradation of RhB (10 ppm) for 3 cycles by synthesized metal peroxides.

## 4. Conclusion

Metal peroxides of Zn, Mg have been synthesized and characterized. These peroxides have been proven to be efficient UV photocatalysts with activity in the sequence  $BaO_2 > MgO_2 > ZnO_2$ .  $BaO_2$  could degrade the dye close to 100% within 30 minutes with high rate of degradation. These peroxides are the first examples of wide band gap semiconductors that perform dual roles of a photocatalyst and chemical source of  $H_2O_2$  with remarkable stability.

## Author contributions

Conceptualization, V. R.; data curation, D. H.; validation V. L. P and D. H.; methodology, V. L. P. and D. H.; roles/writing –

original draft, V. L. P and D. H.; writing – review & editing, D. A. and V. R.; project administration, V. R and D. A. All authors have read and agreed to the published version of the manuscript.

## Conflicts of interest

There are no conflicts to declare.

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