Hydrothermal fabrication and characterization of novel CeO$_2$/PbWO$_4$ nanocomposite for enhanced visible-light photocatalytic performance

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Abstract
In this revision, a series of novel visible-light-driven (VLD) CeO$_2$/PbWO$_4$ nanocomposites (NCs) were effectively fabricated by facile hydrothermal preparation way. The UV–Vis absorption spectra exposed that CeO$_2$ NPs prolonged the adsorption edge of the CeO$_2$/PbWO$_4$ composite to the extensive visible region, which allied to decreases of the bandgap. As-prepared CeO$_2$/PbWO$_4$ NCs revealed superior photocatalytic action under visible-light and could degrade the Methylene Blue (MB) dye solution in 140 min. The photodegradation efficacy of CeO$_2$/PbWO$_4$ NCs was improved catalytic activity, which is around 1.45 and 2.7 times that of CeO$_2$ and PbWO$_4$ nanoparticles (NPs) individually. Besides, the CeO$_2$/PbWO$_4$ catalysts display notable stability and reusability performance in four succeeding cycles. The development in the photocatalytic enactment of combined CeO$_2$/PbWO$_4$ nanocomposite could be recognized not only to the sturdy visible-light absorption responses and separating the photoexcited electron–hole pairs. Also, the plausibly systematic illumination of charge transference and exploitation of reactive species for superior photocatalytic action in visible-light have been discussed. It is projected that the CeO$_2$/PbWO$_4$ NCs could be used as effective photocatalysts for promising applications for environmental wastewater refinement.

Keywords CeO$_2$/PbWO$_4$ · Nanocomposites · Hydrothermal · Visible light · Photodegradation · Active species

Introduction
Over the former few years, water contaminants have industrial wastewater become the greatest challenging ecological concerns and thus aroused abundant courtesy in the progress of modern society (Gour and Jain 2019). Wastewater usually covers a huge amount of organic pollutants (such as reactive dyes, pesticides and antibiotics) which is adverse things on aquatic ecologies equilibrium and human healthiness. The textile, paper-making, cosmetics, food industries and dye houses have used countless organic dyes which are the prime causes for the contamination of environmental wastewater due to its toxicity and non-biodegradability is a vital environmental issue (Dhmees et al. 2019). Various traditional systems, such as electrochemical oxidation, membrane filtration, adsorption, chlorination, reverse osmosis, and photocatalysis, have been agreed to treat the harmful dyes covering wastewater. Amid these skills, semiconductors (SCs) based photocatalysis has drawn increasing interest because it offers a capable substitute strategy to eradicate the dye-containing wastewater since of its high efficacy, green reaction route and moderate reaction settings (Rohini et al. 2017) for solving the recent severe problems of environmental pollution and energy shortages. Unfortunately, the utmost of these physical, chemical and biological systems could custom to secondary impurities simply through degradation manners (Venkatasubramanian et al. 2008). The advanced oxidation practices (AOPs) of semiconductor photocatalysts (PCs) were broadly considered by deprivation of various noxious organic toxins in environment remediation and antimicrobial action (Girase et al. 2011; Depan and Misra 2014; Zhang et al. 2019b; Shanmugam et al. 2020). The photodegradation and mineralization of the dyes by nanoconfiguration semiconductor in visible-light treated progress has engrossed great concern in modern years. Various metal oxides (such as ZnO, TiO$_2$, Fe$_2$O$_3$, CeO$_2$, and WO$_3$) have been repeatedly employed as support in heterogeneous catalysis of organic pollutants degradation in the wastewater and antimicrobial activity (Rana et al. 2006; Rawat et al. 2007a;
As a significant rare earth metal oxide chains, cerium oxide (CeO₂), a wide bandgap SCs which fascinates light in the nearby UV and slightly visible region. Likewise, the CeO₂ has eco-friendly photocatalytic material, has encouraged abundant concern of the researchers owing to its favorable applications, for instance, plentiful oxygen sensors, luminescent things besides admirable chemical constancy, high catalytic action and cost-effective nature (Li et al. 2019; Qi et al. 2019). This material was also functional for solar water splitting (Ce⁴⁺/Ce³⁺) into hydrogen creation and concerned increasing attention used for deletion of organic pollutants from wastewater owed to its strong light captivation (Priyadarsan et al. 2017a). Though, the key weakness of CeO₂ is the absence of visible-light consumption since the large bandgap (2.92 eV) and weak separation efficacy of photoexcited carriers hinders its widespread request in photocatalysis. Hence it is probable to outspread the visible-light captivation skill of CeO₂ either by doping of metals/nonmetals or fashioning a heterojunction between CeO₂ and another narrow bandgap SCs to create VLD PCs (Cano-Franco and Álvarez-Láinez 2019a). Unfortunately, the UV region signifies a little amount (3–5%) of photon flux whereas the visible region attains 45% of daylight. So that, it has required to progress the photocatalytic efficacy by doping or coupling the CeO₂ with narrow bandgap materials which could diminish the recombination of the photogenerated electron/hole pair rate and extend their lifetime important to the excellent light absorption from UV to the visible region for the elimination of organic pollutants (Ma et al. 2019). As a member of the tungstate family, lead tungstate (PbWO₄) is a scientific importance inorganic scintillating semiconductor, which has vast potential applications like humidity identical sensors, solid-state lasers ground, optical fibers, and catalysts (Pourvast et al. 2020; Rajendran et al. 2019). PbWO₄ NPs was also attained via without accumulation of organic pollutants from wastewater owed to its strong light captivation (Priyadarsan et al. 2017a). Advising to this outline, the pristine CeO₂/PbWO₄ NMs, via 0.03 mol of Ce(NO₃)₃·6H₂O; 99%, Sodium tungstate dihydrate (Na₂WO₄·2H₂O, 99%), Ethylene glycol (99%) were procured from Himedia Ltd. Potassium chloride (Merck, 99%), Cerium nitrate, (Ce(NO₃)₃·6H₂O; 98%) were obtained since SRL Chem Limited. Sodium hydroxide (NaOH), isopropanol (IPA), Di-sodium Ethylene Diamine Tetra Acetic Acid (EDTA-2Na), benzoquinone (BQ), and absolute ethanol (CH₃CH₂OH) were acquired from SDFCL Chemical Reagent Co., Pvt. Ltd. Methylene blue (MB; C₁₆H₁₈ClN₃S) dye from SD Fine and was used as received. Deionized water (D.I) was used for the preparation of all solutions. All the chemicals were analytical reagent (A.R) grade also have auxiliary purified before use.

**Preparation of CeO₂/PbWO₄ photocatalyst**

In a typical synthesis, 0.03 mol of Ce(NO₃)₃·6H₂O was ultrasonically dissolved in 100 mL of D.I water, then 10 mL NH₄OH was gradually dropped directly into the above reaction mixture for pH extended at ~12 under constant stirring for 30 min. Lastly, the composed precipitants (Cui et al. 2019) were kept dry at 60 °C for 8 h and extra calcined at 400 °C for 1.5 h to attain CeO₂ NMs. In this research, the CeO₂ blended PbWO₄ NMs, via 0.03 mol of Pb(NO₃)₂·6H₂O and 0.03 mol of Na₂WO₄·2H₂O solution was added by 50 mL of D.I water. And 1 mol (50 mL) of NH₄OH solution was additional in the pioneer solution, although the pH value was touched at ~11–12. Afterwards, being stirred for 3 h, the 0.1 g of as-obtained CeO₂ NMs was auxiliary added in the upstairs produces and formerly stirred for 2 h. Then, the reaction mixer was relocated to heat-treat by 160 °C aimed at 24 h in a 250 mL Teflon-lined stainless steel autoclave. Lastly, the autoclave was then cooled to room temperature, hence the as-attained CeO₂/PbWO₄ precipitate was centrifugated and rinsed carefully with ethanol/D.I. water further dry at 70 °C for 8 h. Besides, the CeO₂/PbWO₄ NCS was attained (Jeyakanthan et al. 2018). Advising to this outline, the pristine PbWO₄ NPs was also attained via without accumulation of CeO₂ NMs.
Characterization of the obtained samples

The crystal organization and phase of as-obtained nanocomposite was estimated by X-ray diffraction (Rigaku Miniflex-II; X-ray diffractometer) over CuKα radiation in the 2θ range from 10 to 80°. FTIR revisions were done by Perkin Elmer RX-1 FTIR spectrophotometer. Surface morphologies and microstructure of as given NMs were scrutinized via high-resolution (HR-SEM; HITACHI S-3000 H) scanning electron microscope and high-resolution transmission electron microscopy (HR-TEM; JEM-2011; JEOL-Japan) instruments. Energy-Dispersive X-ray spectroscopy (EDX-attached with HRSEM) was used to evaluate the elemental compositions of the NCs. To measure the optical assets of the attained samples were considered by a UV–Vis DRS spectrophotometer (UV2550 model, Shimadzu—Japan). Photoluminescence (PL) spectrophotometry was performed with a (Perkin-Elmer-LS 100) to determine the electron–hole recombination rate at an excitation series of ~ 342 nm. The optical absorption of dye degradation samples was performed via a UV–Vis spectrophotometer (UV; Perkin-Elmer Lambda-19). The absorption spectra in the photodegradation process of MB dye solutions also measured with a (Perkin Elmer-Lambda 35) spectrometer.

Description of the photocatalytic activity of MB dye

The photodegradation performing of as-attained samples (50 mg) was measured via deprivation of MB dye (20 ppm; 100 mL solution; 10 mg/L) under visible-light exposure (300 W Xe lamp by λ > 420 nm cutoff filter in a Pyrex photocatalytic vessel). Preceding to exposure, the suspensions stayed constant magnetically stirred for around 30 min in the dark to certify that the dyes might extend the absorption–desorption balance on the photocatalyst superficial and dyes (Ali Baig et al. 2020). At certain time pauses of 20 min irradiation, 2.5 mL of aliquots were collected. The degraded resolutions were explored by UV–Vis absorption peaks of corresponding MB dye (wavelength at ~ 663.5 nm) (Zeleke and Kuo 2019). The photodegradation efficacy was extent as resulting formula, Efficiency (%) = (C₀ – Cₜ)/C₀ * 100, wherever C₀ and Cₜ exist the absorbance rate of dyes solution earlier and afterwards destruction. Finally, through the degradation manner, photocatalyst was separated from the reaction blend and dried to succeed in the reusability trials (Zhang et al. 2017).

Active species trapping experiments

To detect that the reactive species, certain caused/trapping mechanism during the photocatalytic manner, 1 mM of EDTA-2Na IPA and BQ and were added as scavengers of holes (h⁺) hydroxyl radicals (% •OH⁻) and superoxide radical (% O₂•⁻) exclusively surveyed by the photocatalytic valuations, hence to catch the detection of dynamic reactive species (Cardillo et al. 2016).

Results and discussion

Crystal structure investigation

To explore the crystal constructions and phase composition of the as-obtained samples, XRD evaluations were carried out. As exposed in Fig. 1a, the key diffraction peaks are indexed to the (111), (200), (220), (311), (222), (400) and (311) crystal planes, which was in moral contract with the typical cubic crystalline phase structure pattern of CeO₂ (JCPDS card No: 89-8436) (Syed Khadar et al. 2019). For PbWO₄, the diffraction (Fig. 1b) and consistent planes of (112), (004), (204), (220), (116) and (312), respectively, could be well-indexed to the pure tetragonal stolzite phase (JCPDS card No. 19-0708) (Xiong et al. 2015). In Fig. 1c, designating a good crystallinity of CeO₂/PbWO₄ NCs revealed the association with both the distinctive diffraction peaks of CeO₂ and PbWO₄ crystalline phases. The solid and sharp diffraction peaks proposed that the CeO₂/PbWO₄ nanocomposite was fine crystalline in nature. No characteristic impurity peaks from other crystalline forms were detected which proves that the CeO₂/PbWO₄ NCs has high purity. The average crystallite size (D) of as-prepared NCs was intended by the full width half maximum (FWHM) using Scherer’s equation (Ramos-Corella et al. 2019). The average crystalline sizes for the pristine CeO₂, PbWO₄ and CeO₂/PbWO₄ nanocomposite was found to be 24, 28 and 21.5 nm, individually. The intensity variance and peak extending of the CeO₂/PbWO₄ NCs are ascribed to a substantial reduction of crystallite sizes (Table 1).

FT-IR analysis

To decide the proper functional groups in final catalysts samples, FT-IR spectra of as-obtained CeO₂, PbWO₄ and CeO₂/PbWO₄ NCs were perceived in the series of 400–4000 cm⁻¹ and shown in Fig. 2. An exact extensive band of 3100–3650 cm⁻¹ is recognized to the typical surface hydroxyl (O–H) stretching mode (Saravanakumar et al. 2019). The bending vibration group of actually adsorbed water (H₂O) molecules are besides observed at 1635–1670 cm⁻¹ band. An increase in the number of surfaces -OH groups could expand the photocatalytic action. The existence of sharp dominated absorption peaks on 570–730 cm⁻¹ which is linked to the metal-O (Ce–O, W–O, Pb–O) bonds/stretching vibration are confirmed that the prepared NCs (Syed Khadar et al. 2019). Usually, spinel oxide and metal–oxygen broadening frequencies are perceived in
Fig. 1 XRD pattern of as obtained nanomaterials

Table 1 Comparison of visible-light assisted MB dye photodegradation rate (%) over earlier reported nanocomposite materials

| S. No | Nanomaterials       | Irradiation time (mins.) | Degradation efficiency (%) | References                  |
|-------|---------------------|--------------------------|-----------------------------|-----------------------------|
| 1     | CeO₂                | 180                      | 86                          | (Reddy Yadav et al. 2017)   |
| 2     | NiWO₄               | 330                      | 60                          | (AlShehri et al. 2017)      |
| 3     | g-C₃N₄/BaTiO₃       | 360                      | 76                          | (Xian et al. 2015)          |
| 4     | g-C₃N₄/CeO₂         | 120                      | 74                          | (Kumar et al. 2013)         |
| 5     | CdS/TiO₂            | 310                      | 62                          | (Wei et al. 2014)           |
| 6     | α-Fe₂O₃/TiO₂        | 160                      | 80                          | (Li et al. 2016)            |
| 7     | CeO₂/PbWO₄          | 140                      | 94                          | This work                   |
the peak range of 650–850 cm⁻¹. No auxiliary absorption group was sensed in the experimental FTIR spectrum (Rana et al. 2005b).

**Morphology and microstructure analysis**

To acquire detailed evidence about exterior morphology and microstructure of the CeO₂, PbWO₄ and CeO₂/PbWO₄ NCs were inspected by HRSEM and HRTEM. Figure 3a the HRSEM images of pristine CeO₂ demonstrates spherical shaped aggregates morphology. Figure 3b for PbWO₄ shows a uniform ball-shaped structure was obtained. Also the Fig. 3c the CeO₂/PbWO₄ NCs displays the high agglomeration of CeO₂ NPs rendered with non-uniform spherical fashioned aggregates (Ramasamy Raja et al. 2019). The elemental composition and purity analysis of CeO₂/PbWO₄ NCs have been determined from EDX extents. The EDX inquiry authorizes the existence of all essential elements
such as Ce, W, Pb, and O individually from CeO$_2$/PbWO$_4$ NCs as described in Fig. 3d, also the weight % are detected and inserted in Fig. 3d (Lan et al. 2018). Moreover, the EDX elemental mapping analysis characterizes that the distribution of W, Ce, O and Pb elements separately and as illustrated in Fig. 4. It is well evident that PbWO$_4$ and CeO$_2$ are evenly circulated in the CeO$_2$/PbWO$_4$ NCs. Furthermore, the EDX spectra and corresponding elemental mapping outcomes of as-obtained CeO$_2$/PbWO$_4$ NCs which are very pure and no other impurities are found. The HRTEM analysis of CeO$_2$/PbWO$_4$ NCs is publicized in Fig. 5a–b. The HRTEM micrograph indicates that the number of CeO$_2$ fine NPs has indeed deposited compactly on the PbWO$_4$ surface structure and also homogeneous dispersion nature were forming the nano-sized composite (Aboutaleb and El-Salamony 2019). Moreover, the surface has several irregular small granules with additional agglomeration and the shape is more or less spherical. The intimate contact amid PbWO$_4$ and CeO$_2$ facilitates the separation of the photoexcited carriers, which favours the enhancement of photocatalytic concert (Hezam et al. 2017).

**Optical properties**

The optical properties and energy bandgap of the as-obtained samples have very important to determine the
photocatalytic behaviors (Liang et al. 2017) were studied by UV–Vis DRS as exhibited in Fig. 6. The CeO₂, PbWO₄ and CeO₂/PbWO₄ nanomaterials (NMs) were shown in strong absorption ability in the wavelength range of 200–800 nm. Related with pristine CeO₂ and PbWO₄, the CeO₂/PbWO₄ NCs consume broader absorption competence (Rana et al. 2005a; Cano-Franco and Álvarez-Láinez 2019b), which is superior visible-light harvesting capacity and redshift (~290–418) of absorption edge implying that the CeO₂/PbWO₄ NCs own admirable visible-light dynamic photocatalytic action (David et al. 2018; Wang et al. 2019). The bandgap energy (E₉) values are optically deduced from the Tauc plots and the graph plotted by (αhν)² versus the photon energy (hν). The E₉ values of CeO₂, PbWO₄ and CeO₂/PbWO₄ heterojunction NCs are nearly 2.92, 3.52 and 2.68 eV, separately were exposed in insert of Fig. 6. However, the CeO₂ combined PbWO₄ NCs could reduce the bandgap energy of CeO₂/PbWO₄ NCs which is owed to an energy transition since the visible region triggered by an active band of PbWO₄ effectively deposited on the CeO₂ surface (Liu et al. 2019). In the combined effect of light, absorption would have an obvious effect while catalytic action towards the degradation of dyes qualified to absorption of quite visible-light to probably make more charge carriers (Velusamy and Lakshmi 2017).

Photoluminescence analysis

The photoluminescence (PL) system is also an effective approach to assess the separation ability of photoexcited electron–hole (e⁻-h⁺) pairs since it directly related to photocatalytic efficacy. The PL spectrum of the as-synthesized pristine CeO₂, PbWO₄ and CeO₂/PbWO₄ heterojunction NCs were investigated as shown in Fig. 7. The PL emission intensity of CeO₂/PbWO₄ nanocomposite was lesser than that of pristine CeO₂ and PbWO₄, signifying that the coupling of PbWO₄ NPs might reduce the fluorescence from the CeO₂ NPs while the recombination rate of (e⁻-h⁺) pairs is seriously reserved and extend the lifetime of charge carriers (Jeyakanthan et al. 2018). It is well established that coupling of PbWO₄ NPs onto the superficial of CeO₂ donated for reduced recombination rate of photoexcited charges related to CeO₂. This reduction might be accredited to (i) a greater amount of nominal defects and (ii) effectual charge
separation of CeO2/PbWO4 NCs (Koli and Kim 2019). The detected stronger characteristic PL near-band-edge emissions ranges of ~440–510 nm (448, 487 and 503 nm) for the visible region (apparently excitation peak at ~342 nm). Normally, the effective charge separation and inhibited (e−-h+) recombination rate by coupling of CeO2/PbWO4 NCs was auspicious for enhancing the photocatalytic efficacy of CeO2 NPs (Lu et al. 2020).

**Photocatalytic activity**

The photocatalytic performance was verified against the deprivation of MB aqueous dye in the existence of as-synthesized CeO2, PbWO4 and CeO2/PbWO4 PCs under visible-light exposure. It is seen from Fig. 8a, the characteristic UV–Vis absorption peak of MB dye solution at ~663.5 nm has constantly reduced by CeO2/PbWO4 photocatalyst and hence the supreme degradation efficacy almost 94% was degraded within 140 min. The photocatalytic proficiency of pristine CeO2 and PbWO4 for MB dye degradation was 42% and 58% in identical exposure time separately. The C/C0 (where C0 = absorption intensity of the initial dye solution and C = main absorption peak intensity of dye) has schemed vs. the wavelength as exposed in Fig. 8b. Related to the blank photodegradation testing of MB dye showed almost no obvious degradation in presence of a catalyst under the dark condition, along with an absence of catalyst and without catalyst in the light source, hence the curves could be neglected (Wen et al. 2018). Mostly, the MB organic dyes could be photodegraded by three conceivable reactions containing photolysis, photosensitization, and photocatalysis also. Largely, degradation efficacy was improved via accumulation of CeO2/PbWO4 photocatalyst effort might be the outcomes from (i) synergetic influence of the two metal oxides, (ii) leads to the decreases of bandgap energy, (iii) hindrance of the recombination rate of photoexcited (e−-h+) pairs separation amid CeO2 and PbWO4 heterojunction, (iv) accessibility of surface reactive sites, (v) development of light absorption ability of photoexcited charges generated in the visible-light (Rawat et al. 2007b). The primary absorbance of the peak disappeared entirely after 140 min of visible-light exposure in the CeO2/PbWO4 photocatalyst which specifies the cleavage of conjugated chromosphere structure of MB dye and exchange into small aromatic intermediary (Rožić et al. 2019).

**Kinetics of MB dye photodegradation**

The photocatalytic reaction kinetics of MB dye in visible-light, overall the photocatalysts, was considered by a
consistent pseudo-first-order kinetic equation of \( \ln(C_0/C_t) = kt \) using CeO\(_2\), PbWO\(_4\) and CeO\(_2\)/PbWO\(_4\) PCs as shown in Fig. 9a. Here, \( k \) refers to a reaction rate constant, \( C_0 \) and \( C_t \) are the initial and residual concentrations of MB aqueous dye solution at the agreeing time, and \( t \) (min) was initiate to be linear regression (Yu et al. 2013; Xu et al. 2020). The obvious rate constants for CeO\(_2\), PbWO\(_4\) and CeO\(_2\)/PbWO\(_4\) PCs were calculated as 0.0004, 0.0082, and 0.0164 \( \text{min}^{-1} \). The \( k \) value has increased in the order of CeO\(_2\) < PbWO\(_4\) < CeO\(_2\)/PbWO\(_4\). It has decided that CeO\(_2\)/PbWO\(_4\) PCs has a greater rate constant and it has 4.2 and 2.1 fold enrichment linked to that of pristine CeO\(_2\) and PbWO\(_4\) PCs, separately. Also, the CeO\(_2\)/PbWO\(_4\) NCs owns expressively high photocatalytic dye degradation effectiveness as compared with related metal oxides and reported in other nanocomposites (Kumar et al. 2013; Wei et al. 2014; Xian et al. 2015; Li et al. 2016; AlShehri et al. 2017; Reddy Yadav et al. 2017).

**Reusability of the photocatalyst**

To further explore the stability and reusability were of great consequence factor for its practical application, and the Fig. 9(b) has exhibits the recycling investigates of chief CeO\(_2\)/PbWO\(_4\) PCs was repeatedly used (Shanmugam et al. 2019). For both cycles, the CeO\(_2\)/PbWO\(_4\) PCs were recycled via centrifuging, washing and drying for the next cycling runs. For the CeO\(_2\)/PbWO\(_4\) PCs, the MB dye photodegradation still existing good stability with only about 5% decreases from the initial activity (94%) during the 4th recycle. The activity loss has which largely might be owed to the photo-corrosion of the catalyst by light in CeO\(_2\)/PbWO\(_4\) photocatalyst (Yu et al. 2015). As well, the XRD and FTIR analysis of CeO\(_2\)/PbWO\(_4\) PCs were surveyed further to prove the stability of before and after the photocatalytic replies were carried out. As shown in Fig. 10a, b the XRD and FTIR...
outcomes might designate that no notable changes are witnessed after 4th recycles, representing the structural stability of the CeO$_2$/PbWO$_4$ PCs has measured (Saravanakumar et al. 2016). These consequences propose that the CeO$_2$/PbWO$_4$ PCs used as effective superior photo-stability, and suitable recyclable PCs might also be reused constantly for wastewater treatment under visible-light contact (Vignesh et al. 2019).

Reactive species study

As well known, to validate the radicals of nanocomposites in the photodegradation progression, the trapping tests of reactive species are executed by utilizing light drive. Photoexcited ($e^-$-$h^+$) pairs thereby form numerous reactive species for instance (% $O_2$•$^-$) and hydroxyl radical (% •OH$^-$), hence these reactive species could source in the decomposition of the organic toxins (Negi et al. 2019). Figure 11 as could be seen that photodegradation rate of as-obtained PCs has faintly reductions resultant from the adding of EDTA-2Na, hence validating that $h^+$ are not a major reactive species in this concerned systems. Likewise, the degradation rate is slightly declined when the addition of IPA, hence the % •OH$^-$ is minor/deliberate part of the allied photocatalytic system. This is because the (VB) valence band potential of CeO$_2$ and PbWO$_4$ NPs have conjugated into the % OH/•OH$^-$ also being % •OH$^-$ cannot be fashioned. Though, the addition of BQ initiated significantly suppress the photocatalytic movement from 91 to 26% as presented in the tentative results. Based on the trapping investigation effects, it’s resolved that % $O_2$•$^-$ radicals are the dominant reactive species ($O_2$+$e^-$=% $O_2$•$^-$) accountable for the decomposition of CeO$_2$/PbWO$_4$ photocatalytic scheme (Ravishankar et al. 2015).

Possible photocatalytic mechanism

To obtain better consideration on the CeO$_2$/PbWO$_4$ PCs heterojunction, their valence band (VB) and conduction band (CB) edge potentials were intended via Mulliken electronegativity theory from the Eqs. (1) and (2)

$$E_{VB} = X - E_e + 0.5E_g$$

$$E_{CB} = E_{VB} - E_e$$

wherever $\chi$ states the absolute electronegativity of certain semiconductors ($\chi$ is 5.56, 6.15 eV for CeO$_2$ and PbWO$_4$, singly). And the $E_{VB}$, $E_{CB}$, $E_e$ and $E_g$ are VB potential, CB potential, estimated optical bandgap of CeO$_2$ and PbWO$_4$, and energy of free electrons vs. hydrogen scale (4.5 eV), separately (Channei et al. 2019). Agreeing to the beyond equations, the $E_{VB}$ and $E_{CB}$ band edge potential values were assessed to be +2.52 and −0.11 eV for CeO$_2$ and as −0.40 and +3.41 eV for PbWO$_4$, separately. From the above-mentioned results, the probable photocatalytic mechanism (Fig. 12) comprises by visible-light which leads to the conception of a photoexcited electron ($e^-$) flowing towards CB of CeO$_2$ and thereby the VB of PbWO$_4$ acts as a drop for the hole ($h^+$) (Tomova et al. 2015). Thus, the $e^-$ and $h^+$ could be proficiently divided; the $e^-$-$h^+$ pairs are essentially gathered in the CB of CeO$_2$ and the VB of PbWO$_4$, individually. It is important to note that Ce element has two valence state (Ce$^{4+}$ and Ce$^{3+}$), and Ce$^{4+}$/Ce$^{3+}$ combine owns with multiple roles in endorsing the separation of photoexcited $e^-$-$h^+$ pairs of CeO$_2$/PbWO$_4$ PCs, by which the photocatalytic performance is enriched (Misra et al. 2012; Priyadharshan et al. 2017b; Wang and Tian 2020). Essentially, Ce$^{3+}$ could effortlessly trap the $O_2$•$^-$ making chemical adsorption of oxygen on the exterior of CeO$_2$ centered on the Ce$^{3+}$ + $O_2$ = Ce$^{4+}$—% $O_2$•$^-$, which stimulates photocatalytic oxidation response. Instead of Ce$^{3+}$, which comprises oxygen defects could also absorb visible-light to harvest the photoexcited electron ($e^-$) (Ali Baig et al. 2021). All these gathered electrons ($e^-$) and Ce$^{3+}$ own a strong reduction capacity was augmented easily and speedily decrease the absorbed O$_2$ on CeO$_2$ to cause active superoxide (% $O_2$•$^-$) radicals (Cano-Franco and Álvarez-Láinez 2019). This is because the VB band edge potential of CeO$_2$ (+2.52 eV vs. NHE) develops more positive than PbWO$_4$ (-0.11 eV vs. NHE), which is beneficial for MB dye deprivation (Fukumura et al. 2017). While electron in the CB supports an O$_2$ molecule to form an $O_2$•$^-$ radicals and formerly $O_2$•$^-$ will respond with surface water molecules (H$_2$O) to yield the •OH radical. Lastly, the reactive radicals respond with MB dye molecules decayed to the intermediates or degradation yields over the highly oxidizing species ($O_2$•$^-$, •OH$^-$ etc.). The appropriate photocatalytic reaction progression (Reddy

![Fig. 11 Effect of scavengers on the MB dye photodegradation process](image-url)
Yadav et al. 2016; Zhang et al. 2019a) could be also agreed upon by the succeeding Eqs. (3–7)

Conclusions

To sum up, CeO$_2$/PbWO$_4$ heterojunction photocatalyst was effectively formed via a facile and effectual hydrothermal scheme. The CeO$_2$/PbWO$_4$ nanocomposite was characterized by a range of techniques to study its phase purity, surface morphology, chemical composition and optical belongings were examined and debated in detail.

CeO$_2$/PbWO$_4$ + Dye + Light $\rightarrow$ CeO$_2$/PbWO$_4$ + Dye + ($e^-$(CB) + $h^+$ (VB))

$$\text{(3)}$$

Dye + $e^-$ (CB) $\rightarrow$ Reduction Products

$$\text{(4)}$$

Dye + $h^+$ (VB) $\rightarrow$ Oxidative Products

$$\text{(5)}$$

Dye + OH $\rightarrow$ OH$^-$ + Degradation Products

$$\text{(6)}$$

Dye + O$_2$ $\rightarrow$ O$_2^-$ + Degradation Products

$$\text{(7)}$$

Conclusions

To sum up, CeO$_2$/PbWO$_4$ heterojunction photocatalyst was effectively formed via a facile and effectual hydrothermal scheme. The CeO$_2$/PbWO$_4$ nanocomposite was characterized by a range of techniques to study its phase

In specific, CeO$_2$/PbWO$_4$ photocatalyst displayed the utmost photodegradation efficacy for 94% of MB aqueous dye within 140 min in visible-light treatment which is greater than other as-obtained samples. The degradation rate constant was closely 4.2 and 2.1 fold greater than those of pristine CeO$_2$ and PbWO$_4$ PCs singly. Also, •OH radicals were enabled in the key reactive species in the photodegradation route and the plausible degradation pathways have also been projected. Moreover, the optimized CeO$_2$/PbWO$_4$ photocatalyst presented an outstanding photocatalytic steadiness also reusability up to four consecutive cycles. The developed photocatalytic activities were recognized to the pairing of CeO$_2$ and PbWO$_4$ NPs were initiated by superior charge separation/transfer, reduced bandgap, and strong visible-light absorption proficiency thus suppressing the recombination of photoexcited charges. This study promotes the novel CeO$_2$/PbWO$_4$ NCs with outstanding visible-light photocatalytic action.
and admirable stability was estimated to inspire potential environmental applications in may near future.

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Declarations

Conflict of interest The authors have declared no conflict of interest.

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