

Research Article

Preparation of Ni Doped ZnO-TiO₂ Composites and Their Enhanced Photocatalytic Activity

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Herein, Ni doped ZnO-TiO₂ composites were prepared by facile sol-gel approach and were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), UV-visible diffuse reflectance spectroscopy (UV-Vis DRS), X-ray photoelectron spectroscopy (XPS), and photoluminescence spectroscopy (PL). The results indicated that the Ni ions can be incorporated into the lattice of TiO₂ structure and replace Ti. The introduction of Ni expanded light absorption of TiO₂ to visible region, increased amount of surface hydroxyl groups and physically adsorbed oxygen (as the electronic scavenges), and then enhanced separation rate of photogenerated carriers. The photodegradation test of reactive brilliant blue (KN-R) under simulated solar light indicated that Ni doped ZnO-TiO₂ composites have better photocatalytic activities, as compared to those of TiO₂ and ZnO-TiO₂.

1. Introduction

With the rapid development of the industry, the dye pollutants have already been one of the most important sources of environmental contamination. However, these dyes from wastewater cannot be satisfactorily removed by using chemical and biological degradation methods [1]. In the past years, the degradation of dyes pollutants in water by photocatalysis, using semiconductors such as TiO₂, has attracted more interest due to their high photocatalytic efficiency, low-cost, nontoxic nature, and environment friendly features [2–6]. However, the practical application of TiO₂ in semiconductor photocatalytic oxidation for environmental decontamination is still limited because of its wide band gap (3.0–3.2 eV), low solar energy conversion efficiency, and high charge recombination rate of photogenerated electrons and holes [7, 8].

With regard to the improvement of the photocatalytic activity of semiconductors, the coupling of TiO₂ with other semiconductors has been studied widely as an efficient approach with two purposes: (i) extending the light adsorption and improving the efficiency of the light utilization and (ii) enhancing the separation of photogenerated electron/hole pairs [9–13]. A lot of previous researches indicated that the integration of TiO₂ with ZnO is one of the most

promising candidates due to the fact that TiO₂/ZnO heterostructure may increase charge separation rate and extend the photoresponding range [14, 15]. Nevertheless, to the best of our knowledge, previous researches mostly regarded on the binary TiO₂-ZnO composites; few studies have been done on modification of binary TiO₂-ZnO composite with transition metal ion to enhance photocatalytic performance of composites.

It is well known that Ni ion is a more efficient dopant of transition metal elements used to modify the TiO₂ surface [16–18]. Ni²⁺ has similar radius to Ti⁴⁺ (the effective ionic radii are 72 pm and 68 pm, resp.). Thus, Ni²⁺ has easily gone into TiO₂ lattice by substitution of Ti⁴⁺ (also form octahedral coordination as Ti⁴⁺) and created an impurity energy level. The impurity energy would lead to visible light response for TiO₂ photocatalyst. On the other hand, the introduction of Ni ions in TiO₂ can form heterojunctions between *n*-type TiO₂ and *p*-type Ni oxide dopant. The presence of *p-n* junctions can promote the separation of electron-hole pairs through the electric junction field and facilitate the interfacial charge transfer [19–21].

In this study, we have developed a simple sol-gel method to build Ni doped ZnO-TiO₂ composites. Anthraquinone dye (reactive brilliant blue KN-R) is employed as the model

contaminant to evaluate the photocatalytic activity of as-synthesized samples under sunlight illumination. Compared to the single TiO_2 and binary ZnO-TiO_2 composite, Ni doped ZnO-TiO_2 composites showed better photocatalytic activity.

2. Experimental

2.1. Preparation of Samples. Ni doped ZnO-TiO_2 composites with different Ni loadings (ZnO loading was fixed to 8 wt%) were prepared as follows: firstly, 15 ml tetraethyl titanate (TEOT) was dripped into 17.5 ml absolute ethanol under strong stirring to obtain solution A. Desired amounts of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were added into a mixed solution (consisting of 17.5 ml absolute ethanol, 6.5 ml acetic acid, and 2.5 ml deionized water) to obtain solution B. Solution B was added slowly into solution A under vigorous stirring for 2 h to obtain a pale yellow transparent sol. After aging for 48 h, as-prepared sol was dried at 100°C for 12 h and then calcined at 450°C for 2 h in microwave muffle furnace.

For comparison, pure TiO_2 , ZnO-TiO_2 , and NiO-TiO_2 were prepared by the same process as the synthesis of NiO-ZnO-TiO_2 composites; only $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ or $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was absent in this process.

2.2. Characterization of Samples. The products were characterized by X-ray powder diffraction on a Shimadzu XRD-6100 X-ray diffractometer with a graphite monochromatized Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). UV-visible diffuse reflectance spectra were recorded with a Varian Cary-100 spectrophotometer and barium sulfate was used as a standard. The surface information of the as-prepared samples was determined by X-ray photoelectron spectroscopy (XPS) and was performed using VG ESCALAB 250 system (Thermo VG) with Al K α radiation (1486.6 eV). The Cls photoelectron peak (binding energy at 284.6 eV) was used as energy reference. Morphology and particle sizes of the samples were analyzed by transmission electron microscopy (TEM, JEM-2000EX, JEOL). The PL spectra of ZnO microcrystal photocatalyst were measured by using a fluorescence spectrophotometer (PE-LS55, USA) equipped with a xenon lamp at an excitation wavelength of 325 nm.

2.3. Photocatalytic Activity Test. The photocatalytic activity was evaluated by the decolorization rates of reactive brilliant blue KN-R in an aqueous solution. The photocatalysts (200 mg) were suspended in 200 ml reactive brilliant blue KN-R aqueous solution with initial concentration of 50 mg/L, which was exposed to illumination of 350 W Xe lamp (as simulated sunlight source). Before turning on the lamp, the suspension containing reactive brilliant blue KN-R and photocatalysts was magnetically stirred in a dark condition for 30 min till an adsorption-desorption equilibrium was established. Samples were then taken out regularly from the reactor and centrifuged immediately for separation of any suspended solid. The absorbance A of transparent solution was measured by a 721B spectrophotometer and the A value

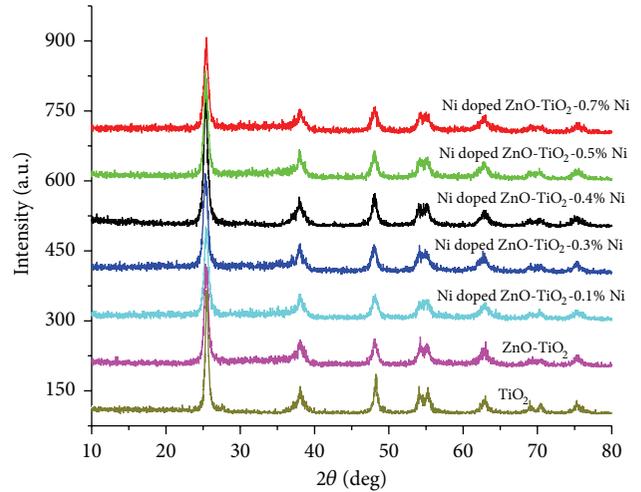


FIGURE 1: XRD patterns of TiO_2 , ZnO-TiO_2 , and Ni doped ZnO-TiO_2 photocatalysts.

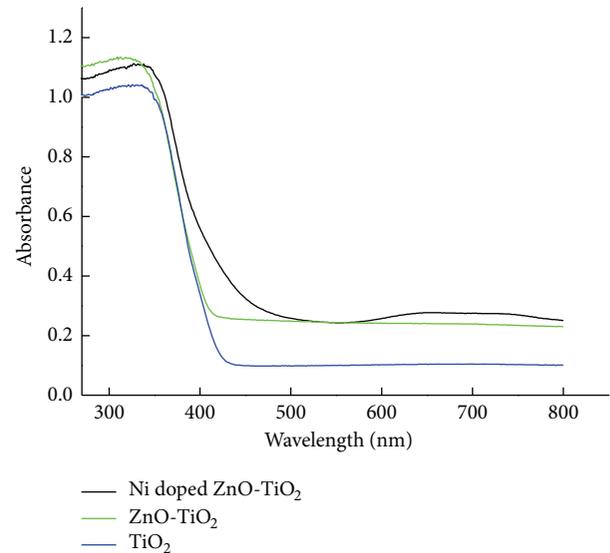


FIGURE 2: DRS spectra of TiO_2 , ZnO-TiO_2 , and Ni doped ZnO-TiO_2 photocatalysts.

was used to estimate the photocatalytic degradation rate D of reactive brilliant blue K-NR according to the equation

$$D = \frac{(A_0 - A_t)}{A_0} \times 100\%, \quad (1)$$

where A_0 is the initial absorbance of reactive brilliant blue K-NR, t is the reaction time, and A_t is the absorbance at time t .

3. Results and Discussion

The XRD patterns of Ni doped ZnO-TiO_2 composites with different Ni loadings are shown in Figure 1. As shown in Figure 1, all diffraction peaks can be attributed to the anatase phase of TiO_2 crystallite and the anatase structure of TiO_2

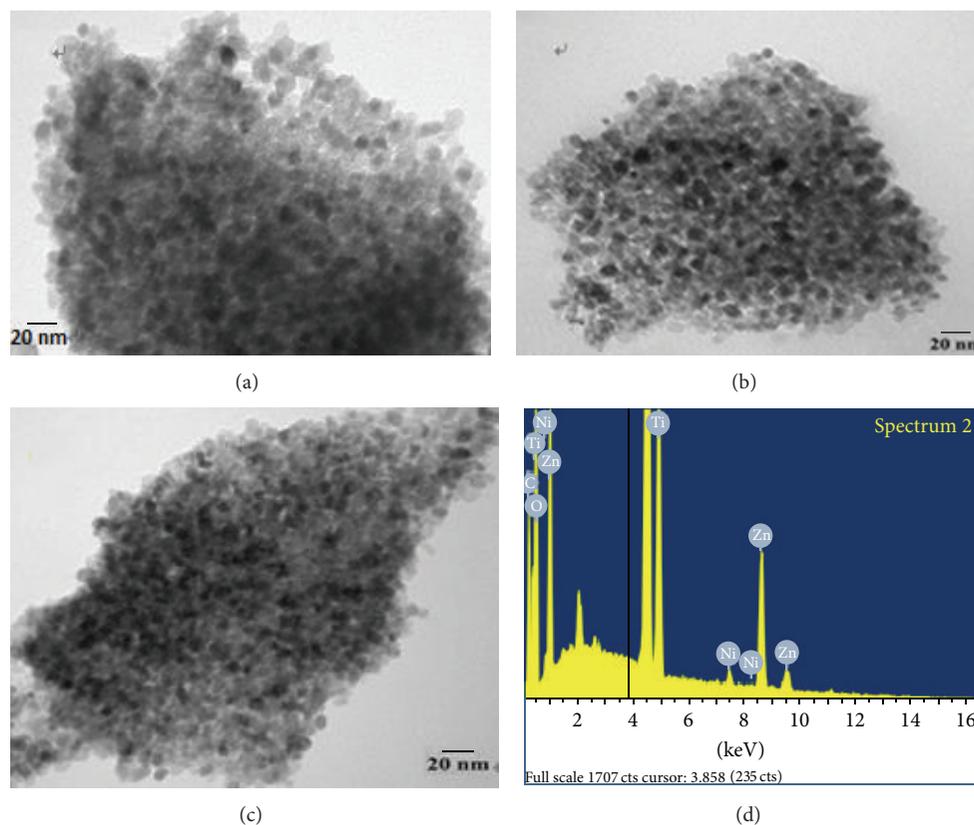


FIGURE 3: TEM micrograph of (a) TiO_2 , (b) ZnO-TiO_2 , and (c) Ni doped ZnO-TiO_2 and (d) EDX spectra obtained from Ni doped ZnO-TiO_2 .

is not changed by introduction of Ni and Zn. Moreover, peaks corresponding to Ni oxides and ZnO phases were not detected in the XRD patterns of the composites. The probable reason is that ZnO is truly amorphous or crystallites size is too small to be detected by X-ray in consideration of the ZnO concentration (8 wt%). On the other hand, the Ni ions might be highly dispersed in the TiO_2 matrix (Ni ions may be incorporated into the lattice of TiO_2 structure and substituting for Ti^{4+}).

In order to understand the optical properties of as-prepared composites, the UV-vis absorption spectra of pure TiO_2 , ZnO/TiO_2 , and Ni doped ZnO-TiO_2 samples are presented in Figure 2. Compared with the pure TiO_2 and ZnO/TiO_2 , the optical absorption of Ni doped ZnO-TiO_2 catalysts in visible light region was increased and the absorption edge of TiO_2 was further shifted to the visible light region after introducing Ni ions. This wide visible light response of composites may be attributed to the formation of surface defect centers, which are associated with existence of oxygen vacancies created by the introduction of metallic ions [22, 23]. The obvious red shift for Ni doped ZnO-TiO_2 sample maybe ascribed to the introduction of new impurity levels between the conduction and the valence band of TiO_2 by substitution of Ti^{4+} for Ni ions in the TiO_2 lattice [24]. The enhancement of optical absorption intensity in the visible region for Ni doped ZnO-TiO_2 samples implied that the Ni doped ZnO-TiO_2 composites have better photocatalytic activities than those of other samples under visible light irradiation.

In order to investigate the morphology and structure of the catalyst, the TEM observation for TiO_2 , ZnO-TiO_2 , and Ni doped ZnO-TiO_2 samples was carried out, and the results are shown in Figure 3. It can be seen from Figure 3 that the introduction of Ni and Zn did not change the morphology of TiO_2 and the grain size of TiO_2 , ZnO-TiO_2 , and Ni doped ZnO-TiO_2 samples was about 10–20 nm. Figure 3(d) is the energy-dispersive X-ray spectrum from Figure 3(c), and it further confirms that the Ni doped ZnO-TiO_2 catalyst is composed of Ti, Zn, Ni, C, and O, which indicated that the Ni and Zn were successfully introduced into TiO_2 .

The X-ray photoelectron spectroscopy (XPS) measurements were carried out for the as-synthesized samples to determine the surface composition and chemical states of the elements. The survey spectra of TiO_2 , ZnO-TiO_2 , and Ni doped ZnO-TiO_2 are shown in Figure 4(a). A detectable Zn2p peak could be observed in the ZnO-TiO_2 and Ni doped ZnO-TiO_2 samples (see Figure 4(a)) compared to that of pure TiO_2 . It is worthwhile to note that Ni element is not found in the Ni doped ZnO-TiO_2 sample, which may be contributed to the fact that Ni has low concentrations beyond the detection capacity of the XPS.

High resolution spectra of Ti2p, Zn2p, and O1s are shown in Figures 4(b)–4(d). As shown in Figure 4(b), the binding energy values of Zn 2p_{3/2} and 2p_{1/2} are observed at 1021.6 and 1044.5 eV, respectively. The spin-orbit splitting of Zn2p with 22.9 eV indicated that Zn ions mainly as Zn^{2+} existed in the ZnO [25]. Figure 4(c) showed the high resolution spectra

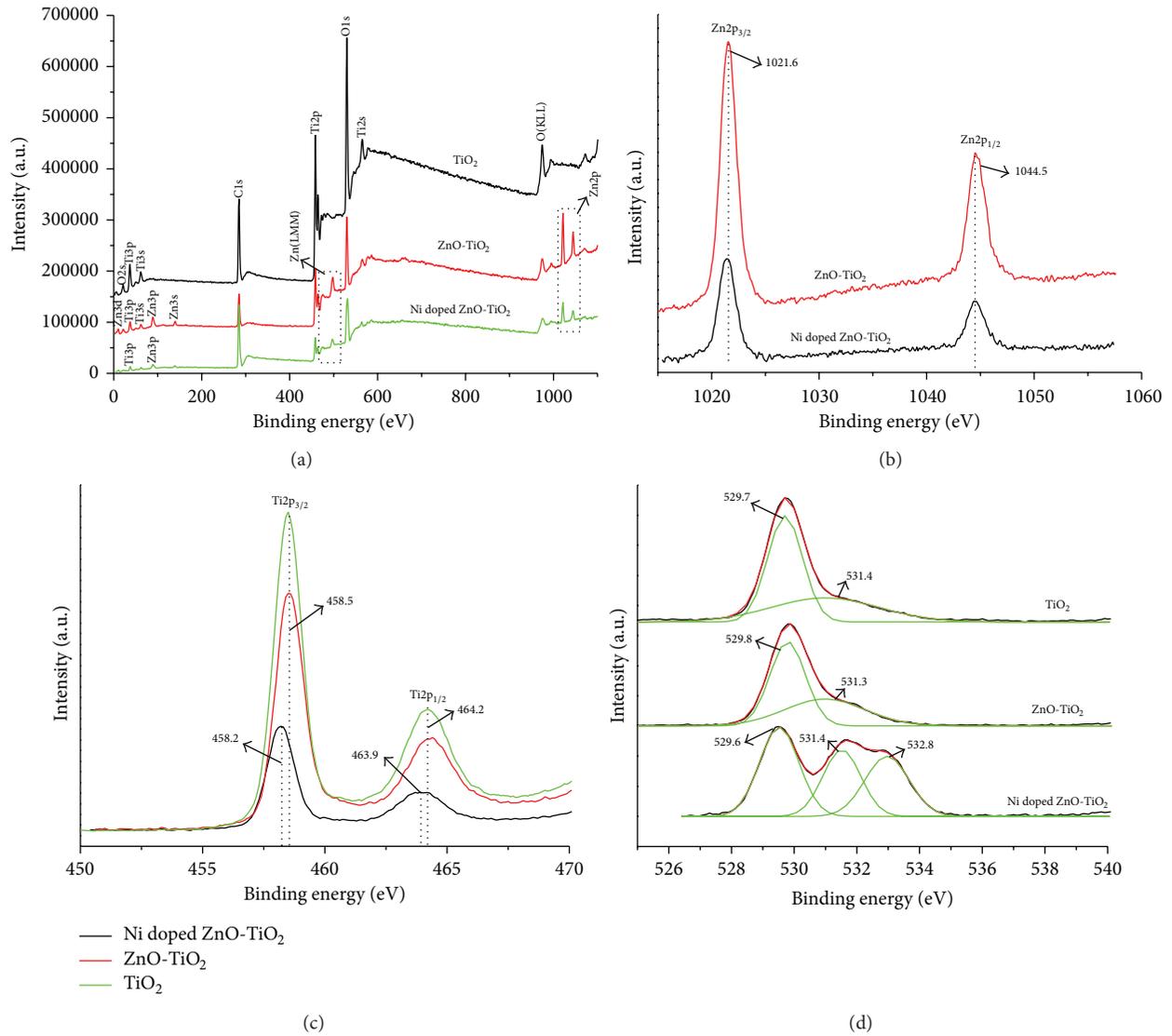


FIGURE 4: XPS spectra of samples: (a) XPS survey spectra, (b) Zn2p, (c) Ti2p, and (d) O1s state.

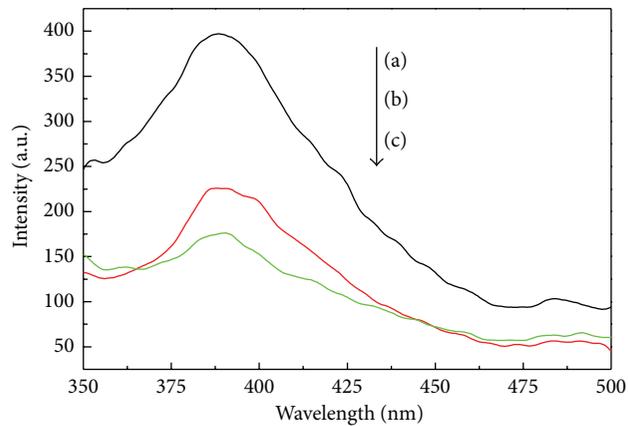


FIGURE 5: Fluorescence spectra of (a) TiO₂, (b) ZnO-TiO₂, and (c) Ni doped ZnO-TiO₂.

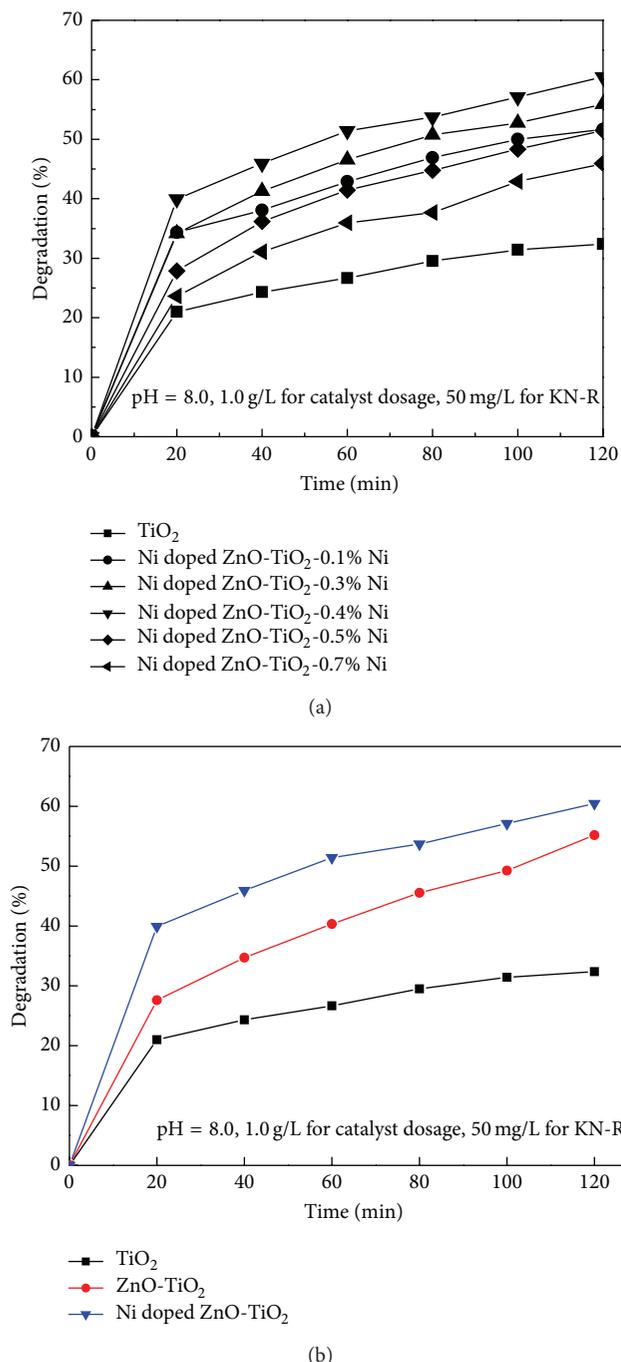


FIGURE 6: Plots of degradation of reactive brilliant blue KN-R over different samples under visible light irradiation.

of Ti2p. It can be seen that the binding energy values of Ti2p_{3/2} and Ti2p_{1/2} in the Ni doped ZnO-TiO₂ composite are observed at 458.2 eV and 463.9 eV, which are slightly lower than those of pure TiO₂ and ZnO-TiO₂. Such a shift can imply that the Ni ions may be incorporated into the lattice of TiO₂ structure and substituting for Ti. The high resolution XPS spectra of O1s peak band of as-synthesized samples are shown in Figure 4(d). The O1s peaks of samples were fitted to three components centered at 529.6–529.8, 531.3–531.4,

and 532.8 eV, respectively. The O1s peak centered at 529.6–529.8 eV could be ascribed to lattice oxygen (Ti–O–Ti) in TiO₂, while the higher binding energy component located at 531.3–531.4 eV could be associated to surface hydroxyl groups (Ti–OH) [26–28]. The other peak at 532.8 eV was attributed to physically adsorbed oxygen [29]. It can be seen from Figure 4(d) that the Ni doped ZnO-TiO₂ composite has abundant hydroxyl groups. The surface hydroxyl groups can trap the photogenerated holes to form hydroxyl radicals, which can suppress electron-hole recombination and improve the photocatalytic efficiency [30, 31]. Moreover, the adsorbed O₂ (as the electronic scavengers) can inhibit the recombination of photoexcited electron-hole pairs. This implies that the Ni doped ZnO-TiO₂ composite was more active than pure TiO₂ and ZnO-TiO₂, which is also in agreement with the photocatalytic test of the as-synthesized samples below.

Figure 5 shows the PL spectra of the as-synthesized samples measured by an excitation wavelength of 325 nm at room temperature. PL peaks were observed at about 390 nm for all samples, which corresponds to the direct recombination between photogenerated electrons and holes [32]. The intensity of the PL spectra decreased in the following order for the photocatalysts: TiO₂, ZnO-TiO₂, and Ni doped ZnO-TiO₂ composite. Generally, the lower PL intensity suggests lower recombination rate of photogenerated electron-hole pairs, which leads to the high photocatalytic activity of semiconductor photocatalysts [33]. This result indicates that the Ni doped ZnO-TiO₂ composite has higher photocatalytic activities as compared to that of others.

The photodegradation of reactive brilliant blue KN-R with the as-prepared samples under visible light irradiation was investigated (see Figure 6). It can be seen that Ni doped ZnO-TiO₂ samples showed higher photocatalytic activity as compared to that of pure TiO₂ and ZnO-TiO₂. The photocatalytic activity was found to be strongly influenced by the amount of Ni. The Ni doped ZnO-TiO₂ composite with 0.4% Ni loading has the best photocatalytic activity in comparison to other samples, and the degradation of reactive brilliant blue KN-R would reach up to 60.5%. When concentration of Ni is low, Ni ions can capture the electrons, create *p-n* junction, and then improve charge separation. However, Ni ions with high concentration may become recombination center of photogenerated carriers and decreased photocatalytic activity. Furthermore, the photocatalytic degradation of KN-R over the as-synthesized samples is in good agreement with the above PL results.

It is well known that heterogeneous photocatalytic reaction is highly dependent on some operating parameters like pH of solution, catalyst dosage, and substrate concentration. Here, effect of above parameters on reaction was investigated and was shown in Figures 7(a)–7(c). It is observed that the degradation rate increases with increase of catalyst dosage and then reaches a flat change. This is probably due to the fact that the increase of catalyst dosage increases the number of absorbed photons and dye molecules. However, addition of extra amount of catalyst is unfavorable for photocatalytic reaction due to increase in opacity and light scattering of nanoparticles which lead to decrease in the passage of irradiation through the sample. The degradation efficiency

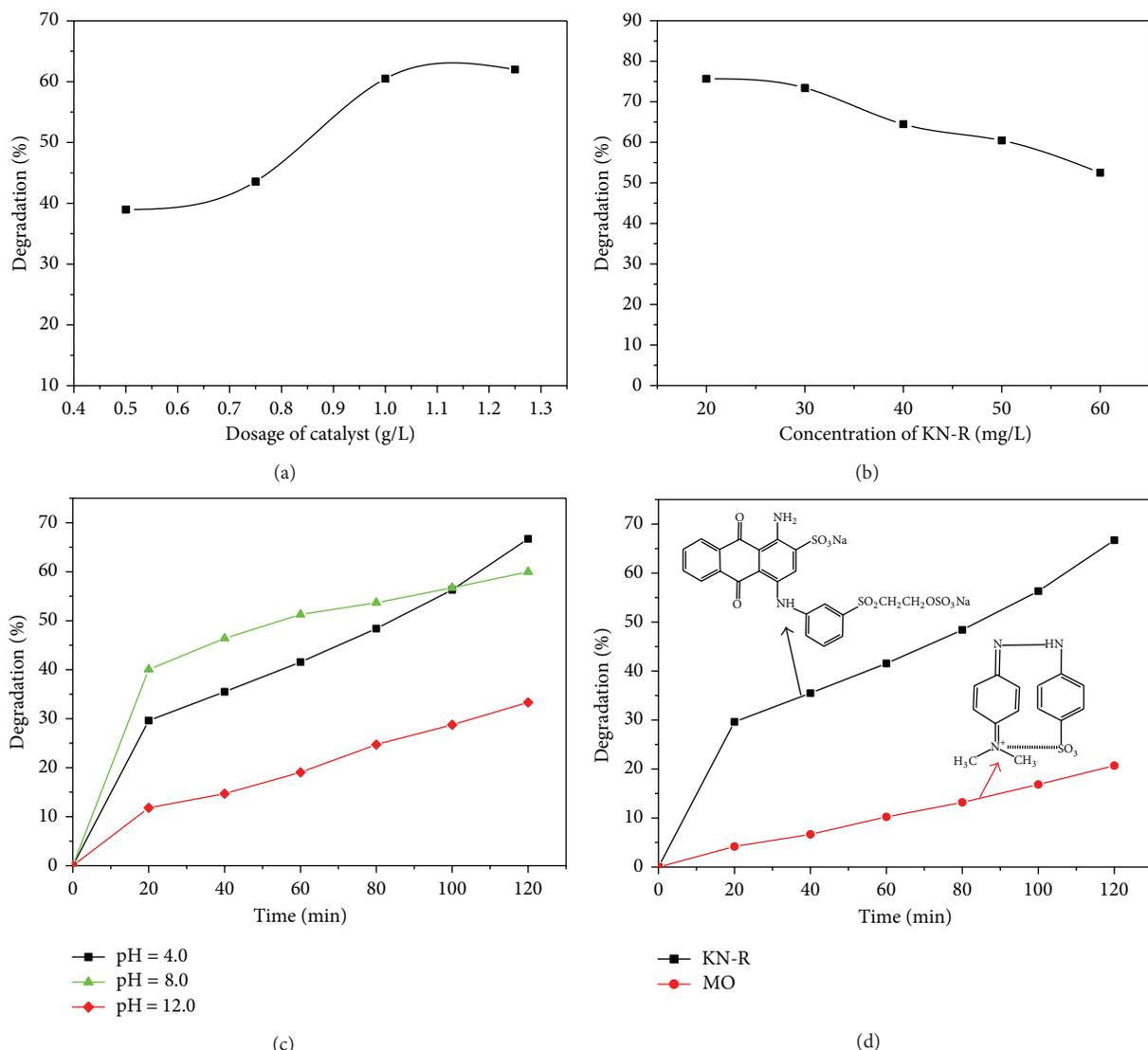


FIGURE 7: Effect of photocatalyst dosage, initial concentration of dye, and pH value of solution and dye species on photocatalytic reaction.

of dye decreased with increasing the initial concentration of dye. The decrease of degradation efficiency can be attributed to two reasons as follows. (1) With increasing the amounts of dye, the more of dye molecules will be adsorbed on the surface of the photocatalyst and the active sites of the catalysts will be reduced. (2) The more of dye can lead to decreasing the number of photons that has arrived to the surface of catalysts and then diminished photodegradation efficiency [34].

It can be seen that the maximum degradation efficiency was obtained at $\text{pH} = 8.0$ for KN-R solution. As far as we know, the surface of photocatalyst is positively charged in acidic solutions and negatively charged in alkaline solution. When solution is in a low pH, positively charged surface of catalyst improved adsorption of dye molecules with negative charge on the surface of photocatalyst but cannot provide hydroxyl groups which are needed for hydroxyl radical formation [35]. Similarly, higher pH value of solution can provide higher concentration of hydroxyl ions (react with the

holes to form hydroxyl radicals), but the adsorption of dye molecules on the surface of photocatalyst is inhibited when the pH value is high [36, 37]. As a result, the optimal pH value of dye solution for photocatalytic reaction can be obtained at $\text{pH} = 8.0$.

Here, we also investigated photodegradation of methyl orange (MO) over the as-synthesized Ni doped ZnO-TiO_2 beside KN-R. As shown in Figure 7(d), the photodegradation rate of methyl orange (MO) over the as-synthesized Ni doped ZnO-TiO_2 is lower than that of KN-R. The low photodegradation rate of methyl orange may be ascribed to formation of stable intramolecular salt with double quinone structure. Furthermore, to evaluate the photocatalytic stability of the as-synthesized Ni doped ZnO-TiO_2 photocatalyst, the photocatalytic cycling tests were carried out under visible light irradiation, and each run lasted for 120 min (see Figure 8). The results in Figure 8 show that the photocatalytic activity of Ni doped ZnO-TiO_2 composite does not exhibit any great

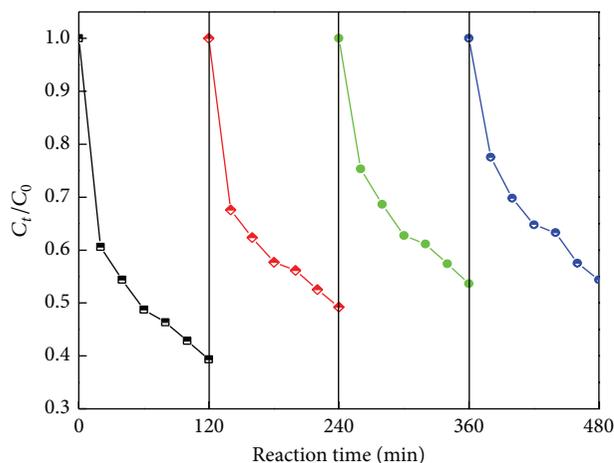


FIGURE 8: Recycling runs in the photocatalytic degradation of reactive brilliant blue KN-R.

loss in activity even after four times, which implied that the stability of Ni doped ZnO-TiO₂ composite is suitable for the photodegradation process of pollutants.

4. Conclusions

Ni doped ZnO-TiO₂ composites with visible light response were fabricated by a facile sol-gel method and its photocatalytic performance was tested by KN-R degradation under xenon lamp irradiation. Doping of Ni shifted the band-gap absorption edge to visible light region and inhibited recombination of photogenerated electron-hole pairs. Hence, the as-synthesized Ni doped ZnO-TiO₂ composites show better photodegradation rate of reactive brilliant blue KN-R as compared to that of pure TiO₂ and ZnO-TiO₂ under sunlight irradiation. Furthermore, no significant decrease of activity was observed after four cycles for photodegradation of KN-R. Considering the photocatalytic ability under sunlight and the stability of Ni doped ZnO-TiO₂, it is believed that Ni doped ZnO-TiO₂ photocatalyst may have potential application in the field of water pollution control.

Conflict of Interests

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

Acknowledgments

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