

The Study of NiO/TiO₂ Photocatalytic Activity for Degradation of Methylene Orange

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ABSTRACT

The NiO/TiO₂ co-photocatalysts were fabricated by chemical-solution-deposition-decomposition process. The photocatalytic activities of different composites were studied by the degradation of methylene orange (MO) under visible light. The absorption edge of NiO/TiO₂ composites shifted towards the visible region with the presence of NiO and the indirect band gap was narrowed. In view of the selectivity of NiO/TiO₂ co-photocatalysts in the degradation of organic dye, we focused on the degradation of MO. The results show that the degradation ability of every NiO/TiO₂ co-photocatalyst is less than that of pristine TiO₂ (P25) nano-particles, and the degradation activity decreases gradually with the increase in the amount of NiO. Also discussed in detail were the mechanisms of degradation activity decrease in the presence of NiO. In addition, our results further confirmed the selective photocatalysis.

KEYWORDS: NiO/TiO₂, P25, Degradation, Methylene Orange, Oxidation Reaction.

1. INTRODUCTION

In recent years, several photocatalytic reactions over various kinds of semiconductors, such as degradation of various kinds of organic and inorganic pollutants, have attracted great attention because this is an ideal route to harvest solar energy in order to perform the reactions.^{1–7} Among the semiconductors which are employed as photocatalysts, titanium dioxide (TiO₂) has been considered as the most promising choice and is widely applied for the mentioned application owing to its non-toxicity, inexpensiveness, high chemical stability, and especially its excellent photocatalytic activity. During the photocatalysis process, the semiconductor is subjected by photon irradiation whose energy is not less than the band gap, then it produces electron-hole pairs, in which the holes in the valence band (VB) and the electrons in the conduction band.^{1,8} Some of these pairs diffuse to the surface of the crystal and react with the adsorbed reactant. Holes with strong oxidizing ability can oxidize the hydroxyl group HO[•] or water (H₂O) absorbed on the surface by the hydroxyl radicals [•]OH. The electrons pick up the absorbed O₂ and transform into highly active superoxide radical [•]O₂⁻. The superoxide radical may also react further to generate other species.

However, there are still some limitations in the use of TiO₂, which can lead to reduction of its photocatalytic efficiency.^{9,10} Factors such as the fast recombination of the electrons and holes photo-generated pairs upon light irradiation, and its wide band gap energy of 3.20 eV limits its application to UV region only and so on. Several researchers have put on a lot effort to improve these defects. As reported that modifications of titanium oxide by doping with transition elements such as Cu, Fe,^{11,12} noble metals Ag etc.¹³ or non-metal elements of N, F, C etc.^{14–16} improves its optical activity by narrowing the energy band gap, extending the absorption to visible region and preventing the electron-hole pair recombination. Among *p*-type co-catalysts, NiO with an indirect band gap of about 3.55 eV,¹⁷ is considered as the most promising choice due to its low cost, unique catalysis effect, special electric and magnetic properties and so on Refs. [18–20]. At present, TiO₂ covered by NiO, served as *p*-*n* junction, is being studied extensively and deeply. For instance, Chou et al. prepared TiO₂/NiO composite particles, which were applied in dye-sensitized solar cells.²¹ Also, Sreethawong et al. reported that NiO/TiO₂ composite prepared by sol-gel enhanced the photocatalytic evolution of hydrogen rather than TiO₂.²²

At the beginning, excellent modification in photocatalytic activity and other properties and wide applications of NiO/TiO₂ composite attracted our attention. Karunakaran Chockalingam et al. reported the selectivity of NiO/TiO₂ in photocatalysis.²³ They found that the photocatalytic

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activity of NiO/TiO₂ on degradation of sunset yellow, rhodamine B, and methylene blue dyes under UV light is less than that of bare TiO₂. However, it degrades phenol faster than its precursor, both under visible and UV light. In addition, it has been reported that the degradation activity of NiO/TiO₂ on degrading *p*-chlorophenol aqueous solution, Cr₂O₇²⁻ etc. is higher than that of TiO₂.^{24,25} Therefore, NiO/TiO₂ as the co-photocatalyst is selective in the degradation of organic dyes. However, the degradation activity of NiO/TiO₂ in degrading methylene orange (MO) is controversial. For instance, Lin et al. systematically reported that NiO/TiO₂ nanobelts exhibit much enhanced photocatalytic activity on degradation of MO,⁴ whereas Shifu et al. reported that degradation activity on MO decreased. But Shifu et al. did not conduct his study systematically.²⁶

In this paper, we prepared the NiO/TiO₂ co-photocatalysts by chemical solution deposition decomposition (CSDD) process, and studied the degradation of methylene orange (MO) under visible light systematically. The NiO/TiO₂ degradation capacity of methylene MO decreased compared with original TiO₂. In addition, we analyzed the reasons for the decrease of photocatalytic degradation activity on the methylene orange (MO).

2. EXPERIMENTAL DETAILS

The NiO/TiO₂ co-photocatalysts were prepared by chemical solution deposition decomposition (CSDD) process. Firstly, the Ni(NO₃)₂ · 6H₂O precursor solutions of 0.1 mol/L, 0.2 mol/L and 0.4 mol/L (designated as 1NiO/TiO₂, 2 NiO/TiO₂, 4NiO/TiO₂) were prepared. Then, 0.35 g P25 TiO₂ was dispersed into each of the Ni (NO₃)₂ solutions and then soaked for 5 h to ensure the P25 powder was completely permeated with the nickel nitrate solution. Subsequently, the soaked samples were collected by centrifugation from the solutions and dried in an oven at 80 °C, forming a layer of nickel nitrate on the P25 TiO₂ surface. Finally, the thermal decomposition process was performed by heating the dried samples in a furnace at 500 °C for 2 h, 1 °C/min.

Photocatalytic degradation of MO was conducted at room temperature under a PLS-LAX500 Xe lamp simulating visible light. In photocatalytic process, 100 mg/L of the obtained composite samples were dispersed in 20 mg/L MO dye solution. For comparison, the experiment was done on P25 in the same way. Before the irradiation, the reaction systems were stirred for 1 h to reach the adsorption balance, and these solutions were used to measure the adsorption ability. Then the mixed solutions were exposed to Xe light irradiation, and each sample's supernatant liquid was extracted every 30 minutes for further measurement.

Scanning electron microscopy (SEM) images and energy dispersive X-ray spectroscopy (EDX) spectra were obtained using a FEI Quanta200F microscope. X-ray powder diffraction (XRD) patterns of samples were examined by a Bruker D8 Focus X-ray powder diffractometer with

Cu K_α radiation ($k = 1.5406 \text{ \AA}$). The photocatalytic experiments and UV-visible diffuse reflectance spectra were carried out using a UV-Vis spectrophotometer (Shimadzu UV2450). The diffuse reflectance spectra were converted to the absorption spectra by using the Kubelka-Munk function.

3. RESULTS AND DISCUSSION

The NiO/TiO₂ co-photocatalysts degradation activity are different in degrading different dyes such as phenol, *p*-chlorophenol aqueous solution, Cr₂O₇²⁻, sunset yellow, rhodamine B, and methylene blue and so on Refs. [23–25]. here we focus on the study of the NiO/TiO₂ degradation of methylene orange (MO). The X-ray diffraction (XRD) patterns of 1NiO/TiO₂, 2NiO/TiO₂, 4NiO/TiO₂ and the pristine P25 nanoparticles at room temperature are shown in Figure 1. We could not detect the peak of NiO from the XRD pattern. However, the EDX spectroscopy shows the existence of NiO, and the content is lower than 2% in every composite. This might be the result of the uniform dispersion of the NiO in very low content, which is similar to the other studies.^{27,28}

The SEM images are shown in Figure 2 for NiO/TiO₂. The TiO₂ and NiO particles are difficult to distinguish from the SEM images because they have similar shapes and sizes. In addition, the crystal phase and morphology of TiO₂ did not change after calcination at 500 °C as shown in Figures 1 and 2. The photocatalytic activity would not be affected by the changing of crystal phase and morphology.

To verify the presence of NiO further, we performed UV-visible diffuse reflectance measurements on the samples. The reflectance spectra were converted to absorption spectra by the Kubelka-Munk function as shown in Figure 3. The results demonstrated that the absorption edge shifted towards visible region with the presence of NiO. In addition, the extension to visible region of the absorption edge reveals that the is good contact between NiO

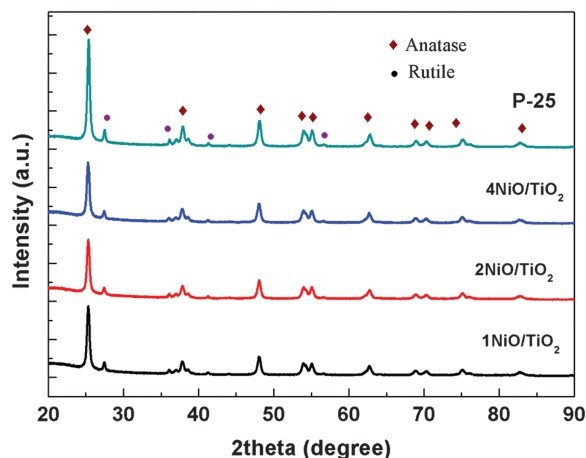


Fig. 1. Room temperature X-ray diffraction (XRD) pattern for 1NiO/TiO₂, 2NiO/TiO₂, 4NiO/TiO₂ and pristine P-25 nanoparticles.

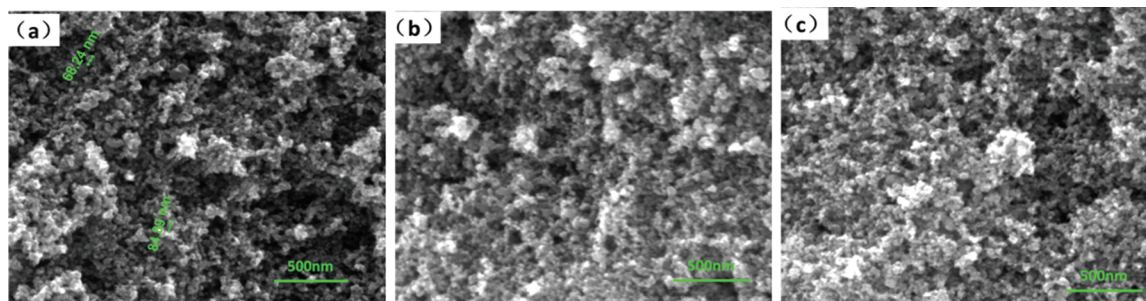


Fig. 2. Scanning electron microscopy (SEM) images of 1NiO/TiO₂ (a), 2NiO/TiO₂ (b), 4NiO/TiO₂ (c).

and TiO₂ in consequence of inter-dispersion of the two oxides.²⁸ The band gap of NiO/TiO₂ narrows when compared with that of TiO₂ as shown in the inset of Figure 3. The indirect band gap is determined by the extrapolation of the absorption tangent to the abscissa. In the NiO/TiO₂ system, NiO cluster derived states lie on the top of the VB edge of the TiO₂ surfaces, which pushes the VB edge of the composite system to higher energy compared to the bare surfaces. Therefore, the overall band gap of the composite is reduced compared to unmodified TiO₂.²⁹

The visible light photocatalytic activities of every composite and original P25 nanoparticles were also evaluated via the photocatalytic degradation of MO under visible light irradiation (Fig. 4). The pristine P25 nanoparticles have good photocatalytic activity under visible light, and the corresponding degradation of MO reaches 95% after 180 min. However, the photocatalytic activity of the NiO/TiO₂ decreased significantly compared with that of P25 nanoparticles and the degradation rate decreases with increasing NiO contents. The result is similar with the study of Shifu et al.²⁶

When *p*-type semiconductor TiO₂ is decorated by *n*-type semiconductor NiO, *p*-*n* junctions are formed at the interface of NiO/TiO₂. The electron and hole carriers

are diffused to *p*-type and *n*-type semiconductor respectively. The inner electric field is established when electron and hole diffusions reach the equilibrium point, which makes the NiO region charged negatively while the TiO₂ region is charged positively. The junction then prevents the combination of electron and hole, acting as a potential barrier. However, the free electrons from *p*-type and free holes from *n*-type semiconductors are allowed to move to the *n*-type and *p*-type semiconductors respectively. Therefore, the photogenerated electron-hole pairs excited by irradiation are separated efficiently by the inner electric field.^{28, 30} In addition, it has been reported that *p*-type NiO semiconductor acts as hole traps and collectors.³¹ Therefore, there are abundant electrons to conduct reduction reaction, but the holes involved in oxidation reaction are inadequate. As a result, the NiO/TiO₂ co-photocatalyst has higher photocatalytic reduction activity and lower photocatalytic oxidation activity than that of TiO₂.²⁶ Just like the study of Yu et al. the degradation of methyl orange is mainly due to the hole or hydroxyl (at low MO concentration) oxidation process.³² Therefore, the degradation activity of MO decreases after TiO₂ is decorated with NiO, and decreases gradually with the increase in the amount NiO.

The TiO₂ decorated with NiO are extensively studied because they are low-cost, non-toxic and especially have wide applications. The application of NiO/TiO₂ co-photocatalytic in photocatalysis has attracted a large

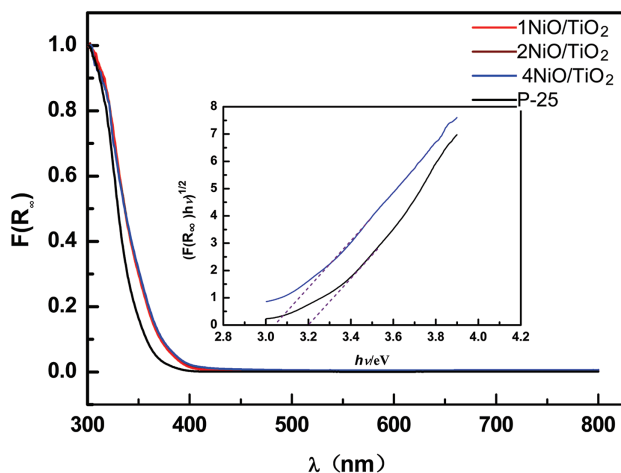


Fig. 3. UV-visible absorption spectra of 1NiO/TiO₂, 2NiO/TiO₂, 4NiO/TiO₂ and P25. The inset is (F(R_∞)hν)^{1/2} versus hν for 4NiO/TiO₂ and P25.

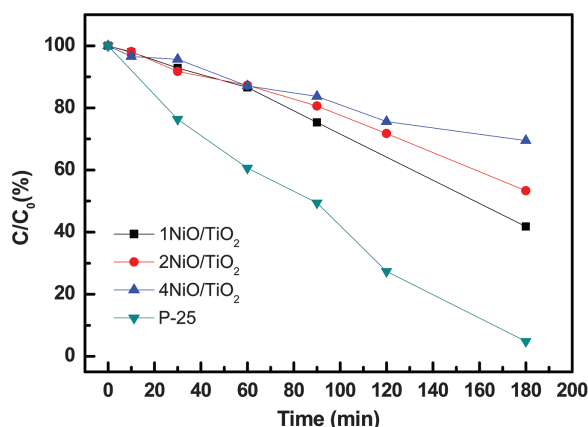


Fig. 4. The visible light photocatalytic degradation of MO for 1NiO/TiO₂, 2NiO/TiO₂, 4NiO/TiO₂ and P25.

number of researchers. The degradation activity of NiO/TiO₂ on degrading phenol, *p*-chlorophenol aqueous solution, Cr₂O₇²⁻ etc. is higher than that of TiO₂. However, the photocatalytic activity on degradation of sunset yellow, rhodamine B, and methylene blue dyes is less than that of bare TiO₂.^{23–25} In this work, we systematically studied the degradation of methyl orange, due to controversial research results for methyl orange. It has been proved that the degradation activity of MO is less than that of P25 after decorating with NiO. Therefore the selectivity in NiO/TiO₂ photocatalytic degradation of organic dye has been confirmed through our experiments, and the mechanisms and factors need to be studied further.

4. CONCLUSION

In summary, NiO/TiO₂ nanoparticles were prepared through the chemical-solution-deposition-decomposition process using Ni(NO₃)₂·6H₂O and P25 TiO₂ as the raw materials. The crystal phase and morphology of TiO₂ did not change, even after calcination at 500 °C. The absorption edge extended to visible region and the narrowing of band gap occurred after TiO₂ was decorated with NiO. We studied systematically the NiO/TiO₂ photocatalysis degradation of methylene orange (MO) under visible light because of selective photocatalysis. The photocatalytic activity decreased significantly compared with that of pristine TiO₂ nanoparticles. Also, the degradation rate decreased as the NiO contents increased. The main reason why photocatalytic degradation of methylene orange (MO) activity reduced with the presence of NiO is that the oxidation activity reduced due to insufficient holes, because NiO acts as holes collector, whereas the degradation of methyl orange mainly depends on the oxidation reaction.

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