Research Article

Preparation, Characterization, and Activity of Y_2O_3 -ZnO Complex Oxides for the Photodegradation of 2,4-Dinitrophenol

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With strong adsorption selectivity and thermal stability, Y_2O_3 was added to ZnO to obtain Y_2O_3 -ZnO complex oxides by a precipitation method. The Y_2O_3 -ZnO complex oxides were characterized by X-ray diffraction, Raman spectroscopy, X-ray photoelectron spectroscopy, UV-vis diffuse reflectance spectroscopy, physisorption analyzer, and terephthalic acid photoluminescence probing techniques and were used for the degradation of 2,4-dinitrophenol. More hydroxyl radicals were generated on the surface of the ZnO after adding moderate Y_2O_3 . The Y_2O_3 -ZnO complex oxides which contained 0.50% Y_2O_3 were proved to be the optimal photocatalyst and achieved a degradation of 81.2% of 2,4-dinitrophenol solution, compared to 57.6% achieved under the same photocatalytic conditions with ZnO alone.

1. Introduction

With the development of human society, wastewater treatment is attracting more and more attention. Phenolics are typical pollutants since these compounds are commonly used in the production of a wide range of industrial products, including dyes, textiles, gunpowder, pesticides, and plastics [1, 2], which has serious toxic effects on many biological resources [3]. Their strong toxicity and stability make it difficult to use traditional methods of biological treatment to degrade phenols [4].

With highly photocatalytic activity under the UV irradiation, ZnO showed good possibilities for application as photocatalyst in sewage treatment [5, 6]. However, the recombination of the electron and hole of ZnO occurs easily, which limits its application in industry [7]. Researchers have tried many preparation methods, such as solvothermal [8], solid state reaction [9], and sol-gel [10] to improve the photocatalytic activity of ZnO. And on the other hand, to improve the physical, chemical, and optical properties, ZnO was modified by doping with metal or nonmetal elements. For example, doping with sulphur can expand the lattice constants of ZnO and increase the oxygen vacancy of ZnO [11], doping with

chromium can decrease the band gap of ZnO and increase the absorption of visible light [12], and doping with gold can inhibit the recombination of photoinduced electrons and holes [13].

The rare earth element yttrium (Y) has one occupied 4d orbital, which easily produces several electron configurations, and its oxides have many advantages, such as many crystal types, strong adsorption selectivity, good thermal stability, and electronic conductivity [14, 15]. At present, Y has been used to improve the photocatalytic activity of a number of metal oxides, for example, Y^{3+}/TiO_2 [16], $Y^{3+}/Bi_5Nb_3O_{15}$ [17], PbYO [18], and $InYO_3$ [19]. There are reports about Y being used to improve the optical performance of ZnO [20]; however, there is no report about Y_2O_3 -ZnO being used as a photocatalyst.

Based on the previous studies of PbYO [18] and $InYO_3$ [19], Y_2O_3 -ZnO complex oxides were prepared by a precipitation method and characterized by X-ray diffraction (XRD), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), UV-vis diffuse reflectance spectroscopy, physisorption analyzer, and terephthalic acid photoluminescence (TA-PL) probing techniques. And the photocatalytic activity of the Y_2O_3 -ZnO complex oxides was studied using

2,4-dinitrophenol (2,4-DNP) as simulate phenolic wastewater.

2. Experimental

2.1. Materials. Yttrium nitrate, zinc nitrate, ammonium bicarbonate, and 2,4-dinitrophenol, all reagents and solvents, were of analytical grade and were obtained commercially.

2.2. Preparation of Y_2O_3 -ZnO Complex Oxides. The Y_2O_3 -ZnO complex oxides were prepared by a precipitation method. To prepare the Y_2O_3 -ZnO complex oxides, a $0.5 \text{ mol}\cdot\text{L}^{-1}$ $Y(NO_3)_3$ solution was added to a $0.3 \text{ mol}\cdot\text{L}^{-1}$ $Zn(NO_3)_2$ solution until the $Y(NO_3)_3$ content reached 0.50%, 1.00%, 1.50%, and 2.00% (mole fraction) of the $Zn(NO_3)_2$, respectively. Next, a $0.6 \text{ mol}\cdot\text{L}^{-1}$ NH_4HCO_3 solution was added to the mixture while stirring to yield a white precipitate. The precipitate was filtered and washed with distilled water several times and dried at 120°C for 12 h, resulting in the Y_2O_3 -ZnO precursors. These precursors were ground to pass through a 100-mesh sieve mesh and calcined at 800°C for 2 h to obtain Y_2O_3 -ZnO photocatalysts. In our experiment, four samples with initial Y_2O_3 content of 0.25%, 0.50%, 0.75%, and 1.00% were defined as 0.25%- Y_2O_3 -ZnO, 0.50%- Y_2O_3 -ZnO, 0.75%- Y_2O_3 -ZnO, and 1.00%- Y_2O_3 -ZnO, respectively. For comparison, a sample of ZnO was also prepared by the same method as described above just without the addition of $Y(NO_3)_3$.

2.3. Characterization of Y_2O_3 -ZnO Complex Oxides. XRD was performed using a D8 ADVANCE X-ray powder diffraction instrument (Bruker Corporation), equipped with a Cu $K\alpha$ radiation source. Raman spectrum was obtained on a LabRAM HR UV-NIR Raman spectrometer (HORIBA Jobin Yvon) with a laser source of excitation wavelength 488 nm. UV-vis diffuse reflectance spectra were obtained using an UV-vis spectrometer (U4100, Hitachi High-Technologies Corporation) with $BaSO_4$ used as the reflectance standard. XPS analyses were conducted on a thermo ESCALAB 250XI multifunctional imaging electron spectrometer (Thermo Fisher Scientific Inc.) equipped with an Al $K\alpha$ radiation source. The energy resolution of the spectrometer was 0.48 eV. The peak positions were corrected for sample charging by setting the Cls binding energy at 284.8 eV. The XPS analysis was conducted at 150 W and at a pass energy of 40 eV. N_2 adsorption-desorption was performed at liquid nitrogen temperature with a ASAP 2020 physisorption analyzer (Micromeritics Instrument Corporation), based on the adsorption branches of N_2 sorption isotherms; the Brunauer-Emmett-Teller (BET) method was used to calculate the surface area of the catalyst.

The photoluminescence (PL) technique with terephthalic acid as a probe molecule was used to detect the formation of $\bullet\text{OH}$ on the surface of the UV-illuminated photocatalyst. The experiment produced at ambient temperature, 0.1 g of the Y_2O_3 -ZnO complex oxides which contained different content of Y_2O_3 , was dispersed in a 20 mL of the $5 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ terephthalic acid aqueous solution with a concentration

of $2 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ NaOH in a dish with a diameter of about 9.0 cm. A 15 W, 365 nm UV lamp (6 cm above the dishes) was used as a light source. After UV irradiated for 30 min, the reaction solution was centrifuged and filtrated to measure the increasing amount in the PL intensity on a fluorescence spectrophotometer (Shimadzu. RF-5301PC) at 425 nm excited by 315 nm light of 2-hydroxyterephthalic acid, as was described in the previous work [18].

2.4. Photocatalytic Degradation of 2,4-DNP. The photocatalytic degradation reaction was carried out in a SGY-1 photochemical reactor (Nanjing Stonetech Electric Equipment Co., Ltd.). 0.2 g of ZnO or Y_2O_3 -ZnO complex oxides were dispersed in 200 mL of 2,4-DNP aqueous solution ($10 \text{ mg}\cdot\text{L}^{-1}$) and stirred in the dark for 40 min to reach adsorption equilibrium. Then, the mixed solution was transferred to the photochemical reactor and irradiated by a 500 W xenon lamp. Every 20 minutes, 2 mL of the reaction mixture was removed by pipette and centrifuged to remove the photocatalyst particles prior to the analysis of the concentration of the remaining 2,4-DNP. The concentration of 2,4-DNP in the solution was determined by monitoring group absorbance at 358 nm, using a TU1901 UV-vis spectrophotometer (Beijing Purkinje General Instrument CO., Ltd.).

3. Results and Discussion

3.1. Photocatalysts Characterization. Figure 1(a) shows that the characteristic diffraction peaks of ZnO are corresponding to (100), (002), (101), (102), (110), (103), (200), (112), and (201) planes, which indicated the crystal structure of ZnO is hexagonal wurtzite structure (JCPDS: 36-1451) [21]. The grain size of the Y_2O_3 -ZnO was calculated by the Scherrer equation according to the full width at half maximum (FWHM) of the (101) crystals; the results displayed that the grain size of ZnO, 0.25%- Y_2O_3 -ZnO, 0.50%- Y_2O_3 -ZnO, 0.75%- Y_2O_3 -ZnO, and 1.00%- Y_2O_3 -ZnO was 56.24, 48.35, 42.62, 42.61, and 40.52 nm, respectively, which indicated that the grain size decreased with the increasing of Y_2O_3 content. When 0.25% Y_2O_3 was added to the ZnO, no Y_2O_3 characteristic diffraction peak was observed, which was due to the low composition of Y_2O_3 [22]. However, when the Y_2O_3 content was increased to 0.50%, 0.75%, and 1.00%, a very weak Y_2O_3 (JCPDS: 65-3178) diffraction peak was found at $2\theta = 29.2^\circ$, which indicated that the Y_2O_3 -ZnO complex oxides were formed.

Figure 1(b) shows that the positions of Raman bands for Y_2O_3 -ZnO do not change and no new band is observed. However, obvious ZnO phonon modes appear at 331, 380, 438, and 575 cm^{-1} , which has been assigned to the $2E_2$, A_1 (transverse optical), E_2 , and A_1 (longitudinal optical) mode of ZnO, respectively. Among these phonon modes, E_2 and $2E_2$ are related to the oxygen vacancies, surface states, and defects. The intensity of Raman band at E_2 was changed, which due to the Y_2O_3 was added to ZnO [23, 24]. Combined with the XRD results, the Y_2O_3 -ZnO complex oxides were formed, and compared to ZnO, the Raman bands of the Y_2O_3 -ZnO complex oxides are broadening, which may be

FIGURE 1: XRD patterns (a) and Raman spectra (b) of ZnO (E), 0.25%- Y_2O_3 -ZnO (D), 0.50%- Y_2O_3 -ZnO (C), 0.75%- Y_2O_3 -ZnO (B), and 1.00%- Y_2O_3 -ZnO (A), JCPDS Card number 36-1451 (F) and JCPDS Card number 65-3178 (G).

FIGURE 2: TEM image (a) and energy dispersive X-ray spectrum (EDS) of 0.50%- Y_2O_3 -ZnO (b).

caused by the three-dimensional confinement of phonons in the smaller size of the Y_2O_3 -ZnO complex oxides that will produce more oxygen defects [25].

Figure 2 shows the morphology of the 0.50%- Y_2O_3 -ZnO sample. From Figure 2(a) it can be seen that the compound is composed of generally spherically shaped particles of irregular diameter, ranging from 25 nm to 200 nm. Figure 2(b) shows the energy dispersive X-ray spectrum (EDS) of the sample particles. Sharp peaks of Zn, Y, and O were obtained; no other peak related to any other element was detected in the spectrum within the detection limit which confirms that synthesized material is composed of Zn, Y and O only. Furthermore, the ratio from Zn to Y in the sample was 54.9 : 0.9, which is lower than the theoretical value 100. This result may be caused by an uneven distribution of Y in the catalyst.

The UV-visible diffuse reflectance spectra of ZnO and Y_2O_3 -ZnO can be seen from Figure 3(a). Compared to ZnO,

the 0.25%- Y_2O_3 -ZnO, 0.50%- Y_2O_3 -ZnO, and 0.75%- Y_2O_3 -ZnO exhibit stronger absorption in the ultraviolet than the ZnO and the 1.00%- Y_2O_3 -ZnO, and the 0.50%- Y_2O_3 -ZnO showed the strongest absorption in the ultraviolet. When the amount of Y_2O_3 is above 0.75%, excessive Y_2O_3 is possible to create aggregation phenomenon in the ZnO. And the band gap of the Y_2O_3 is wider which is unfavorable for light absorption, which will reduce the effective absorption surface of the samples; therefore, the absorption in the ultraviolet decreased with the increasing amount of Y_2O_3 when the Y_2O_3 content was above 0.75%.

The differentiated absorption spectra are shown in Figure 3(b), which gained from the first order differential equations, and accentuate the slight differences seen in Figure 3(a). The absorption edge and maximum absorption strengths of the Y_2O_3 -ZnO complex oxides are shown in Table 1. The band gap of the Y_2O_3 -ZnO samples is between

FIGURE 3: UV-visible diffuse reflectance spectrum of Y_2O_3 -ZnO complex oxides contained different Y_2O_3 content (a) and the corresponding first derivative of the spectrum (b).

TABLE 1: The absorption edge and absorb intensity of ZnO and Y_2O_3 -ZnO complex oxides contained different Y_2O_3 content.

Y_2O_3 content/%	Absorb edge (nm)	Band gap (eV)	Absorption intensity (a.u.)
0	383	3.24	6.74
0.25	381	3.26	8.31
0.50	378	3.28	10.63
0.75	379	3.27	7.67
1.00	382	3.25	3.89

3.24 eV and 3.28 eV, indicating the absorption edge of catalyst depends on the structure of ZnO itself.

Figure 4(a) shows the Zn 2p XPS spectrum of ZnO and Y_2O_3 -ZnO complex oxides. The Zn 2p peaks of ZnO and Y_2O_3 -ZnO complex oxides are around 1021.1 eV and 1044.2 eV, which are attributed to the $2p_{3/2}$ and $2p_{1/2}$ of Zn^{2+} states in ZnO [26]. A ternate peak was observed from Figure 4(b) which was corresponding to Y 3d; peak pairs with binding energies around 156.4 eV and 158.3 eV were for Y $3d_{5/2}$ and Y $3d_{3/2}$, respectively, which are related to Y-O bonding in the Y_2O_3 , and another peak pairs are noticed around 160.0 eV which may be attributed to the Y-OH bonding of $\text{Y}(\text{OH})_3$ [27]. The XPS spectrum of O1s of all the samples is not symmetrical (Figure 4(c)), the peaks around 530.0 eV may be attributed to the oxygen (O^{2-}) in the lattice of ZnO, while the others around 531.1 eV are associated with the oxygen in the hydroxyl group ($-\text{OH}$) on the surface of ZnO [26, 28].

From Table 2, the content of oxygen in the lattice of the 0.25%- Y_2O_3 -ZnO, 0.50%- Y_2O_3 -ZnO, and 0.75%- Y_2O_3 -ZnO

was less than that of ZnO and 1.00%- Y_2O_3 -ZnO. However, the content of oxygen in the hydroxyl group of the 0.25%- Y_2O_3 -ZnO, 0.50%- Y_2O_3 -ZnO, and 0.75%- Y_2O_3 -ZnO was higher in comparison to the ZnO and 1.00%- Y_2O_3 -ZnO.

In the photocatalytic oxidation reaction, the adsorbed oxygen species play an important role. Oxygen species of chemical adsorption, such as surface hydroxyl groups, are scavengers of photoinduced holes and can generate active species $\bullet\text{OH}$. $\bullet\text{OH}$ in the adsorbed phase and solution phase is a strong oxidant and can easily initiate an oxidation reaction [28]. Therefore, increasing the adsorption of the hydroxyl groups on a photocatalyst surface benefits to the photocatalytic oxidation reaction. Table 2 shows that the surface hydroxyl groups content of the 0.50%- Y_2O_3 -ZnO is higher than that of the other samples. Thus, it may be observed that the 0.50%- Y_2O_3 -ZnO has a higher level of photocatalytic activity.

From the surface area of Y_2O_3 -ZnO complex oxides (Table 3), it can be seen that the surface area of ZnO ($11.82 \text{ m}^2 \cdot \text{g}^{-1}$) was almost the same after adding 0.25% Y_2O_3 ($11.48 \text{ m}^2 \cdot \text{g}^{-1}$). After 0.50% Y_2O_3 was added to ZnO, the surface area increased to $14.25 \text{ m}^2 \cdot \text{g}^{-1}$ due to its smaller grain size which was confirmed by the results of XRD. The photocatalytic process mainly occurs on the surface of the photocatalyst. Among these samples, the 0.50%- Y_2O_3 -ZnO has the highest surface area, which may have the highest photocatalytic activity.

Hydroxyl radicals are an important reactive species in the photocatalytic process [29, 30]. In general, terephthalic acid reacts with $\bullet\text{OH}$ readily to produce a highly fluorescent product, 2-hydroxyterephthalic acid, whose PL peak intensity is proportional to the amount of $\bullet\text{OH}$ produced in water [29, 30]. Figure 5 shows the PL spectra of the Y_2O_3 -ZnO complex oxides contained with different amounts of Y_2O_3 .

FIGURE 4: XPS spectra of (a) Zn 2p; (b) Y 3d; and (c) O 1s in ZnO (A), 0.25%-Y₂O₃-ZnO (B), 0.50%-Y₂O₃-ZnO (C), 0.75%-Y₂O₃-ZnO (D), and 1.00%-Y₂O₃-ZnO (E).

For the 0.50%-Y₂O₃-ZnO, the amount of •OH produced on its surface is much higher than that of the other samples. From the above discussion, the surface area of the 0.50%-Y₂O₃-ZnO is the highest, considering the fact that photocatalytic reactions mainly occur on the surface of catalyst, and the 0.50%-Y₂O₃-ZnO shows a little stronger light absorption than other Y₂O₃-ZnO complex oxides according to the UV-visible diffuse reflectance spectra; thus, more •OH can be produced on the surface of the 0.50%-Y₂O₃-ZnO. These data suggest that the photocatalytic activity is the greatest when the Y₂O₃ content is 0.50%.

3.2. Photocatalytic Degradation of 2,4-DNP. Figure 6(a) shows the adsorption of 2,4-DNP on the surface of Y₂O₃-ZnO complex oxides. After adsorption for 40 min, the 2,4-DNP solution reaches adsorption equilibrium, and the saturated adsorption amount of 2,4-DNP on ZnO, 0.25%-Y₂O₃-ZnO, 0.50%-Y₂O₃-ZnO, 0.75%-Y₂O₃-ZnO, and 1.00%-Y₂O₃-ZnO is 3.04%, 2.98%, 3.33%, 3.18%, and 2.87%, respectively. The 0.50%-Y₂O₃-ZnO shows the strongest adsorption of 2,4-DNP which corresponds to its larger surface area, and this may improve its photocatalytic activity. Figure 6(b) shows the results of using ZnO and

TABLE 2: Binding energy and the percent of valence state of O 1s in ZnO and Y_2O_3 -ZnO complex oxides contained different Y_2O_3 content^a.

Y_2O_3 content/%	0	0.25	0.50	0.75	1.00
O ²⁻	530.0 (55.25)	529.9 (44.34)	529.9 (35.67)	530.0 (37.44)	530.0 (62.70)
•OH	531.1 (44.75)	531.2 (55.66)	531.0 (64.33)	531.0 (62.56)	531.6 (37.30)

^aSurface concentration of different O states is in parentheses.

TABLE 3: Surface area of ZnO and Y_2O_3 -ZnO complex oxides contained different Y_2O_3 content.

Y_2O_3 content/%	Surface area/m ² ·g ⁻¹
0	11.82
0.25	11.48
0.50	14.25
0.75	13.73
1.00	9.67

TABLE 4: Degradation rate as a function of the concentration of Y_2O_3 and pseudo-first order rate constants derived from fitting experimental data to computer model.

Y_2O_3 content/%	Rate constant (10 ⁻³ min ⁻¹)	Correlation coefficient, R ²
0	8.6	0.996
0.25	14.3	0.985
0.50	16.4	0.982
0.75	12.8	0.989
1.00	9.6	0.969

Y_2O_3 -ZnO complex oxides with different contents of Y_2O_3 as photocatalysts for photocatalytic degradation of 2,4-DNP under light irradiation. The data show that the amount of Y_2O_3 has a great effect on the degradation of 2,4-DNP. When without catalyst, a very small amount of degradation of 2,4-DNP is observed under the light irradiation. Specifically, after light irradiation for 100 min, the degradation of 2,4-DNP was 57.6%, 78.0%, 81.2%, 73.0%, and 63.3% when using the ZnO, 0.25%- Y_2O_3 -ZnO, 0.50%- Y_2O_3 -ZnO, 0.75%- Y_2O_3 -ZnO, and 1.00%- Y_2O_3 -ZnO, respectively. These results indicated that when 0.50%- Y_2O_3 -ZnO was used as the photocatalyst and after reaction for 100 min, the degradation of 2,4-DNP was 81.2%, which was higher than that of TiO₂ [31] and ZnO [32] on the photocatalytic degradation of 2,4-DNP. These degradation data of 2,4-DNP show that the optimal amount of Y_2O_3 in the Y_2O_3 -ZnO photocatalyst is 0.50%.

The kinetics of the 2,4-DNP degradation was found to fit a pseudo-first order model by plotting $-\ln(c/c_0)$ versus reaction (t), as shown in Table 4.

The above results show that the reaction rate constant of the photocatalytic degradation of 2,4-DNP by the 0.50%- Y_2O_3 -ZnO was 0.0164 min⁻¹, which is 1.7 times higher than that of the 1.00%- Y_2O_3 -ZnO. Compared with ZnO, the reaction rate constant of 0.50%- Y_2O_3 -ZnO is 1.9 times higher than that of ZnO photocatalyst.

FIGURE 5: Fluorescence spectra observed after illumination of ZnO, 0.25%- Y_2O_3 -ZnO, 0.50%- Y_2O_3 -ZnO, 0.75%- Y_2O_3 -ZnO, and 1.00%- Y_2O_3 -ZnO in 2×10^{-3} mol·L⁻¹ NaOH solution of terephthalic acid (excitation at 315 nm) and the fluorescence spectrum of pure terephthalic acid. Each fluorescence spectrum was recorded after 30 min of UV irradiation.

Combined with the results from the PL intensity of the samples, it can be seen that the amount of •OH produced on the surface of the 0.50%- Y_2O_3 -ZnO is larger than that of the other samples. Oxidized by more •OH, the 2,4-DNP was degraded faster when the 0.50%- Y_2O_3 -ZnO was used as the photocatalyst. It can be deduced that the photocatalytic activity of ZnO for the degradation of 2,4-DNP can be enhanced by adding moderate amount of Y_2O_3 and the 0.50%- Y_2O_3 -ZnO exhibited the highest photocatalytic activity.

4. Conclusions

The photocatalytic activity of ZnO can be enhanced by adding a moderate amount of Y_2O_3 . Compared with ZnO, after adding moderate amount of Y_2O_3 , the surface area of the photocatalysts was increased and more hydroxyl free radicals were generated on the surface of the photocatalysts, thus promoting the photocatalytic reaction. The optimal amount of Y_2O_3 in the Y_2O_3 -ZnO complex oxides was 0.50%, achieving 81.2% degradation of 2,4-DNP.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

FIGURE 6: The adsorption of 2,4-DNP in the dark (a) and the effect of the Y_2O_3 content of the Y_2O_3 -ZnO on the photocatalytic degradation of 2,4-DNP (b).

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References

- [1] Y.-Z. Ren, Z.-L. Wu, M. Franke et al., "Sono-electrochemical degradation of phenol in aqueous solutions," *Ultrasonics Sonochemistry*, vol. 20, no. 2, pp. 715–721, 2013.
- [2] L. J. Kennedy, J. J. Vijaya, K. Kayalvizhi, and G. Sekaran, "Adsorption of phenol from aqueous solutions using mesoporous carbon prepared by two-stage process," *Chemical Engineering Journal*, vol. 132, no. 1–3, pp. 279–287, 2007.
- [3] X. Jin, J. Gao, J. Zha et al., "A tiered ecological risk assessment of three chlorophenols in Chinese surface waters," *Environmental Science and Pollution Research*, vol. 19, no. 5, pp. 1544–1554, 2012.
- [4] R. Blasco and F. Castillo, "Characterization of 2,4-dinitrophenol uptake by *Rhodobacter capsulatus*," *Pesticide Biochemistry and Physiology*, vol. 58, no. 1, pp. 1–6, 1997.
- [5] S. Senthilvelan, V. L. Chandraboss, B. Karthikeyan, L. Natana-patham, and M. Murugavelu, " TiO_2 , ZnO and nanobimetallic silica catalyzed photodegradation of methyl green," *Materials Science in Semiconductor Processing*, vol. 16, no. 1, pp. 185–192, 2013.
- [6] N. Kaneva, I. Stambolova, V. Blaskov, Y. Dimitriev, A. Bojinova, and C. Dushkin, "A comparative study on the photocatalytic efficiency of ZnO thin films prepared by spray pyrolysis and sol-gel method," *Surface and Coatings Technology*, vol. 207, pp. 5–10, 2012.
- [7] J. B. Zhong, J. Z. Li, Y. Lu et al., "Fabrication of Bi^{3+} -doped ZnO with enhanced photocatalytic performance," *Applied Surface Science*, vol. 258, no. 11, pp. 4929–4933, 2012.
- [8] Y. Zhang, Q. Wang, J. Xu, and S. Ma, "Synthesis of Pd/ZnO nanocomposites with high photocatalytic performance by a solvothermal method," *Applied Surface Science*, vol. 258, no. 24, pp. 10104–10109, 2012.
- [9] X. Jia, H. Fan, M. Afzaal, X. Wu, and P. O'brien, "Solid state synthesis of tin-doped ZnO at room temperature: characterization and its enhanced gas sensing and photocatalytic properties," *Journal of Hazardous Materials*, vol. 193, pp. 194–199, 2011.
- [10] M. Fu, Y. Li, S. Wu, P. Lu, J. Liu, and F. Dong, "Sol-gel preparation and enhanced photocatalytic performance of Cu-doped ZnO nanoparticles," *Applied Surface Science*, vol. 258, no. 4, pp. 1587–1591, 2011.
- [11] A. B. Patil, K. R. Patil, and S. K. Pardeshi, "Ecofriendly synthesis and solar photocatalytic activity of S-doped ZnO," *Journal of Hazardous Materials*, vol. 183, no. 1–3, pp. 315–323, 2010.
- [12] L. Li, W. Wang, H. Liu, X. Liu, Q. Song, and S. Ren, "First principles calculations of electronic band structure and optical properties of Cr-doped ZnO," *Journal of Physical Chemistry C*, vol. 113, no. 19, pp. 8460–8464, 2009.
- [13] M. de Lourdes Ruiz Peralta, U. Pal, and R. S. Zeferino, "Photoluminescence (PL) quenching and enhanced photocatalytic activity of Au-decorated ZnO nanorods fabricated through microwave-assisted chemical synthesis," *ACS Applied Materials & Interfaces*, vol. 4, no. 9, pp. 4807–4816, 2012.
- [14] V. H. Mudavakkat, M. Noor-A-Alam, K. K. Bharathi et al., "Structure and AC conductivity of nanocrystalline Yttrium oxide thin films," *Thin Solid Films*, vol. 519, no. 22, pp. 7947–7950, 2011.
- [15] N. Li and K. Yanagisawa, "Sub-micrometer sized yttrium oxide fibers prepared through hydrothermal reaction," *Materials Research Bulletin*, vol. 46, no. 3, pp. 428–431, 2011.
- [16] X. Niu, S. Li, H. Chu, and J. Zhou, "Preparation, characterization of Y^{3+} -doped TiO_2 nanoparticles and their photocatalytic

- activities for methyl orange degradation," *Journal of Rare Earths*, vol. 29, no. 3, pp. 225–229, 2011.
- [17] J. Zhao, B. Yao, Q. He, and T. Zhang, "Preparation and properties of visible light responsive Y^{3+} doped $Bi_5Nb_3O_{15}$ photocatalysts for Ornidazole decomposition," *Journal of Hazardous Materials*, vol. 229–230, pp. 151–158, 2012.
- [18] T.-M. Su, Z.-L. Liu, Y. Liang, Z.-Z. Qin, Y. Liu, and Y.-Q. Huang, "Preparation of $PbYO$ composite photocatalysts for degradation of methyl orange under visible-light irradiation," *Catalysis Communications*, vol. 18, pp. 93–97, 2012.
- [19] Z.-Z. Qin, Y. Liang, Z.-L. Liu, and W. Q. Jiang, "Preparation of $InYO_3$ catalyst and its application in photodegradation of molasses fermentation wastewater," *Journal of Environmental Sciences*, vol. 23, no. 7, pp. 1219–1224, 2011.
- [20] P.-T. Hsieh, R.-K. Chuang, C.-Q. Chang, C.-M. Wang, and S.-J. Chang, "Optical and structural characteristics of yttrium doped ZnO films using sol-gel technology," *Journal of Sol-Gel Science and Technology*, vol. 58, no. 1, pp. 42–47, 2011.
- [21] K. Zhou, Q. Zhang, Y. Shi, S. Jiang, Y. Hu, and Z. Gui, "A facile method for preparation ZnO with different morphology and their optical property," *Journal of Alloys and Compounds*, vol. 577, pp. 389–394, 2013.
- [22] C. Karunakaran, P. Gomathisankar, and G. Manikandan, "Preparation and characterization of antimicrobial Ce-doped ZnO nanoparticles for photocatalytic detoxification of cyanide," *Materials Chemistry and Physics*, vol. 123, no. 2–3, pp. 585–594, 2010.
- [23] W. Baiqi, S. Xudong, F. Qiang et al., "Photoluminescence properties of Co-doped ZnO nanorods array fabricated by the solution method," *Physica E: Low-Dimensional Systems and Nanostructures*, vol. 41, no. 3, pp. 413–417, 2009.
- [24] J. Kong, D. Fan, and Y. Zhu, "Synthesis and Raman spectra of hammer-shaped ZnO nanostructures via thermal evaporation growth," *Materials Science in Semiconductor Processing*, vol. 15, no. 3, pp. 258–263, 2012.
- [25] M. Yuan, J. Zhang, S. Yan et al., "Effect of Nd_2O_3 addition on the surface phase of TiO_2 and photocatalytic activity studied by UV Raman spectroscopy," *Journal of Alloys and Compounds*, vol. 509, no. 21, pp. 6227–6235, 2011.
- [26] R. Saravanan, K. Santhi, N. Sivakumar, V. Narayanan, and A. Stephen, "Synthesis and characterization of ZnO and Ni doped ZnO nanorods by thermal decomposition method for spintronics application," *Materials Characterization*, vol. 67, pp. 10–16, 2012.
- [27] P. S. Das, G. K. Dalapati, D. Z. Chi, A. Biswas, and C. K. Maiti, "Characterization of Y_2O_3 gate dielectric on n-GaAs substrates," *Applied Surface Science*, vol. 256, no. 7, pp. 2245–2251, 2010.
- [28] M. Fan, Z. Qin, Z. Liu, and T. Su, "Preparation of $Bi_xY_{(2-x)}O_3$ and its photocatalytic degradation of molasses fermentation wastewater under visible-light irradiation," *Advanced Materials Research*, vol. 287–290, pp. 1640–1645, 2011.
- [29] S. S. Shinde, C. H. Bhosale, and K. Y. Rajpure, "Hydroxyl radical's role in the remediation of wastewater," *Journal of Photochemistry and Photobiology B: Biology*, vol. 116, pp. 66–74, 2012.
- [30] Q. Xiao and L. Ouyang, "Photocatalytic activity and hydroxyl radical formation of carbon-doped TiO_2 nanocrystalline: effect of calcination temperature," *Chemical Engineering Journal*, vol. 148, no. 2–3, pp. 248–253, 2009.
- [31] R. Chand and F. Shiraishi, "Reaction mechanism of photocatalytic decomposition of 2, 4-dinitrophenol in aqueous suspension of TiO_2 fine particles," *Chemical Engineering Journal*, vol. 233, pp. 369–376, 2013.
- [32] J. J. Vora, S. K. Chauhan, K. C. Parmar, S. B. Vasava, S. Sharma, and L. S. Bhutadiya, "Kinetic study of application of ZnO as a photocatalyst in heterogeneous medium," *E-Journal of Chemistry*, vol. 6, no. 2, pp. 531–536, 2009.