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Facile synthesis of monodisperse porous ZnO nanospheres for organic pollutant degradation under simulated sunlight irradiation: The effect of operational parameters

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Graphical Abstract



Highlights

- Monodisperse porous ZnO nanospheres were succesfully synthesized.
- The material featured excellent photocatalytic activity towards degradation of various organic pollutants.
- The operational parameters affecting dye degradation were studied in detail.
- The photodegradation of RhB followed the pseudo-first-order kinetics.
- O_2^{-} are the main reactive species during the photocatalytic process.

ABSTRACT

Monodisperse porous ZnO nanospheres were successfully fabricated through a facile and cost-effective polyol-mediated preparation approach, followed by annealing at 400 °C for 2 h. The photocatalytic activity of the ZnO products was evaluated by the

decolorization of rhodamine B (RhB) solution under simulated sunlight irradiation. The effects of operational parameters on the photo-degradation reaction progress, including catalyst dosage, initial dye concentration, reaction temperature, initial pH value, and the addition of inorganic oxidants, transition-metal ions and inorganic anions were investigated in detail. In addition, reactive species in the oxidation of RhB solution were pinpointed by adding a series of scavengers into the photocatalytic reaction system and O_2^{\bullet} were determined to be the main reactive species. A potential mechanism of photocatalysis of RhB under simulated sunlight irradiation is proposed. The catalyst is found to be reusable.

Keywords: A. Nanostructures; A. Semiconductors; B. Chemical synthesis; D. Catalytic properties

1. Introduction

Discharge of large amount of wastewater containing various kinds of organic contaminants, such as synthetic dyestuffs, halocarbons, and phenol derivatives, is extremely harmful to environment and human health owing to their non-biodegradability, toxicity and potential carcinogenic nature [1, 2]. It is estimated that approximately 10,000 different types of commercial available textile dyes with an annual production rate of over 7×10^5 metric tonnes are produced; additionally, 30 %

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of these dyes are consumed over 1,000 tonnes and 90 % of the textile products are utilized at the level of 100 tonnes annually. As reported [3, 4], approximately 2–20 % of textile dyes are directly released as aqueous effluents and another 10–25 % are lost during the dyeing process, which cause serious pollution to the environment. In general, the complex molecular structure and persistence in nature of synthetic dyes render them difficult to be efficiently degraded by natural means. Up to now, many remedial strategies have been developed as approaches for eliminating recalcitrant pollutants from industrial effluents, including adsorption [5], biological treatment [6], membrane filtration [7], ultrasound irradiation [8] and heterogeneous photocatalytic oxidation [9, 10]. Among the aforementioned wastewater treatment technologies, semiconductor-assisted photocatalytic technology has drawn considerable attention, due to its potential application in the removal of recalcitrant organic and inorganic pollutants of contaminated effluents by utilizing solar energy to completely convert them into innocuous or less harmful compounds [11–13].

Zinc oxide (ZnO) is one of the most important semiconductor photocatalysts used extensively in the field of environmental remediation because of its high catalytic activity, superior photochemical stability, non-toxicity, low cost, and ability to make use of ample sunlight [11, 14, 15]. ZnO has approximately the same band gap energy as TiO₂, and presents photocatalytic capability similar to or better than that of TiO₂. Moreover, it is suggested that ZnO semiconductor exhibits a higher efficiency than TiO₂ for photocatalytic oxidation of pulp mill bleaching wastewater [16], phenol [17] and 2-phenylphenol [18]. Over the last few decades, the photocatalytic degradation of

organic contaminants under artificial solar light (or direct solar light) irradiation with ZnO has been pervasively used in environmental photocatalysis [19–24]. For instance, Jia et al. [19] investigated the influencing parameters of cibacron brilliant yellow 3G-P dye degradation using nanosized ZnO as a photocatalyst and found the dye solutions with concentration of 50 ppm were 98 % decolorized after 60 min of UV-vis light irradiation. In another development, Meng et al. [25] reported that an ordered porous ZnO inverse opal structure exhibited promising photocatalytic activity for the degradation of methyl orange under UV-vis light illumination, due to the synergistic effect of the inverse opal structure and the photonic crystal effect.

In previous works [26–28], we have stated the formation mechanism of the monodisperse spherical ZnO nanomaterials via the developed two-stage solution approach and examined the effects of calcination temperature and particle size on the photocatalytic decolorization of aqueous MB dye over as-synthesized porous ZnO products. However, to the best of our knowledge, few efforts have been devoted to explore the effects of operational parameters, especially the detailed photocatalytic mechanism, over the as-synthesized porous ZnO nanospheres for the photodegradation of organic azo dyes and 4-nitrophenol under UV-vis light illumination, and thus, this area is necessary for further study. In the present study, monodisperse porous ZnO nanospheres were firstly synthesized via a facile and cost-effective polyol-mediated preparation route using zinc acetate dihydrate and diethylene glycol as starting materials. The structure, morphology and

optical property of the as-made ZnO products were investigated using various

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analytical techniques. Furthermore, the effects of operational parameters, such as the catalyst dosage, initial dye concentration, reaction temperature, initial pH value and in the presence of inorganic oxidants, metal ions and inorganic anions on photocatalytic activity of as-synthesized ZnO as photocatalyst in treating organic pollutants under simulated sunlight irradiation have been examined. It was found that RhB dye could be efficiently bleached by the as-synthesized ZnO products under the irradiation of UV-vis light, 97.30 % of RhB decolorization was achieved after 140-min irradiation under certain experimental conditions. The possible roles of the additives on the photocatalytic decolorization of aqueous RhB dye solution were analyzed carefully. In addition, a mechanism by which RhB dye was decolorized over the as-obtained ZnO products under UV-vis light illumination was proposed.

2. Experimental

2.1. Materials

Zinc acetate dihydrate (Zn(CH₃COO)₂·2H₂O), diethylene glycol (DEG), absolute ethanol, methylene blue (MB), 4-nitrophenol, coumarin (C₉H₆O₂), p-benzoquinone, triethanolamine, isopropyl alcohol, potassium periodate (KIO₄), potassium peroxydisulfate (K₂S₂O₈), hydrogen peroxide (H₂O₂), potassium bromate (KBrO₃), potassium chlorate (KClO₃), manganese (II) chloride (MnCl₂), cobalt chloride (CoCl₂), nickel chloride (NiCl₂), zinc chloride (ZnCl₂), sodium carbonate (Na₂CO₃), sodium dihydrogen phosphate (NaH₂PO₄), sodium chloride (NaCl), and sodium nitrate (NaNO₃) were purchased from Sinopharm Chemical Reagent Co., Ltd. Methyl orange (MO) and rhodamine B (RhB) were supplied by Aladdin Industrial

Corporation. Sodium sulfate (Na₂SO₄) was obtained from Xilong Chemical Co., Ltd. Copper chloride (CuCl₂) was purchased from Tianjin Basf Chemical Co., Ltd. Iron chloride (FeCl₂) was purchased from Xiya Chemical Industry Co., Ltd. All chemicals were of analytical reagent grade and used as such without further purification. Double-distilled water was employed throughout for all aqueous solution, as a component of the mixed water and organic pollutant solutions. TiO₂-P25 was received from Degussa (Germany). It has a mean particle size of 30 nm and BET specific surface area of 50 m²/g. The characteristics and chemical structure of RhB, MB, MO and 4-nitrophenol were given in Table S1 of supporting information.

2.2. Synthesis of porous ZnO nanospheres

Monodisperse porous ZnO nanospheres were prepared through a facile and cost-effective polyol-mediated preparation approach as described earlier [26]. In the first stage, Zn(CH₃COO)₂·2H₂O (10 mmol) was dissolved to DEG (100 mL) in a 250 mL three-necked flask. The above reaction mixtures were stirred thoroughly using a magnetic stir-plate while it was heated to 160 °C and maintained at this temperature for 1 h. Reflux with water cooling was utilized to prevent solvent evaporation. The resultant milk-like suspension was centrifuged (Xiangyi Centrifuge Instrument Co., Ltd., China, TG16-WS) at 7000 rpm for 90 min, after which the solution was separated into two gradations. The supernatant was decanted off and washed with ethanol for several times by a repeated sonication-centrifugation process. The solid phase formed from the supernatant was redispersed in 20 mL of ethanol by sonication to form a stable colloidal suspension, which was stored for use in the next

stage. The reaction in the second stage was started in a similar way as the first. One difference was that some volume of the suspension was added to the solution at 150 °C. The remaining steps were the same as the above mentioned in the first stage. After the reaction was completed, a large amount of milky slurry was formed. The resulting solution was cooled naturally to room temperature, after which it was separated by centrifugation and subjected to successive washing with doubly distilled water and ethanol for several times, and then dried in an oven at 60 °C for 12 h. Lastly, the solid was annealed at 400 °C for 2 h in a muffle furnace to obtain the nanostructured ZnO samples.

2.3. Characterization

The morphology and particle size of the as-synthesized products were collected by transmission electron microscopy (TEM) and high resolution TEM using a JEM-2100 system with selected area electron diffraction (SAED). Moreover, the crystal phase and crystal size were determined using powder X-ray diffraction (XRD, D/max-2500, Rigaku, Japan) with CuK α monochromatized radiation ($\lambda = 1.54$ Å) in the 2 θ range from 20° to 80°. Fourier transform infrared spectrometer (FT-IR) was carried out on a Nexus spectrometer (Nicolet, USA) from 4000 to 400 cm⁻¹ at room temperature. The sample was prepared as KBr pellet for FT-IR spectroscopy. The specific surface area was obtained through nitrogen adsorption at 77 K on the basis of BET (Brunauer-Emmett-Teller) equation with a Micrometrics ASAP 2010 instrument. Diffuse reflectance UV-vis spectroscopy (DRS) was recorded on a Shimadzu UV-2600 spectrophotometer (Japan) equipped with an integrated sphere diffuse

reflectance accessory, and BaSO₄ was used as a reference.

2.4. Photocatalytic evaluation

The photocatalytic activities of the prepared porous ZnO products were investigated by photooxidation of the organic azo dyes and 4-nitrophenol in aqueous solution. The photocatalytic oxidation reaction was carried out using a 300 W xenon lamp (Perfectlight Scientific Pty Ltd., Beijing, China) equipped with a 100-mL jacketed beaker reactor (Pyrex) of 4.5 cm i.d. 7.0 cm o.d. and 9.0 cm length. The distance between the light and solution was about 10 cm. In a typical test, a certain amount of as-prepared ZnO nanoparticle was placed in 50 mL of aqueous RhB solution with known initial concentration. The pH of the solution was adjusted by 0.1 mol/L of HCl or 0.1 mol/L of NaOH to the required pH. The reactor vessel was surrounded by circulation of water through the external jacket from a thermostatic bath, which maintained the temperature of the aqueous solution at 25 °C during the photoreaction. Before the light illumination, the reaction mixture was magnetically stirred for 30 min in the dark to attain adsorption-desorption equilibrium between dye and ZnO products. The decolorization rate of RhB was assessed by measuring the absorbance of the reaction liquid at 20 min interval. Approximately 3 mL of solution were syringed out from the reaction suspension, centrifuged at 7000 rpm for 20 min, and subsequently filtered through a Millipore filter (pore size, 0.45 µm) to separate the solid particles, and the corresponding UV-vis spectra were recorded to monitor the progress of the oxidation of the organic dyes by a UV-vis spectrophotometer (Shanghai Lengguang Technology Co., Ltd., China, 759S) with doubly distilled water as a reference.

To explore the universality of the obtained products on the photocatalytic oxidation of organic pollutants, identical operations were performed except that the RhB solution was replaced by 50 mL of MB (10 mg/L), MO (10 mg/L) and 4-nitrophenol (5 mg/L) aqueous solutions, respectively. The absorbance of RhB, MB, MO, and 4-nitrophenol was monitored at the wavelengths of 553, 664, 462 and 400 nm, respectively.

2.5. Estimation of hydroxyl radicals

Coumarin can readily react with 'OH radicals to generate highly fluorescent hydroxyl products, 7-hydroxycoumarin, as displayed in Eq. (1). As a result, the generation of 'OH radicals at the surface of catalyst under the UV-vis light irradiation can be detected by a fluorescence technique reported by Ishibashi et al [29]. The detailed experimental procedure was similar to that of the photocatalytic oxidation experiment, except that the aqueous solution of dye was replaced by a solution of coumarin (50 mL, 0.1 g/L). After the reaction, the solution was centrifuged, subsequently filtered with a 0.45 µm Millipore filter to separate the ZnO particles, and the PL spectra of generated 7-hydroxycoumarin were determined in the intensity of peak at about 453 nm by a fluorescence spectrophotometer (Shanghai Lengguang Technology Co., Ltd., China, F97Pro) with an excitation wavelength of 340 nm.



3. Results and discussion

3.1. Characterization of as-synthesized porous ZnO nanospheres

Fig. S1(a) illustrates the representative XRD pattern for the ZnO products. All of the diffraction peaks can be well indexed as the hexagonal wurtzite crystal structure of ZnO (JCPDS card No. 36-1451). The absence of characteristic peaks corresponding to impurities indicated high purity of the products [10, 30, 31]. Again, the sharp and strong diffraction peaks further revealed the ZnO products were of good crystallinity. Moreover, the average crystallite size was calculated using the Debye-Scherrer equation [32], $D = k\lambda/\beta \cos\theta$, where D is the average crystallite size, k is a dimensionless shape factor, with a typical value of around 0.89, λ is wavelength of X-ray radiation, β is full width at half maximum (FWHM) of the (101) peak and θ is Bragg's diffraction angle. The average crystallite size obtained from the XRD data was estimated to be 12.6 nm. The FT-IR spectrum of the sample is shown in Fig. S1(b). The well resolved strong and sharp band centered at around 451 cm^{-1} was ascribed to characteristic vibration mode of Zn-O bond, which further corroborated the formation of ZnO. A relatively weak absorption band at 3442 cm⁻¹ corresponded to the O-H stretching vibration of water adsorbed at the surface of ZnO photocatalyst. The structure and morphology of the ZnO nanoparticles were investigated by TEM and HRTEM. As shown in Fig. 1(a), the as-synthesized samples were mainly constituted of uniform sphere-like nanoparticles. Fig. 1(b) shows a histogram of the particle diameters, which clearly illustrates that the average diameter of the as-prepared ZnO nanoparticles was approximately 168 nm. Fig. 1(c) shows the typical TEM image of the ZnO products, and it can be seen that the ZnO particles consisted of many small ZnO grains, and the surface of the ZnO nanoparticles was rough.

Moreover, a careful observation under higher magnification (Fig. 1(d)) confirms that each ZnO nanosphere was assembled by many small primary nanocrystals with an average diameter of approximately 14 nm, which was in accordance with the above XRD analysis. Noticeably, it can be found that there were a large number of irregular cavities inside the nanoparticle (marked with green circles), which resulted from the release of carbon dioxide and water during annealing process. This feature endows the porous ZnO nanospheres with a high surface area. The BET surface area of porous ZnO products was 43.9 m²/g, which is higher than that of the reported nanostructured ZnO [22, 33]. Furthermore, the lattice fringes of ZnO nanoparticles are clearly observed in Fig. 1(e) and its insets. The lattice spacings were about 0.250 and 0.281 nm, corresponding to the (101) and (100) planes of hexagonal wurtzite-structure ZnO nanoparticles, respectively [14, 30]. The bright rings in the corresponding SAED pattern (Fig. 1(f)) revealed the polycrystalline nature of the synthesized ZnO architectures.

The as-synthesized ZnO was subjected to DRS analysis to provide information on the optical quality of reaction products. As displayed in Fig. S2(a), the as-synthesized ZnO products exhibited a strong absorption wavelength shorter than 400 nm, mainly concentrated in UV region, with a tail extending to the visible light region, being attributed to the intrinsic band gap absorption of ZnO [14, 30]. The band gap energy (Eg) was estimated from Fig. S2(b) by extrapolation of linear part of the spectrum to the energy axis [10, 32]. The Eg value for the synthesized ZnO products was estimated to be 3.13 eV, which was approximately located at 396 nm. Thus, compared with the

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absorption edge (386 nm) of pure ZnO [19], the as-synthesized ZnO products in our work presented a red shift, suggesting that it might result in a higher photocatalytic activity under visible light.

3.2. Photocatalysis under simulated sunlight irradiation

3.2.1. Evolution of UV-vis spectra during photocatalysis process

We also investigated the potential application of the obtained porous ZnO products to be used as a photocatalyst in wastewater treatment. The photooxidation behavior of rhodamine B (RhB), a hazardous dye as well as a common model to test the photooxidation capability, over porous ZnO products as function of irradiation time under simulated sunlight illumination is illustrated in Fig. 2. The spectrum of RhB in visible region displayed a main peak with a maximum at 553 nm. It can be also found that the absorption bands of RhB showed two types of spectral changes. One was a slight hypsochromic shift ($\Delta \lambda = 34$ nm) in the absorbance maximum, and the other was a decrease in the absorbance. The gradual hypsochromic shifts of the absorption maximum were caused by deethylation of RhB during irradiation because of the attack by one of the active oxygen species on the N-ethyl group, reminiscent of similar phenomena observed by Zhao's group on a RhB/TiO₂ system illuminated under visible irradiation [34] and Zhu's group for visible-light-induced photooxidation of RhB over nanosized Bi₂WO₆ [35], while the reduction of the characteristic absorption band indicated that a rapid cleavage of the conjugated chromophore structure of RhB molecules occurred simultaneously, and the color of the solution changed from pink to colorless after 140 min of irradiation (inset of Fig.

2), indicating the gradual decomposition of RhB dye molecules during UV-vis light irradiation [36].

3.2.2. Effect of light irradiation and porous ZnO products

The profiles of the photocatalytic oxidation of 10 mg/L RhB dye aqueous solution containing 10 mg ZnO as function of irradiation time under varied conditions are displayed in Fig. 3. It is evident from the figure that approximately 97.30 % of RhB dye was bleached at the irradiation time of 140 min in the presence of both ZnO and light (curve d). This was contrasted with only 10.49 % decolorization for the identical experiment in the presence of light illumination without the ZnO products (curve b), and the negligible RhB decolorization (4.28 %) in the presence of ZnO products, but without light illumination (curve a). These experiments demonstrated synergistic degradation of RhB dye by the simulated solar light and a photocatalyst. Using a UV cut-off filter ($\lambda > 420$ nm) caused the reduction of the RhB loss from 97.30 % to 82.67 % (curve c). Hence, it can be concluded that simulated solar light is more effective than visible light for ZnO particle to activate the RhB dye decolorization. It is well known that ZnO is a wide-gap semiconductor, which theoretically cannot be excited under visible light illumination. The reason for the high removal ratio (~ 82.67 % RhB loss) over ZnO catalysts in visible light region may be due to the presence of dye sensitization mechanism along with the usual ZnO sensitization [33, 36-38]. Furthermore, the degradation kinetics (curve e) revealed a similar trend as discussed above. The function of $\ln(C_0/C)$ versus reaction time (t) showed a strong linear relationship (regression coefficient of 0.9976), indicating the pseudo-first-order

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reaction kinetics of RhB decolorization catalyzed by the as-synthesized porous ZnO products under UV-vis light irradiation:

$$\ln \mathbf{C}_{o} \quad C \Rightarrow k, \tag{2}$$

where C_0 is the initial concentration of RhB before irradiation, C is the concentration of RhB at any reaction time, and k is the pseudo-first-order reaction rate constant. Via a linear fit, the degradation apparent rate constant k value for the as-synthesized ZnO products can be determined to be 0.025 min⁻¹.

The photocatalytic activity of the as-prepared ZnO products was compared with the commercial TiO₂-P25 under simulated sunlight irradiation at constant dye concentration (10 mg/L, pH = 6.5) and catalyst dosage (10 mg). As depicted in Fig. S3, TiO₂-P25 exhibited a slightly high reaction rate of RhB decolorization compared to the synthesized ZnO products within 140 min, whereas the values of percent RhB removal over TiO₂-P25 and synthesized ZnO products are 82.74 % and 85.36 %, respectively, at the time of 80 min, indicating that the obtained ZnO products and commercial TiO₂-P25 have almost the same decolorization reaction rate. For practical application, the sedimentation properties of the photocatalysts are extensively concerned. For the tested ZnO products, the sedimentation properties were preliminarily compared by suspending 3 mg of the catalyst in 3 mL double-distilled water under ultrasonic process, followed by static sedimentation for 80 min. As presented in Fig. S4, compared with TiO₂-P25 powders, ZnO products possessed faster sedimentation velocity, and nearly all ZnO products were precipitated from the suspension, implying its easy separation for recycle usage. Thus subsequent

experiments were performed with the as-synthesized ZnO as a photocatalyst due to its high photocatalytic activity, superior sedimentation property and low cost. Fig. S5 presents the comparison of porous ZnO products on the photocatalytic oxidation of RhB, MO, MB and 4-nitrophenol aqueous solutions under simulated sunlight irradiation, where the data starts from the initial concentration of pollutants after the adsorption-desorption equilibrium. As can be seen, the obtained ZnO products exhibited better removal performance on the photocatalytic oxidation of these organic pollutants. In addition, it can be found from Figs. S6, S7 and S8 that the changes of UV-vis spectra and colors of aqueous MO, MB and 4-nitrophenol solutions demonstrated similar trends when compared to that of RhB dye. The above results suggested that the porous ZnO photocatalysts had no selectivity and could effectively degrade different kinds of organic contaminants. Consequently, it can be a prospective alternative applied in environmental purification.

3.3. Effect of various factors on photocatalytic process

3.3.1. Effect of photocatalyst amount

To investigate the influence of photocatalyst amount, photocatalytic oxidation experiments were carried out by employing different amounts of ZnO (5, 10, 20 or 30 mg) under constant process conditions: dye concentration = 10 mg/L, reaction temperature = 25 °C and initial pH = 6.5. The percentage of RhB loss as a function of photocatalyst amount is shown in Fig. 4. The catalytic efficiency was studied in terms of reaction rates, turnover number (mole reacted RhB per mole catalyst), and quantum yield (reacted dye molecules per incident photon). It can be seen that there was

appreciable increase in the reaction rate of RhB decolorization with increasing catalyst amount. The reason of this observation is thought to be the fact that increasing photocatalyst dosage results in an increase in the number of active sites that are available at the surface of the catalyst [39]. Another acceptable explanation is that the density of catalyst particles in the area of illumination is improved after the ZnO dosage is increased [11, 40, 41]. However, turnover number values, measured after 140 min, relatively decreased as catalyst amount was increased. This suggested that the relative efficiency of the catalyst was lowered by increasing catalyst amount. Similar phenomena were observed in earlier reports and this was attributed to screening the radiations away from the ZnO particle surfaces [24, 42]. The quantum yield value, measured after 140 min, showed an increase with increasing catalyst amount at the beginning, but then decreased. The reduction in quantum yield was another evidence of light screening effect associated with higher catalyst amount. The above results suggested that the photocatalyst concentration is one of the most important factors in the photocatalytic oxidation of RhB dye.

3.3.2. Effect of initial dye concentration

In order to examine the impact of various dye concentrations on the photocatalytic degradation, experiments were conducted by varying the concentration of RhB from 5 to 30 mg/L. The values of ZnO dosage, reaction temperature and initial pH were constant at 10 mg, 25 °C and 6.5. As it appears in Fig. 5, the RhB loss percentage was significantly lowered with an increase in the initial concentration of RhB. The decolorization rate of the RhB dye aqueous solution with 5 mg/L concentration

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increased sharply in the initial 60 min (93.31 %). In contrast, for the more highly concentrated solutions, such as the solution with 30 mg/L concentration, only 27.82 % RhB loss was observed after the same reaction time. This negative effect can be interpreted by the following reasons: (1) The number of RhB molecules that adsorbed on the active sites of the catalyst surface, increases with rise in the initial concentration of RhB dye. Therefore, competitive adsorption of O₂ and OH⁻ on the same sites decreases, meaning a lower generation rate of O_2^{-} and 'OH radicals, which are the principal oxidants necessary for the high degradation rate [11, 42]. (2) On the other hand, by increasing the dye concentration, a large number of dye molecules along with the intermediates generated may compete for the constant total active sites available for adsorption at a fixed concentration of ZnO [22, 35]. (3) Additionally, with increase in the initial dye concentration, the solution becomes more intensely colored and the path length of photons entering into the solution decreases, so the absorption of photos by the catalysts decreases, and consequently the decolorization rate is reduced [39, 43, 44]. Despite the lowering in removal percentage of RhB with increased initial concentration, the values of turnover number and quantum yield calculated after 140 min increased. Lower values were observed at the concentration of 5 mg/L, which is ascribed to the fact that all added RhB molecules were degraded with no more remaining.

3.3.3. Effect of reaction temperature

The oxidation of aqueous RhB solution by ZnO under UV-vis light illumination was carried out under different temperature (15, 25, 35 and 45 °C). The values of ZnO

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dosage, initial dye concentration and initial pH were constant at 10 mg, 10 mg/L and 6.5, respectively. As displayed in Fig. 6, the RhB loss percentage was found gradually improved with an increase in temperature from 15 to 35 °C. It is well known that the mass transfer of different species increases as the reaction temperature rises, thus improving the reaction rate [45]. Nevertheless, it should be pointed out that the rate of RhB decolorization decreased slightly with the reaction temperature further increased to 45 °C, which can be attributed to possible escape of the oxygen molecules dissolved inside oxygen [24]. The oxygen molecules are involved with the mechanism of photocatalytic degradation reaction. Further, the activation energy (E_a) of the photocatalytic degradation reaction is calculated according to the Arrhenius equation followed as:

$$k = k_{o} \exp(\frac{-E_{a}}{RT}), \qquad (3)$$

$$L n \quad k = L_{o} n \frac{E_{a}}{RT}, \qquad (4)$$

where k and k_o are the reaction rate constant and frequency factor, respectively. T and R represent the absolute temperature and ideal gas constant (8.314 J/(mol K)), respectively. The function plot is depicted in Fig. S9 and the value of activation energy for the degradation of RhB was 6.81 KJ/mol, which was small and close to the value (~6.1 KJ/mol) reported by Hilal's group for the degradation of phenazopyridine over naked ZnO catalyst [46]. This is contrary to thermally induced catalytic reactions where the rates progressively increase with higher temperature. Photochemical degradation reaction rates, with wide band gap semiconductor catalysts, are known to

be insensitive to temperature [46, 47]. Energy provided by heating at ambient temperatures (~ 45 °C) is far less than 3.0 eV, viz. heat energy is only in IR region, not UV. Furthermore, higher temperatures are responsible for removal of oxygen from the reaction solution, which is necessary for pollutant oxidation.

3.3.4. Effect of solution pH

The solution pH is an important parameter in photocatalytic degradation reactions for industrial applications. It has been reported that the pH of zeropoint charge for ZnO is approximately 9.0 (denoted as pHzpc) [48]. At pH lower than the pHzpc of the ZnO, the stable suspension forms because their net positive charge prevents agglomeration. Similar phenomena are observed when pH is higher than the pH_{zpc} of ZnO, where ZnO particles are surface negatively charged by adsorbing OH⁻ ions. The effect of pH values on the percentage of RhB loss was studied in the pH range of 3-11 at a 10 mg/L dye concentration and 10 mg catalyst dosage and the obtained results are depicted in Fig. 7. The pH of the reaction solution was adjusted before light irradiation and it was not controlled during the course of the photocatalytic reaction. It was apparently found that alkaline condition was very beneficial to the photocatalytic oxidation of RhB dye. The rate of RhB decolorization was significantly enhanced with increasing pH value of the dye solution, which may be due to the increase in adsorption of dye molecules. RhB is an aromatic amino acid with amphoteric characteristics because of the presence of both amino and carboxyl groups and it exists in three distinct monomeric molecular forms (cation, zwitterions and lactone) depending on the solvent environment [49]. Thus, the charge state of RhB is

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determined by solution pH. The pKa value for the aromatic carboxyl group presented on RhB molecule is approximately 4.0. When the solution pH is less than 4.0, the RhB ion takes on a positive charge on one of the nitrogens while the carboxyl group is unionized. ZnO has a point of zero charge at pH 9.0 [24, 48], below which the ZnO surface is predominantly positively charged. The electrostatic repulsion between cationic RhB and positively charged ZnO leads to the reduced percentage of RhB adsorption. When solution pH is higher than 4.0, the carboxyl group gets ionized and the zwitterions form of RhB is generated. The zwitterions form of RhB in water may increase dimerization of RhB [50], which makes the molecule difficult to enter most of the pore structure of ZnO nanoparticles. When the solution pH increases above 9.0, excessive OH⁻ compete with COO⁻ in binding with -N⁺ and the aggregation of RhB reduced. Hence, an increase in the adsorption of RhB dye on the ZnO photocatalyst can be inferred at pH > 9. The results obtained are in accordance with previous report, and a similar increase in degradation rate was observed by Kaur et al. [51] for photocatalytic oxidation of safranin O (SO) using highly robust ZnO as catalyst. An experiment to verify the dark adsorption of RhB onto ZnO nanoparticles with different pH value was carried out, as shown in Fig. S10. The percentage of adsorption at pH 3, 5, 6.5, 9 and 11 were found to be 7.95, 11.93, 13.97, 21.10 and 34.25 %, respectively, after the attainment of adsorption equilibrium (30 min). As a result, the improvement in the photocatalytic decolorization rate in the basic region is possibly due to the high adsorption of RhB molecules on the catalyst surface. On the other hand, ZnO is an amphoteric oxide able to react as a base at strong acidic

aqueous solution according to the Eq. 5 [22].

$$ZnO_{(S)} + 2H_{(aq)}^{+} = Zn_{(aq)}^{2+} + H_2O,$$
(5)

So, part of ZnO dissolved at pH 3, resulting in the relatively lower decolorization rate [33]. Because of the amphoteric property of ZnO semiconductor, water molecules in alkaline solution adsorbed on its excited surface and decomposed by oxidative potential of the hole, generating OH⁻. The formed OH⁻ could be oxidized further by the hole to form more 'OH radicals. The 'OH radicals lead to partial or complete dye decomposition. Therefore, alkaline conditions were beneficial to photocatalytic oxidation.

3.3.5. Influence of inorganic oxidants on photocatalytic oxidation of RhB dye In the irradiated aqueous ZnO suspensions, molecular oxygen on the ZnO surface provides a natural sink for the photogenerated electrons to prevent the electron-hole pair recombination process. The inorganic oxidants such as IO_4^- , BrO_3^- , CIO_3^- , $S_2O_8^{2-}$ and H_2O_2 , can compensate for the lack of oxygen either because of oxygen consumption or slow oxygen mass transfer to improve the oxidation rates of organic substrates via quenching the conduction band electrons and via formation of reactive radicals intermediates. The influence of addition of these inorganic oxidants on photocatalytic decolorization rate of RhB dye was studied at the different concentrations and illustrated in Fig. 8. We can observe that all of the added inorganic oxidants had a promotional effect on the photocatalytic process and enhanced the photocatalytic decolorization rate of RhB dye. The positive effect of these inorganic oxidants involved in photocatalytic system was found to be in the order of IO_4^- >

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 $S_2O_8^{2-} > H_2O_2 > BrO_3^{-} > ClO_3^{-}$.

The enhancement in photocatalytic oxidation of RhB dye may be ascribed to the following three factors:

(1) The enhancement of RhB dye removal by the addition of oxidants may be due to the trapping of the photogenerated conduction-band electrons, thus increasing the electron-hole separation time [13, 52, 53, 54].

(2) On the other hand, the oxidant with higher UV absorption is more effective toward degradation of organic compounds in industry effluent, which is due to high absorption of UV light resulting in the generation of reactive radical species. As reported by Swaminathan's group [43], the UV absorption of the above oxidants followed an order of $IO_4^- > S_2O_8^{2-} > H_2O_2 > BrO_3^- > ClO_3^-$. It can be inferred that the higher photocatalytic decolorization rate of IO4⁻ than other oxidants may be attributed to its high absorption capacity toward UV light, while ClO₃, with the least reaction rate, has no UV absorption.

(3) In addition, the combination of some inorganic oxidants and simulated sunlight irradiation provides a strong oxidant system via formation of other oxidizing species. IO₄⁻ can produce several powerfully reactive intermediate radicals (IO₃⁻, 'OH, IO₄⁻ and O⁻) in aqueous solution through the following reactions depicted in Eqs. 6–8, resulting in the increase of photocatalytic decolorization rate of the RhB dye [52].

$$IO_{4}^{-} + hv \rightarrow IO_{3}^{\bullet} + O^{\bullet}, \qquad (6)$$

$$O^{\bullet-} + H^{\dagger} \rightarrow \bullet O, \qquad (7)$$

$$^{\bullet}OH + IO_{4}^{-} \rightarrow OH^{-} + IO_{4}^{\bullet}, \qquad (8)$$

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When $S_2O_8^{2^-}$ undergoes thermolysis or photolysis in an aqueous solution, it can produce sulfate radical anion (SO₄^{•-}) (Eq. 9) [55]. The radical, as a highly reactive oxidant with a standard redox potential of 2.6 V vs. NHE (normal hydrogen electrode) [1, 43, 53, 56], could react with H₂O to generate [•]OH radicals (Eq. 10).

$$S_{2}O_{8}^{2^{-}} + heat / hv \rightarrow 2SO_{4}^{\bullet^{-}}, \qquad (9)$$

$$SO_{4}^{\bullet^{-}} + H_{2}O \rightarrow {}^{\bullet}OH + SO_{4}^{2^{-}} + H^{+}, \qquad (10)$$

As is well known, H_2O_2 is a strong oxidizing agent with high reactive oxygen content which is widely used in advanced oxidation technique for degradation of organic pollutants. Some literatures reported that H_2O_2 may split photolytically to generate hydroxyl radicals directly under UV light irradiation via the following reaction (Eq. 11) [52, 57]:

$$H_2O_2 + hv \rightarrow 2^{\bullet}OH \tag{11}$$

However, H_2O_2 has extremely low absorption of solar light. Thus, the oxidation of the dye by photolytic H_2O_2 will be insignificant. Under the solar light irradiation, H_2O_2 can also react with superoxide radical anions to produce 'OH radicals shown in the equation (Eq. 12).

$$H_2O_2 + O_2^{\bullet} \rightarrow \bullet OH + H^+ + O_2$$
(12)

In the cases of BrO_3^- and ClO_3^- , both oxidants cannot produce other oxidizing species, since they have lower solar light absorption [43].

To further explore the effects of these inorganic oxidant concentrations on the photocatalytic activity over porous ZnO photocatalysts, the experiments were conducted with oxidant concentration ranging from 50 to 400 mg/L, as presented in

Fig. 8. It is noticeable that as the concentration of inorganic oxidant was increased, the photocatalytic decolorization rate of RhB dye was improved, which can be explained by the above three reasons. But when the concentration of these oxidants (i.e., IO₄⁻, BrO₃⁻ and ClO₃⁻) was higher, the photocatalytic removal rate decreased. This observation may be due to the generation of excessive 'OH radicals in the presence of higher concentration of some oxidants, which recombines excessive 'OH radicals to produce less-reactive substances. On the other hand, employing of higher concentration of IO₄⁻, BrO₃⁻ and ClO₃⁻ oxidants may result in adsorption effect of I⁻, Br⁻ and Cl⁻ ions at the surface of ZnO in the breakdown solution, respectively, thereby inhibiting surface photochemistry from occurring to some extent [53].

3.3.6. Influence of transition-metal ions on photocatalytic oxidation of RhB dye The impacts of different transition-metal ions on the photocatalytic activity of obtained porous ZnO products were investigated using RhB as a model dye under UV-vis light irradiation. As shown in Fig. 9, it is clearly seen that all of the added transition-metal ions had a beneficial influence on the photocatalytic decolorization rate of RhB dye. The enhancement effect of these metal ions was ranked as follows: $Zn^{2+} > Mn^{2+} > Ni^{2+} > Cu^{2+} > Fe^{2+} > Co^{2+}$. The common anion of all of the added metal ions is Cl⁻; therefore, only metal ions are involved in the promotional effect. As some authors stated that transition-metal ions could behave as a scavenger of electron from ZnO surface, thus inhibiting the recombination of electron-hole pairs according to the equation below [43, 53, 58].

$$M^{n_{+}} + e_{CB} \to M^{(n-1)_{+}}$$
 (13)

Where M^{n+} represents Zn^{2+} , Mn^{2+} , Ni^{2+} , Cu^{2+} , Fe^{2+} , Co^{2+} metal ions.

To examine the influence of transition-metal ion concentration on the photocatalytic oxidation of RhB dye, a series of experiments were performed with metal ion concentration ranging from 50 to 400 mg/L. As the concentration of added transition-metal ions was increased, the photocatalytic decolorization rate of RhB dye was enhanced, but further increase in transition-metal ion concentration in reaction solution resulted in a reduction in the decolorization rate of RhB dye. The retardation influence of high transition-metal ion concentration may be attributed to the following two factors: (1) The high concentration of transition-metal ions has a filter effect because of UV light absorption and decreases the light intensity in the reaction solution, thus reducing the decolorization rate of RhB dye [32]. (2) On the other hand, when the concentration of added metal ions is higher, the M⁺ cations generated via the electrons existed as the dominating ions in the reaction solution, and the M⁺ cations can be oxidized to M^{2+} ions through the photoinduced holes at the surface of photocatalyst or by 'OH radicals based on the following equations (Eqs. 14 and 15), thus leading to the decrease in photocatalytic decolorization rate of the RhB dye [53, 59].

$$M^+ + h^+ \rightarrow M'$$
, (14)

 $M^{+} + OH + H^{+} \rightarrow M^{2+} + H_2O$, (15)

3.3.7. Influence of inorganic anions on photocatalytic oxidation of RhB dye Dye-containing wastewater usually contains not only organic contaminants but also abundant inorganic anions such as sulfate, carbonate, nitrate and so on [60]. Hence, it

is necessary to investigate the impact of these ions on the photocatalytic process. The effects of added inorganic anions on the removal of RhB dye was studied at different concentrations varying in the range of 0.2–1.0 g/L and displayed in Fig. 10. It can be found that all of added inorganic anions had an inhibition effect on the photocatalytic process and lowered the photocatalytic decolorization rate of RhB dye. The detrimental effect of these inorganic anions was found to rank in the order of $H_2PO_4^- > CO_3^{-2-} > CI^- > SO_4^{-2-} > NO_3^-$. Since the common cation of all the added inorganic anions (Na⁺) is inert; hence, only anions are involved in the retardation effect. In the meanwhile, it can be seen that as the concentration of inorganic anions was increased, and the photocatalytic decolorization of RhB dye became slower.

The inhibitive influence of these inorganic anions on the photocatalytic reaction could be attributed to the following possible reasons: (1) The retardation effect of inorganic anions may be due to a competitive adsorption of these anions and the target organic substance at the surface of catalyst, leading to blockage of the active sites at the surface of photocatalyst, thus inhibiting the photooxidation of organic substance by reactive species [61, 62]. (2) Another possible reason to explain the inhibition effect in the presence of inorganic anions is that an inorganic salt layer forms at the ZnO nanoparticle surface, which obstructs the approach of RhB molecules, thus resulting in the reduction of RhB dye molecules adsorption [13, 60]. (3) Additionally, these negatively charged inorganic anions can react with holes (h⁺) and hydroxyl radicals ('OH) to produce less-reactive species due to their lower oxidation potentials, and those inorganic anions behaved similar to h⁺ and 'OH scavengers, which is a great

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impediment to the progress of the reaction, thus leading to a reduction in the photocatalytic decolorization rate [56].

As has been widely reported [32], dihydrogen phosphate ions could react with h^+ and 'OH to generate less reactive H₂PO₄' radicals through the following equations (Eqs. 16 and 17), leading to a reduction in the decolorization rate of RhB dye.

$$H_{2}PO_{4}^{-} + {}^{\bullet}OH \rightarrow H_{2}PO_{4}^{-} + OH^{-},$$

$$H_{2}PO_{4}^{-} + h^{+} \rightarrow H_{2}PO_{4}^{-}$$
(16)
(17)

Carbonate ions can act as 'OH radical scavenger to produce CO_3 ' radicals which has less oxidizing potential than the hydroxyl radicals (Eq. 18), thus resulting in the reduction of decolorization rate of RhB dye [8, 39, 44].

$$\operatorname{CO}_{3}^{2^{-}} + {}^{\bullet}\operatorname{OH} \to \operatorname{CO}_{3}^{\bullet^{-}} + \operatorname{OH}^{-}$$
(18)

Chloride ions can also act as scavengers of h^+ and 'OH according to the following equations (Eqs. 19 and 20). Moreover, the recombination of two Cl' would terminate the radical generation (Eq. 21) [8, 13, 54, 61].

$$Cl^{+} \bullet OH \rightarrow Cl^{\bullet} + OH^{-},$$
 (19)

$$\operatorname{Cl}^{-} + \operatorname{h}^{+} \to \operatorname{Cl}^{\bullet},$$
 (20)

$$\operatorname{Cl}^{\bullet} + \operatorname{Cl}^{\bullet} \to \operatorname{Cl}_{2},$$
 (21)

Sulfate anions can also retard the photocatalytic decolorization rate of the RhB dye via scavenging 'OH and h⁺ to generate SO₄⁻ radicals (Eqs. 22 and 23). Since SO₄⁻ is less reactive than 'OH radicals and h⁺, the addition of SO₄²⁻ inhibits the photocatalytic oxidation of the RhB dye [8, 41, 61].

$$\mathrm{SO}_4^{2-} + \mathrm{^{\bullet}OH} \rightarrow \mathrm{SO}_4^{-} + \mathrm{OH}^{-}$$
 (22)

$$\mathrm{SO}_4^{2-} + \mathrm{h}^+ \to \mathrm{SO}_4^{\bullet-}$$
 (23)

In case of the nitrate ions, we can observe that the addition of NO_3^- did not affect the photocatalytic decolorization rate of RhB dye appreciably. The role of NO_3^- in the photooxidation process can be interpreted through two factors:

(1) Nitrate ions are known to generate 'OH radicals under UV light irradiation through the following equations (Eqs. 24 and 25) [63].

$$NO_{3}^{\bullet} + h\nu \rightarrow NO_{3}^{\bullet-} \rightarrow NO_{2}^{\bullet} + O^{\bullet-}, \qquad (24)$$
$$O^{\bullet-} + H_{2}O \rightarrow {}^{\bullet}OH + OH^{-} \qquad (25)$$

(2) On the other hand, NO_3^- , especially at high concentrations, would exert an inner filter effect and reduce the UV light intensity acting on the target molecules, thus inhibiting the photocatalytic oxidation of RhB dye [13, 57]. It is obvious that the detrimental effect of NO_3^- was dominant on its promotional effect.

3.4. Discussion of photocatalysis mechanism

3.4.1. Influences of different scavengers

It is important to ascertain the main active species in the photocatalytic process for elucidating the photocatalytic mechanism. The reactive species in photocatalytic process could be detected trough trapping experiments of hydroxyl radicals ('OH), holes (h⁺) and superoxide radical anions (O_2^{\bullet}) by introducing isopropanol (IPA), triethanolamine (TEOA) and p-benzoquinone (BQ) [64, 65], respectively, in the system at the beginning of the photocatalytic reaction. Effects of a series of scavengers on the photocatalytic oxidation toward RhB dye over ZnO photocatalysts are shown in Fig. 11. Under simulated sunlight illumination, the percentage of RhB loss decreased the most rapidly from 97.30 % to 33.71 % after the addition of BQ

(0.001 mol/L), indicating O_2^{\bullet} were the main active species in the photocatalytic process. When TEOA (0.01 mol/L) and IPA (0.02 mol/L) were added, it reduced to 73.79% and 85.96 %, respectively, which implied h⁺ and 'OH radicals also played an important role on the photooxidation of RhB dye in the ZnO system. The conclusion could be drawn that O_2^{\bullet} are the main reactive species, and h⁺ and 'OH radicals also contribute to the photocatalytic oxidation reaction.

3.4.2. Hydroxyl radical analysis

The PL spectra variation of hydroxyl radical formed with irradiation time in the presence of ZnO during simulated sunlight irradiation in a 0.1 g/L coumarin aqueous solution were measured, as presented in Fig S11. It is clearly seen that the PL intensity of photogenerated 7-hydroxycoumarin at about 453 nm enhanced with increasing irradiation time, which indicated that the fluorescence was caused by chemical reaction of coumarin with 'OH radicals generated during photocatalytic process. The 'OH radicals predominantly result from the oxidation of H₂O by positive holes in the valence band of ZnO. The above results infer that 'OH radicals in solution, although detectable, are only a small part of the active oxygen radicals produced under simulated solar light irradiation and not the main active species for the photocatalytic oxidation of the dye, which is in accordance with the previous reports [35, 66].

3.4.3. Proposed mechanism discussion

Based on the above results, we tentatively propose the schematic of photooxidation of RhB dye by ZnO catalyst under simulated sunlight irradiation depicted in Fig. 12. In

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the early stage of photooxidation, RhB dyes are first adsorbed onto the ZnO surface, and then excited by visible light, which promote electrons from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) to generate singlet and triplets (marked as RhB^{*}), leading to electrons injection from the LUMO band of RhB into the conduction band (CB) of ZnO. This process is known as dye sensitization mechanism [36, 38]. Meanwhile, ZnO is illuminated by solar irradiation with photon energy equal to or greater than the band gap energy of ZnO, electrons in the valence band (VB) can be excited to the CB with simultaneous formation of the same amount of holes left behind. In general, part of the charge carriers rapidly underwent recombination, thus retarding the photocatalytic oxidation reaction. However, the transferred and photogenerated electrons in the CB of ZnO was picked up by the O_2 adsorbed on the surface of the catalyst to yield O_2^{-} and h^+ may react with surface-bound H₂O molecular to produce 'OH radicals. Subsequently, the excited dye was decomposed via attack by these reactive species, thus resulting in the decolorization and mineralization of RhB [67]. In order to prove this dye sensitization mechanism, we designed control experiments for the degradation of 4-nitrophenol solution (5 mg/L) by ZnO products with simulated solar light and visible light. We found that 88.34 % of 4-nitrophenol was removed at the irradiation of 140 min in the presence of both ZnO and simulated solar light. This was contrasted with only 12.50 % degradation for the identical experiment in the presence of ZnO products, but with visible light. This result indicated that high decolorization of RhB under visible light arises from a photosensitized process.

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3.5. The stability evaluation

The long-term stability of the photocatalyst is a significant issue for the photocatalytic process, so it is essential to assess the stability and consistency of the catalyst for practical application [40]. To evaluate the photocatalytic stability, the as-synthesized ZnO product was taken for five cyclic stability tests, as depicted in Fig. S12. It has been observed that there was no apparent decrease of photocatalytic activity after five-time recycling for RhB photooxidation. Consequently, the obtained ZnO photocatalyst exhibited excellent stability and reusability during the photocatalytic process.

4. Conclusion

In summary, the successful fabrication of monodisperse porous ZnO nanospheres has been achieved through a facile and cost-effective polyol-mediated preparation route followed by annealing at 400 °C for 2 h. The as-made ZnO nanoparticles were spherical with an average diameter of about 168 nm and were assembled by numerous small primary nanocrystals which had the crystallite size of about 14 nm. Meanwhile, a large number of irregular cavities existed inside the nanoparticles, which contributed to improvement in the specific surface area. Furthermore, porous ZnO products had no selectivity and could effectively degrade different organic pollutants. The RhB dye solution with a concentration of 10 mg/L was up to 97.30 % decolorization over the as-made ZnO products within 140 min under simulated sunlight irradiation. Alkaline condition was beneficial to the oxidation of RhB aqueous solution. As the reaction temperature increased from 15 to 35 °C, the decolorization rate was found gradually improved; whereas, at 45 °C, the decolorization rate decreased slightly. The addition

of inorganic oxidants and transition-metal ions improved the photocatalytic reaction but inorganic anions showed detrimental effect. The promotional effect for inorganic oxidants was found to rank in the order $IO_4^- > S_2O_8^{2-} > H_2O_2 > BrO_3^- > CIO_3^-$, and transition-metal ions was found to be in the order $Zn^{2+} > Mn^{2+} > Ni^{2+} > Cu^{2+} > Fe^{2+} >$ Co^{2+} , whereas the retardation effect for inorganic anions was ranked as follows: $H_2PO_4^- > CO_3^{2-} > CI^- > SO_4^{2-} > NO_3^-$. At last, reactive species in RhB oxidation were pinpointed by adding a series of scavengers into the photocatalytic reaction and O_2^{--} were determined to be the main reactive species in the photocatalytic process. The ZnO products could be easily separated and reused. Therefore, it is concluded that solar light induced photocatalysis over the as-obtained ZnO catalyst in wastewater treatment and remediation of polluted environment is a viable technique in the fields of environmental purification and water disinfection.

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Figure captions

Fig. 1 Characterization of the as-synthesized porous ZnO nanospheres. (a) TEM image at low magnification; (b) the histogram of particle diameters; (c) TEM image of the as-prepared porous ZnO products; (d) TEM image at high magnification of a single ZnO nanosphere; (e) typical HRTEM image of porous ZnO nanosphere and (f) the SAED pattern of the ZnO nanosphere. The insets of (e) are the corresponding magnified images of the region by a circle.



Fig. 2 Temporal changes in the UV-vis absorption spectra of aqueous RhB solution (10 mg/L) over porous ZnO products (10 mg) during irradiation with simulated sunlight; (a) 0 min, (b) 20 min, (c) 40 min, (d) 60 min, (e) 80 min, (f) 100 min, (g) 120 min and (h) 140 min. The inset is the visible color change for the RhB dye aqueous solution during photocatalytic degradation.



Fig. 3 Photodegradability of aqueous RhB aqueous (10 mg/L) over porous ZnO products (10 mg). (a) dye solution treated with ZnO in dark, (b) dye solution irradiated with simulated sunlight irradiation in the absence of ZnO, (c) dye solution irradiated with visible light irradiation in the presence of ZnO products, (d) dye solution irradiated with simulated sunlight irradiation in the presence of ZnO products and (e) pseudo-first-order linear plot of $\ln(C_0/C)$ versus reaction time for the degradation kinetics of RhB solution over ZnO under simulated sunlight irradiation .



Fig. 4 Effect of catalyst amount on RhB loss in the presence of porous ZnO products (experimental conditions: $[RhB]_0 = 10 \text{ mg/L}$, PH= 6.5 and reaction temperature = 25 °C). (a) 5 mg, (b) 10 mg, (c) 20 mg and (d) 30 mg. Turnover number (and quantum yield) values are: $1.17 \times 10^{-2} (1.54 \times 10^{-6})$, $5.91 \times 10^{-3} (1.56 \times 10^{-6})$, $2.58 \times 10^{-3} (1.36 \times 10^{-6})$ and $1.60 \times 10^{-3} (1.26 \times 10^{-6})$ respectively.



Fig. 5 Effect of initial dye concentration on RhB loss in the presence of ZnO products (experimental conditions: Catalyst amount = 10 mg, pH= 6.5 and reaction temperature = 25 °C). (a) 5 mg/L, (b) 10 mg/L, (c) 15 mg/L, (d) 20 mg/L and (e) 30 mg/L. Turnover number (and quantum yield) values are: $2.11 \times 10^{-3} (5.56 \times 10^{-7}), 5.91 \times 10^{-3} (1.56 \times 10^{-6}), 9.18 \times 10^{-3} (2.42 \times 10^{-6}), 1.21 \times 10^{-2} (3.19 \times 10^{-6}) and 1.44 \times 10^{-2} (3.80 \times 10^{-6}) respectively.$



Fig. 6 Effect of reaction temperature on RhB loss in the presence of ZnO products (experimental conditions: $[RhB]_0 = 10 \text{ mg/L}$, catalyst amount = 10 mg and



pH= 6.5).

Fig. 7 Effect of initial pH on RhB loss in the presence of ZnO products (experimental conditions: $[RhB]_o = 10 \text{ mg/L}$, catalyst amount = 10 mg and reaction temperature = 25 °C).





Fig. 8 Effect of inorganic oxidants concentration on photocatalytic decolorization



Fig. 9 Effect of transition-metal ions on the photocatalytic decolorization rate of



Fig. 10 Effect of inorganic anion concentration on photocatalytic decolorization rate

Fig. 11 Trapping experiment of active species for the photocatalytic oxidation of



RhB with ZnO under simulated sunlight irradiation.

Fig. 12 Schematic drawing illustrates the mechanism of charge separation and photocatalytic reaction process in a semiconductor ZnO particle with the presence of RhB dye pollutant, under simulated sunlight irradiation.

