ZnFe$_2$O$_4$/MWCNTs composite with enhanced photocatalytic activity under visible-light irradiation

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ABSTRACT

Zinc ferrite/multi-walled carbon nanotubes (ZnFe$_2$O$_4$/MWCNTs) composite was prepared by a hydrothermal process and characterized by X-ray diffraction, transmission electron microscopy, and ultraviolet–visible diffusion reflectance spectroscopy. Compared with pure ZnFe$_2$O$_4$, the ZnFe$_2$O$_4$/MWCNTs composite exhibits stronger absorption in visible-light range and higher photocatalytic activity, with 99% degradation ratio of methylene blue after 6 h visible-light irradiation in the presence of H$_2$O$_2$. The enhanced photocatalytic activity is attributed to the strong interaction between ZnFe$_2$O$_4$ and MWCNTs which inhibits the recombination of photo-generated charge carriers, and the formation of highly active species •OH on the surface of MWCNTs. Therefore, more radicals are formed for degradation of the dye. The enhancing mechanism of the photocatalytic activity of ZnFe$_2$O$_4$ in the presence of MWCNTs is also discussed.

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1. Introduction

Titanium dioxide (TiO$_2$) has been extensively studied as a photocatalyst for the degradation of organic pollutants [1]. However, the fatal drawback of TiO$_2$ is that it can only absorb UV light due to its wide band gap of 3.2 eV, which prevents it from utilizing solar energy efficiently. Other traditional visible-light photocatalysts (e.g. CdS, Fe$_2$O$_3$ and WO$_3$) bear drawbacks of either photocorrosion or low activity [2,3], which result in difficult application. In contrast, a great number of novel visible-light photocatalysts have been developed, such as BiVO$_4$ [4], CaBi$_2$O$_4$ [5], Bi$_2$WO$_6$ [6], Bi$_2$Fe$_4$O$_9$ [7]. Despite their absorption ability of visible light, most of these complex oxides were prepared by solid-state reaction under high temperature. They usually have small specific surface areas, which is liable to lower photocatalytic activities. Therefore, developing efficient methods to fabricate novel visible-light catalysts with excellent photocatalytic activity is urgently needed. Zinc ferrite (ZnFe$_2$O$_4$) is regarded as a promising visible-light photocatalyst with band gap of 1.9 eV that makes it possible to utilize solar energy [8]. In addition to its photochemical stability and low toxicity, ZnFe$_2$O$_4$ has been applied to degrade organic pollutants [9]. However, the poor quantum efficiency of ZnFe$_2$O$_4$ results in low photocatalytic activity. This can be improved by loading Ag on ZnFe$_2$O$_4$ surface [10]. However, the content of Ag is as high as 22.7%, which is impractical for application.

Recently, multi-walled carbon nanotubes (MWCNTs) have attracted great attention as supports for photocatalysts because of their large surface area, special aperture structure, high chemical stability and good electron conductivity. It has been reported that MWCNTs' supports for TiO$_2$ [11], WO$_3$ [12] and CdS [13] have greatly enhanced these oxides' activities. Inspired by these studies, the authors believe that it is worthwhile to attempt to add MWCNTs to ZnFe$_2$O$_4$ in the hope of improving its photocatalytic activity.

In this paper, ZnFe$_2$O$_4$ nanoparticles were coated on MWCNTs by a hydrothermal process. The effect of MWCNTs on photocatalytic activity was studied by degrading methylene blue (MB) dye under visible-light irradiation. Furthermore, the possible mechanism of the enhanced photocatalytic activity of ZnFe$_2$O$_4$ in the presence of MWCNTs was also discussed.

2. Experimental

2.1. Synthesis of the ZnFe$_2$O$_4$/MWCNTs

MWCNTs were prepared by catalytic chemical vapor deposition (CVD) of methane over Co/MgO catalysts [14]. The MWCNTs were further processed in a mixture of concentrated sulfuric acid (98%) and nitric acid (65%) with volume ratio at 1:2 [15].

All chemicals were purchased from local chemical agents with analytical grade and were used without further purification. For the synthesis of ZnFe$_2$O$_4$/MWCNTs, 5 mmol Zn(NO$_3$)$_2$·6H$_2$O and 10 mmol Fe(NO$_3$)$_3$·9H$_2$O were dissolved in 15 mL distilled water. 10 mg MWCNTs was added into the solution and sonicated for 10 min. An appropriate 6 M NaOH solution was added to the mixture until the pH reached 13. Then the volume of the solution was adjusted to 40 mL with distilled water. The mixture was stirred vigorously for 30 min and transferred into a 50 mL Teflon-lined stainless autoclave. The autoclave was sealed and maintained at 180 °C for 12 h. After that, the product was filtered, washed, and dried. The same procedure was applied to produce ZnFe$_2$O$_4$ without adding MWCNTs.
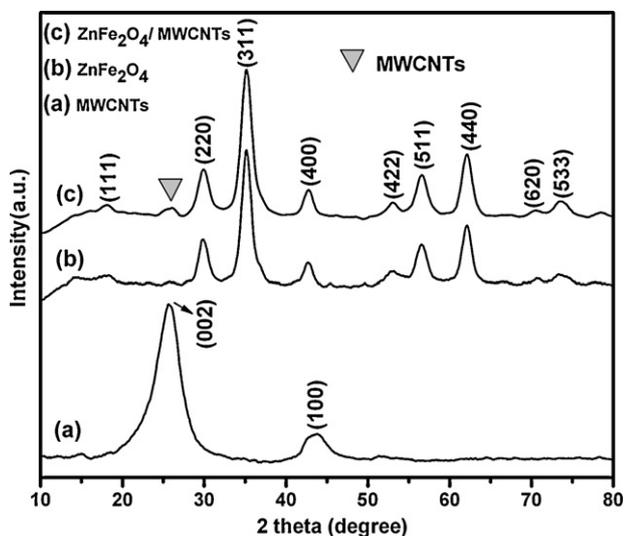
Fig. 1. XRD patterns of MWCNTs (a), $ZnFe_2O_4$ (b) and $ZnFe_2O_4$/MWCNTs (c).

2.2. Characterization of the $ZnFe_2O_4$/MWCNTs

The XRD patterns were recorded using an X-ray diffractometer (X'Pert PRO, Philips, The Netherlands). The morphology of the samples was investigated by transmission electron microscopy (TEM, JEM-2010, JEOL Japan). The optical absorption of the powders was performed on a UV–vis spectrophotometer (U-3010, Hitachi, Japan). The Brunauer–Emmett–Teller (BET) surface area of the samples was determined using a specific surface area apparatus (ST-08, Beifen, China). The photoluminescence (PL) spectra of the samples were detected with a Fluorescence Spectrophotometer (F-4500, Hitachi, Japan).

2.3. Photocatalytic activity of the $ZnFe_2O_4$/MWCNTs

The photocatalytic reaction was conducted by adding 100 mg catalyst into 100 mL MB solution with concentration of 10 mg L^{-1}. To reach the balance of adsorption and desorption, the suspension was stirred in dark for 30 min. The light source was a 400 W metal halide lamp with a filter to cut off all wavelengths shorter than 420 nm. After adding 2.0 mL 30% H_2O_2 to the suspension, the lamp was turned on. Samples were taken out at regular time intervals and the changes of MB concentration were monitored using a UV–vis spectrometer (U-3010, Hitachi, Japan). The total organic carbon (TOC) in the solution before and after the photocatalytic reaction over the $ZnFe_2O_4$/MWCNTs composite was determined by a TOC analyzer (Liqui, Germany). Furthermore, we investigated the ability of different photocatalysts to produce $^{\bullet}$OH by means of the terephthalic acid (TA)–fluorescence (FL) method [16] with a Fluorescence Spectrophotometer F-4500.

3. Results and discussion

3.1. XRD analysis of the $ZnFe_2O_4$/MWCNTs

XRD technique was used to investigate phase composition of the synthesized samples (Fig. 1). The peaks at 25.7° and 43.2° are attributed to the characteristic peaks of MWCNTs (Fig. 1a). The diffraction peaks in Fig. 1b correspond well to the reported values of spinel $ZnFe_2O_4$ (JCPDS 22-1012). As shown in Fig. 1c, the main peaks of the $ZnFe_2O_4$/MWCNTs composite are in good accordance with pure $ZnFe_2O_4$, which indicates that incorporation of a small amount of MWCNTs into $ZnFe_2O_4$ cannot lead to the change of its phase. One peak of MWCNTs at 25.7° is very low due to trivial amount of addition [17]. The other peak of MWCNTs at 43.2° might be overlapped by the main peak of spinel $ZnFe_2O_4$ at 42.8°, since they are so close.

3.2. TEM characterization of the $ZnFe_2O_4$/MWCNTs

The direct evidence of the formation of $ZnFe_2O_4$ nanoparticles on the surface of MWCNTs is given by TEM and HRTEM in Fig. 2. It can be seen that most of the MWCNTs have been covered with $ZnFe_2O_4$ nanoparticles with an average size of 10 nm (Fig. 2a). Fig. 2b shows the HRTEM image of the composite. The lattice fringe spacings of nanocrystals are indexed as (4 0 0) and (3 1 1) planes of spinel $ZnFe_2O_4$. In addition, $ZnFe_2O_4$ particles are firmly anchored on the surface of MWCNTs even after ultrasonic treatment. The strong combination of $ZnFe_2O_4$ and MWCNTs could be attributed to electrostatic interaction and chemical bonding through the functional groups on the surface of the modified MWCNTs [18]. As shown in Fig. 2c, most of the bare $ZnFe_2O_4$ nanoparticles are flaky and their size is about 15 nm. The $ZnFe_2O_4$ particles on the MWCNTs are obviously smaller than the bare ones, which could be attributed to the restriction effect of MWCNTs on the size of the attached nanoparticles [13,19], and they are also dispersed very well, resulting in a large surface area.

3.3. Diffuse reflectance UV–vis spectra of the $ZnFe_2O_4$/MWCNTs

The UV-vis absorption spectra of $ZnFe_2O_4$, MWCNTs and $ZnFe_2O_4$/MWCNTs are provided in Fig. 3. MWCNTs exhibit a very broad spectrum (Fig. 3a). The absorption of the $ZnFe_2O_4$/MWCNTs composite (Fig. 3b) is stronger than that of the bare $ZnFe_2O_4$ particles (Fig. 3c) in the range of wavelength of 250–800 nm. In addition, the threshold of absorption band of the $ZnFe_2O_4$/MWCNTs composite occurs at about 650 nm, which is a significant blue shift compared with the $ZnFe_2O_4$ (700 nm). The blue-shift absorption of the $ZnFe_2O_4$/MWCNTs composite could be attributed to the quantum-size effects, which is consistent with the fact demonstrated by TEM.

3.4. Photocatalytic activity of the $ZnFe_2O_4$/MWCNTs

Photocatalytic activity was evaluated by measuring the degradation of MB. Fig. 4A shows the changes in the absorbance profiles of MB solution in the presence of $ZnFe_2O_4$/MWCNTs composite and H_2O_2 under visible-light irradiation. The spectrum at $t = 0$ h was taken on the starting solution of MB with a concentration of 10 mg L^{-1} (without H_2O_2). Four characteristic peaks (246, 291, 615, 664 nm) are observed, which are similar to those reported by Zhang et al. [20]. After stirring for 0.5 h, about 24% of the MB was adsorbed. As soon as H_2O_2 was added, the MB bands at 291 and 246 nm were masked by the strong absorption of H_2O_2 in the range of 185–300 nm [21]. With the irradiation time increasing, the peaks at 615 and 664 nm were reduced quickly. In addition, the original absorption maximum at 664 nm shifted to 660, 655, 651, 641, 620 nm after reaction for 1, 2, 3, 4 and 5 h, respectively. The blue shift of the absorption band indicates the photocatalytic degradation of MB [20,22]. The band at 620 nm became very weak and disappeared in 6 h, suggesting almost complete degradation of MB. Fig. 4B displays the photocatalytic degradation efficiency of MB monitored at 664 nm over the $ZnFe_2O_4$, MWCNTs, $ZnFe_2O_4$/MWCNTs composite and the mechanically mixed $ZnFe_2O_4$ and MWCNTs (with the same ratio of $ZnFe_2O_4$ to MWCNTs as in the $ZnFe_2O_4$/MWCNTs composite) in the presence of H_2O_2. Obviously, the $ZnFe_2O_4$/MWCNTs composite exhibits the highest adsorption capacity and strongest photocatalytic activity among all the samples, with the MB degradation rate reaching 99% in 6 h. The TOC of this sample decreases from 15.23 to 1.49 mg L^{-1}, which confirms that 90% of MB is mineralized. Photocatalytic degradation of MB must have occurred here, because simple adsorption on the surfaces of the $ZnFe_2O_4$/MWCNTs composite can only account for 24% of the decoloration. No appreciable degradation of the dye has been observed in the presence of neat MWCNTs or under direct photolysis for the same irradiation (data not shown). In the absence of any catalyst (only MB + H_2O_2), no obvious dye degradation is observed after 6 h. MWCNTs show great adsorption for MB but without distinct degradation of MB. It can be seen that the presence
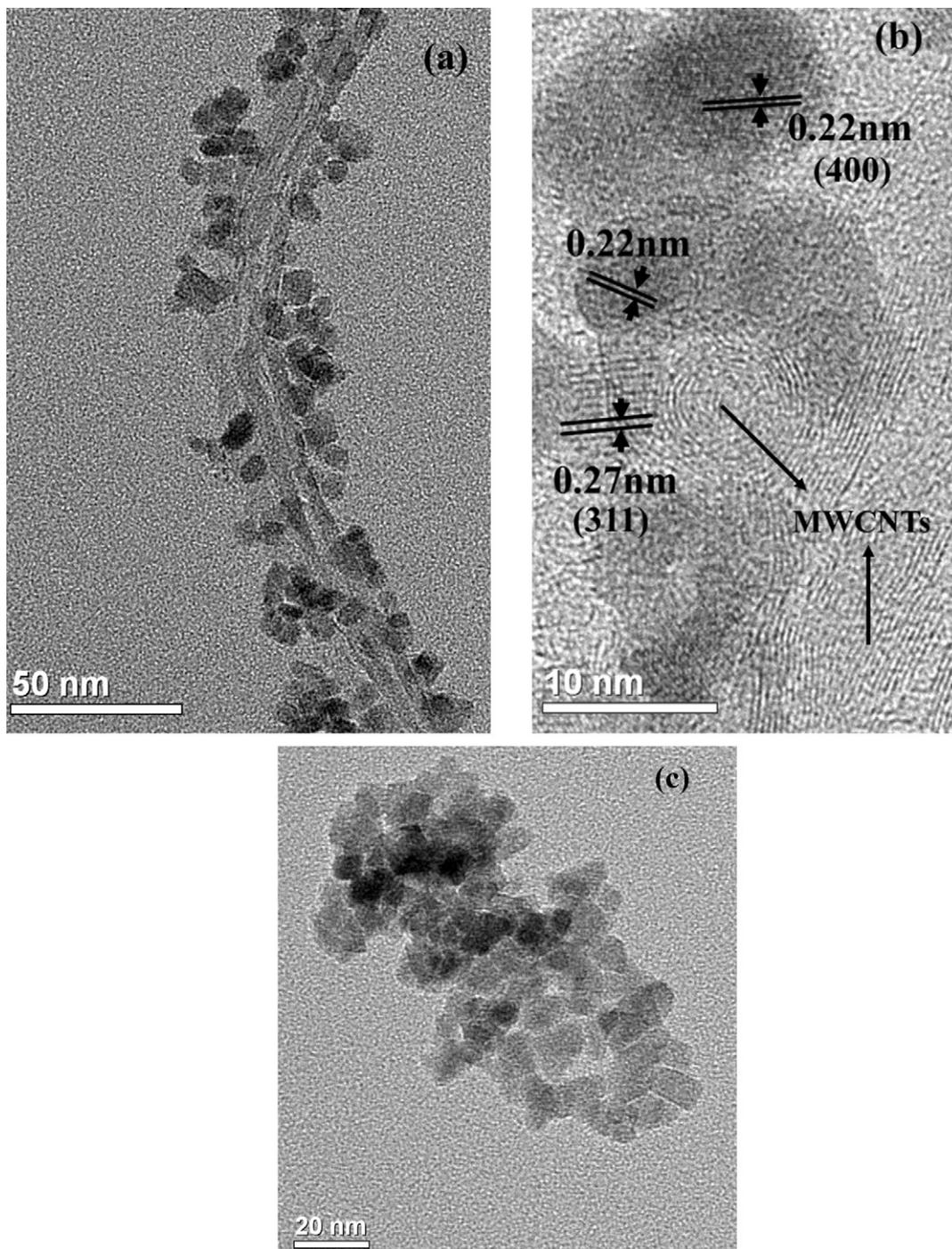
Fig. 2. TEM and HRTEM images of $ZnFe_2O_4/MWCNTs$ (a, b) and $ZnFe_2O_4$ (c).

of MWCNTs enhanced the photocatalytic activity of $ZnFe_2O_4$ by comparing with the $ZnFe_2O_4$ and the mechanically mixed $ZnFe_2O_4$ and MWCNTs. No strong bonding between $ZnFe_2O_4$ and MWCNTs in the mechanical mixture intermits the transfer of electrons from $ZnFe_2O_4$ to MWCNTs. Moreover, $ZnFe_2O_4$ and MWCNTs are not uniformly distributed in the solution, and the enrichment of dye on the surfaces of MWCNTs cannot enhance its oxidation on the $ZnFe_2O_4$. Therefore, the photocatalytic activity of the mechanical mixture of $ZnFe_2O_4$ and MWCNTs is low. Although the degradation of MB over $ZnFe_2O_4$ and $ZnFe_2O_4/MWCNTs$ in the presence of H_2O_2 happened in dark due to the formation of $\bullet OH$ from the decomposition of H_2O_2 on some transition metal oxides [23], they showed lower photocatalytic activity than those under irradiation respectively, which

demonstrates that the degradation reaction is definitely driven by visible light.

The BET surface area of the $ZnFe_2O_4/MWCNTs$ composite is $72.9\,m^2\,g^{-1}$, which is larger than that of the $ZnFe_2O_4$ powder ($56.9\,m^2\,g^{-1}$). The enlarged BET is attributed to the introduction of MWCNTs, which can improve the adsorption of MB.

The photoluminescence (PL) emission spectra are useful to disclose the migration, transfer, and recombination processes of the photo-generated electron–hole pairs in the semiconductor [24]. The PL emission mainly results from the recombination of the excited electrons and holes. In this study, the PL emission spectra of $ZnFe_2O_4$ and $ZnFe_2O_4/MWCNTs$ were examined, as displayed in Fig. 5. One can see that $ZnFe_2O_4$ has a broad green emission peak at
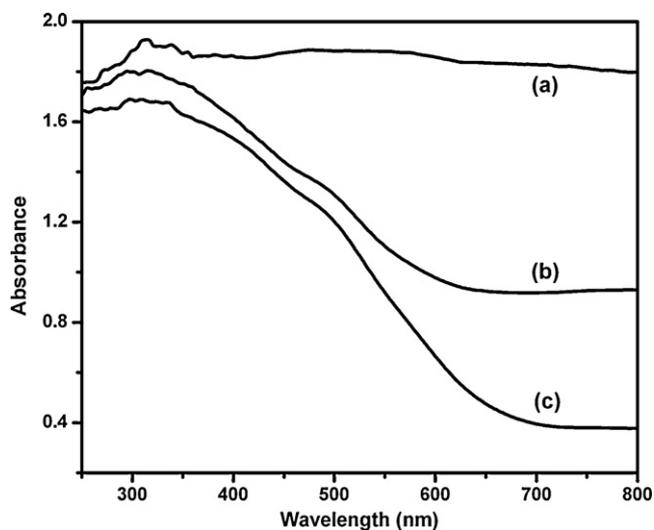
Fig. 3. UV–vis absorption spectra of (a) MWCNTs, (b) ZnFe$_2$O$_4$/MWCNTs and (c) ZnFe$_2$O$_4$.

Fig. 5. The PL spectrum of ZnFe$_2$O$_4$ (a) and ZnFe$_2$O$_4$/MWCNTs (b) (λ_{Ex} = 315 nm).

538–547 nm, which is attributed to the recombination of holes and electrons in the valence band and conduction band. The PL intensity of the ZnFe$_2$O$_4$/MWCNTs composite is lower than that of pure ZnFe$_2$O$_4$, which shows that the recombination of photo-generated charge carriers is inhibited greatly, leading to the increase of highly reactive species for degradation of MB.

Fig. 6 represents linear relationship between the fluorescence intensity of 2-hydroxyterephthalic acid (TAOH) and the duration of visible-light irradiation. The concentration of •OH was estimated by comparing the fluorescence intensity to that of the known concentration of TAOH [25]. The formation rate of •OH ($r_{•OH}$) of ZnFe$_2$O$_4$/MWCNTs in the presence of H$_2$O$_2$ under visible-light irradiation was about 4 times that of pure ZnFe$_2$O$_4$ under the same condition. Contrastively, in the case of ZnFe$_2$O$_4$ or ZnFe$_2$O$_4$/MWCNTs in the absence of H$_2$O$_2$, the $r_{•OH}$ was extremely low. The ZnFe$_2$O$_4$/MWCNTs in the presence of H$_2$O$_2$ in dark shows higher $r_{•OH}$ than the mixture of ZnFe$_2$O$_4$ and MWCNTs. These experimental results indicate that the surface condition of ZnFe$_2$O$_4$/MWCNTs is more favorable than that of pure ZnFe$_2$O$_4$ or the mixture of ZnFe$_2$O$_4$ and MWCNTs in the formation of •OH for oxidizing the dye in the system, which is consistent with the photocatalytic performance discussed above.

Fig. 4. (A) Absorption spectra of the (MB + H$_2$O$_2$ + ZnFe$_2$O$_4$/MWCNTs composite) solution taken at different reaction time. (B) Effect of different catalysts on photocatalytic decomposition of Methylene blue.
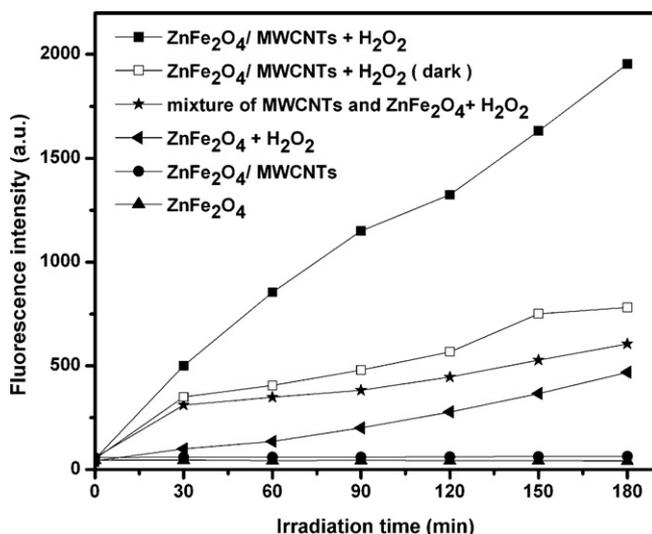
Fig. 6. The changes of the fluorescence intensity of 2-hydroxyterephthalic acid at 425 nm under various conditions.

The enhanced photocatalytic activity of the $ZnFe_2O_4$/MWCNTs for degradation of MB presumably results from the following reasons. Firstly, MWCNTs improve the absorption of dye and H_2O_2 due to their large surface area and special aperture structure. Secondly, when visible light is illuminated on the $ZnFe_2O_4$ nanocrystalline, electrons are excited from the valence band to the conduction band. Then, the excited electrons transfer from $ZnFe_2O_4$ to the MWCNTs, thus the recombination of electron-hole pairs are effectively hindered [26]. As a result, more photo-generated holes can react with adsorbed water to form $^\bullet OH$, which is available to promote the decomposition of MB. Thirdly, H_2O_2 can act as an effective electron scavenger to form $^\bullet OH$ on the surface of MWCNTs [27], which not only enhances oxidation ability but also fleetly reduces electronic accumulation on the surface of MWCNTs. Therefore, the $ZnFe_2O_4$/MWCNTs composite exhibits enhanced photocatalytic activity under visible-light irradiation in the presence of H_2O_2.

4. Conclusion

The $ZnFe_2O_4$/MWCNTs composite was prepared by hydrothermal method. This composite shows higher ability of visible-light absorption and lower PL intensity than that of pure $ZnFe_2O_4$. The presence of MWCNTs improved the photocatalytic activity of $ZnFe_2O_4$ significantly. On the basis of PL spectra and $^\bullet OH$ measurement, the enhancing mechanism for photocatalytic activity of the $ZnFe_2O_4$/MWCNTs composite is probably attributed to effective separation of electron–hole pairs and the formation of $^\bullet OH$. This study is believed to be useful not only for understanding the photocatalytic mechanism but also for developing effective photocatalyst in pollutant decomposition.

Acknowledgement

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